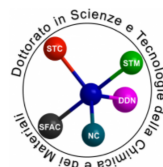




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di Genova**



UNIVERSITÀ DEGLI STUDI DI GENOVA

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Chemistry and Materials (STCM)

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Curriculum: Material Science and Technology

**Effects of Thermal Annealing on
Amorphous Oxides for Gravitational-Wave
Detector Mirror Coatings:
a Real-Time Spectroscopic Ellipsometry
Approach**

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*“La realtà non è sufficiente all’essere umano, un mondo non gli basta.
Perciò lui stesso deve fabbricarne altri, sempre nuovi.”*

— Leena Krohn, *Lo stupore del pellicano*

*“Il mondo non è solo più strano di quanto immaginiamo:
è più strano di quanto possiamo immaginare.”*

— J. B. S. Haldane

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Abstract

The direct detection of gravitational waves in 2015 marked a major milestone in physics and opened the era of gravitational-wave astronomy. These spacetime ripples, predicted by Einstein in 1916, are generated by extreme astrophysical events such as black hole mergers and neutron star collisions. Their observation has provided access to phenomena that cannot be studied with electromagnetic telescopes. Current interferometric detectors, such as the European Virgo and the American LIGO observatories, can resolve measurable strain amplitudes of 10^{-21} , corresponding to length variations of 10^{-18} meters over kilometer-scale baselines. A major limitation to the sensitivity of current detectors is coating thermal noise, which originates from thermally driven mechanical dissipation within the multilayer dielectric coatings that form the mirror surfaces. Such structures, composed of alternating high- and low-index amorphous oxides, must achieve extremely high reflectivity while minimizing optical absorption and mechanical loss. In current detectors, titania-doped tantala is the standard high-index material, but it remains the dominant source of this noise, motivating the search for alternative high-index oxides that exhibit lower mechanical dissipation, while strictly preserving comparable or superior optical properties. Thermal annealing is essential for reducing mechanical losses in amorphous films, yet it induces metastable structural and optical transformations that must be understood to design optimized coatings for next-generation detectors. This thesis introduces a comprehensive method for real-time, in-situ optical characterization of amorphous oxide coatings during thermal annealing. The approach combines spectroscopic ellipsometry with precise thermal control and automated data acquisition. A thorough evaluation of the experimental setup was conducted, including a systematic identification and mitigation of all setup-related and analysis-related sources of error. To establish accurate baseline conditions, temperature-dependent optical models for the substrate and its native silica

were developed over the 30–600 °C range, providing a reliable description of the layers underlying each coating. In addition, a suite of automated scripts was implemented to standardize data acquisition and analysis, ensuring reproducibility and allowing the method to be applied across multiple samples. This approach provides direct access to key material parameters — such as refractive index, layer thickness, and optical gap — and to their evolution under heat treatment. It thus offers a rigorous and sensitive route for characterizing the optical and structural evolution of the material during the annealing process. The method was applied to the most relevant high-index oxides used in gravitational-wave detector coatings, namely the current standard (titania-doped tantala) and two promising alternatives, hafnia–tantala and titania–germania. Titania–tantala and hafnia–tantala exhibit similar overall trends, with structural evolution initiating around 200 °C and the largest variations occurring during the heating ramp, followed by comparatively minor changes in the subsequent high-temperature plateau. A more extensive investigation was carried out on titania–germania, with multiple annealing cycles designed to isolate the effects of heating rate, annealing temperature, and plateau duration. The material showed a stronger response to temperature than to the other parameters. While at 500 °C the coating still behaves in close analogy with titania–tantala and hafnia–tantala, at 600 °C it undergoes a thermal response not previously observed in any oxide used for gravitational-wave detector coatings. This regime is characterized by a rapid inversion of both thickness and refractive index at the onset of the high-temperature plateau, accompanied by a pronounced reduction in the optical gap and a substantial release of argon. We propose that this inversion reflects a structural reorganization driven by the enhanced atomic mobility that develops as the material approaches the glass-transition region of germania. At 550 °C, the system enters an intermediate regime whose response is neither fully conventional nor as extreme as the behavior observed at 600 °C. Taken together, these results demonstrate that the thermal response of high-index oxides is strongly material dependent and that effective optimization of coating performance requires material-specific annealing strategies. They also highlight the capability of real-time optical monitoring to reveal relaxation mechanisms that remain inaccessible to ex-situ analyses. The insights obtained are directly relevant to improving the optical and mechanical performance of future interferometric mirrors.

Chapter 1

Interferometric Gravitational-Wave Detectors: Operating Principles, Sensitivity, and Noise Sources

This chapter offers a concise introduction to the broader context of the thesis and is structured as follows:

- Section [1.1](#) introduces the origin of gravitational waves and their polarization states, highlighting how these signals can be detected through interferometric techniques.
- Section [1.2](#) presents the first direct observation of a gravitational wave, a milestone that marked the beginning of gravitational-wave astronomy.
- Section [1.3](#) provides an overview of the Virgo and LIGO gravitational-wave interferometers:
 - Subsection [1.3.1](#) outlines the basic operating principles of interferometry, emphasizing the key technological features and instrumental configurations of the detectors.
 - Subsection [1.3.2](#) examines their sensitivity and the principal noise sources that limit their performance.

1.1 From Einstein's Field Equations to the Prediction of Gravitational Waves

In 1916, Albert Einstein, proposed the theory of General Relativity, re-defining the concept of gravity: no longer a force of attraction between masses, as formulated by Newton in 1687 in his celebrated treatise *Philosophiæ Naturalis Principia Mathematica* [1], but rather a manifestation of the curvature of spacetime induced by the presence of mass and energy. In this formulation, bodies move along geodesics of spacetime, their trajectories determined by the local geometry. The relation between matter and curvature is described by Einstein's field equations [2]:

$$R_{\mu\nu} - \frac{1}{2}R g_{\mu\nu} = \frac{8\pi G}{c^4}T_{\mu\nu}, \quad (1.1)$$

where:

- $R_{\mu\nu}$: Ricci tensor, describing local curvature;
- R : Ricci scalar, obtained by contracting $R_{\mu\nu}$;
- $g_{\mu\nu}$: metric tensor, defining the geometry of spacetime;
- $T_{\mu\nu}$: energy-momentum tensor, representing the distribution of matter and energy;
- G : Newton's gravitational constant;
- c : speed of light (in vacuum).

In absence of matter and energy sources (vacuum), these reduce to

$$R_{\mu\nu} - \frac{1}{2}R g_{\mu\nu} = 0, \quad (1.1)$$

In the weak-field limit, the metric is expressed as a perturbation of flat Minkowski spacetime:

$$g_{\mu\nu} = \eta_{\mu\nu} + h_{\mu\nu}, \quad |h_{\mu\nu}| \ll 1, \quad (1.2)$$

where $\eta_{\mu\nu}$ denotes the Minkowski metric and $h_{\mu\nu}$ is a small perturbation. For technical convenience, it is useful to introduce the *trace-reversed perturbation*, defined as

$$\bar{h}_{\mu\nu} = h_{\mu\nu} - \frac{1}{2}\eta_{\mu\nu} h, \quad h = h^\lambda{}_\lambda. \quad (1.3)$$

This redefinition simplifies the structure of the linearized Einstein equations. Upon imposing the harmonic (Lorenz) gauge condition,

$$\partial^\mu \bar{h}_{\mu\nu} = 0, \quad (1.4)$$

the linearized Einstein equations in vacuum reduce to the wave equation

$$\square \bar{h}_{\mu\nu} = 0, \quad (1.5)$$

for which a particular solution is a plane-wave mode:

$$\bar{h}_{\mu\nu}(x) = \epsilon_{\mu\nu} e^{ik_\rho x^\rho}, \quad k_\rho k^\rho = 0, \quad (1.6)$$

where:

- $\epsilon_{\mu\nu}$ is the polarization tensor;
- k_ρ is the four-dimensional wave vector;
- x^ρ are the spacetime coordinates.

For a gravitational wave propagating along the z -axis, the residual gauge freedom allows one to impose the *transverse-traceless (TT) condition*. In this gauge, the spatial components of the metric perturbation reduce to the two independent degrees of freedom, which can be written as

$$h_{ij} = h_+ \hat{e}_{ij}^{(+)} + h_\times \hat{e}_{ij}^{(\times)}, \quad (1.7)$$

where,

- h_+ is the amplitude of the “plus” mode,
- $h_\times$ is the amplitude of the “cross” mode.

The corresponding polarization patterns are illustrated in Figure 1.1.

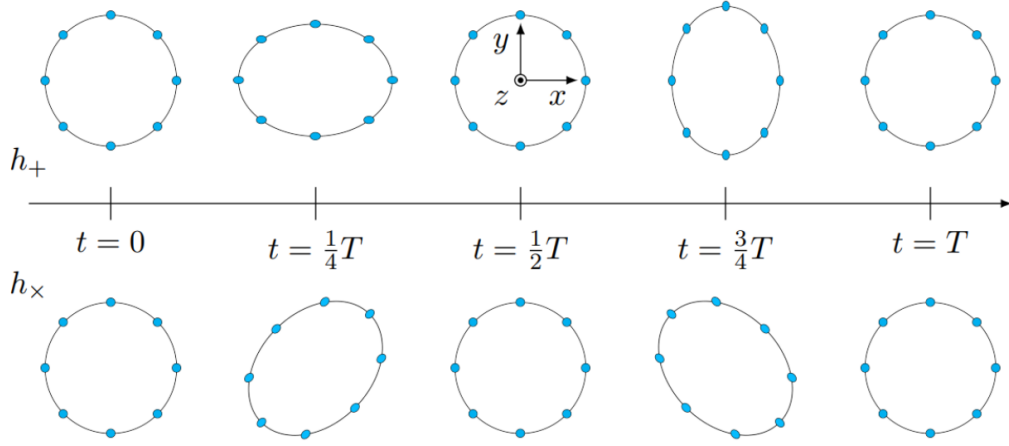


Figure 1.1: Effect of gravitational waves on a ring of test particles. The top row shows the deformation produced by the plus polarization h_+ , while the bottom row shows the deformation due to the cross polarization $h_\times$. Each column corresponds to a different time in the wave cycle. Both polarizations have the same amplitude and differ only by a 45° rotation. Image reproduced from [3].

The h_+ polarization produces an alternating deformation along the x and y axes, while the $h_\times$ polarization induces a distortion rotated by 45° with respect to h_+ . These effects manifest as infinitesimal variations in the relative distances between test masses arranged along orthogonal directions, making Michelson-type interferometers - such as LIGO and Virgo - particularly well suited for the direct detection of gravitational waves. The perpendicular arm configuration enables the measurement of the phase shift induced by gravitational wave on the laser beam, thereby translating spacetime deformations into an observable optical signal.

1.2 GW150914: The First Direct Detection of Gravitational Waves

Since Einstein's theoretical studies in 1916 [4], the existence of gravitational waves remained unconfirmed by direct experimental evidence for decades. A major indirect confirmation came in 1974, when Hulse and Taylor observed the binary system PSR B1913+16 [5], composed of two neutron stars, one of which manifests as a pulsar through periodic radio signals. The gradual decrease in the orbital period and eccentricity of the system, interpreted as the

result of energy loss through gravitational-wave emission, provided strong indirect evidence for general relativity [6]. This discovery earned the researchers the Nobel Prize in Physics in 1993. A decisive breakthrough occurred on September 14, 2015, with the first direct detection of a gravitational-wave signal, designated GW150914 [7], simultaneously recorded by the Advanced LIGO interferometers located in Hanford (Washington) and Livingston (Louisiana). The event was interpreted as the coalescence of a binary black hole system, with component masses of approximately 36 and 29 solar masses. The observed waveform showed excellent agreement with theoretical predictions derived from general relativity. In the months and years that followed, numerous additional signals were recorded. Among them, one of the most significant was *GW170817* [8], associated with the merger of two neutron stars. This event was accompanied by the detection of electromagnetic counterparts observed by both ground-based telescopes and space missions, representing one of the first demonstrations of multimessenger astronomy. These discoveries accelerated technological progress in the field and contributed to the consolidation of a global network of interferometric detectors, among which the most prominent are the U.S.-based LIGO [9], the European Virgo [10], and the Japanese KAGRA [11], currently operational ground-based observatories. Looking ahead, next-generation detectors such as the underground Einstein Telescope [12], the U.S. project Cosmic Explorer [13], and the space-based mission LISA [14] (Laser Interferometer Space Antenna) are being designed to expand the observable frequency band and the accessible cosmological volume. In this thesis, centred on the materials forming the optical coatings of the mirrors employed in Virgo and LIGO-like detectors, the discussion will focus exclusively on the Virgo and LIGO interferometers.

1.3 LIGO and Virgo: Large Ground-Based Interferometers

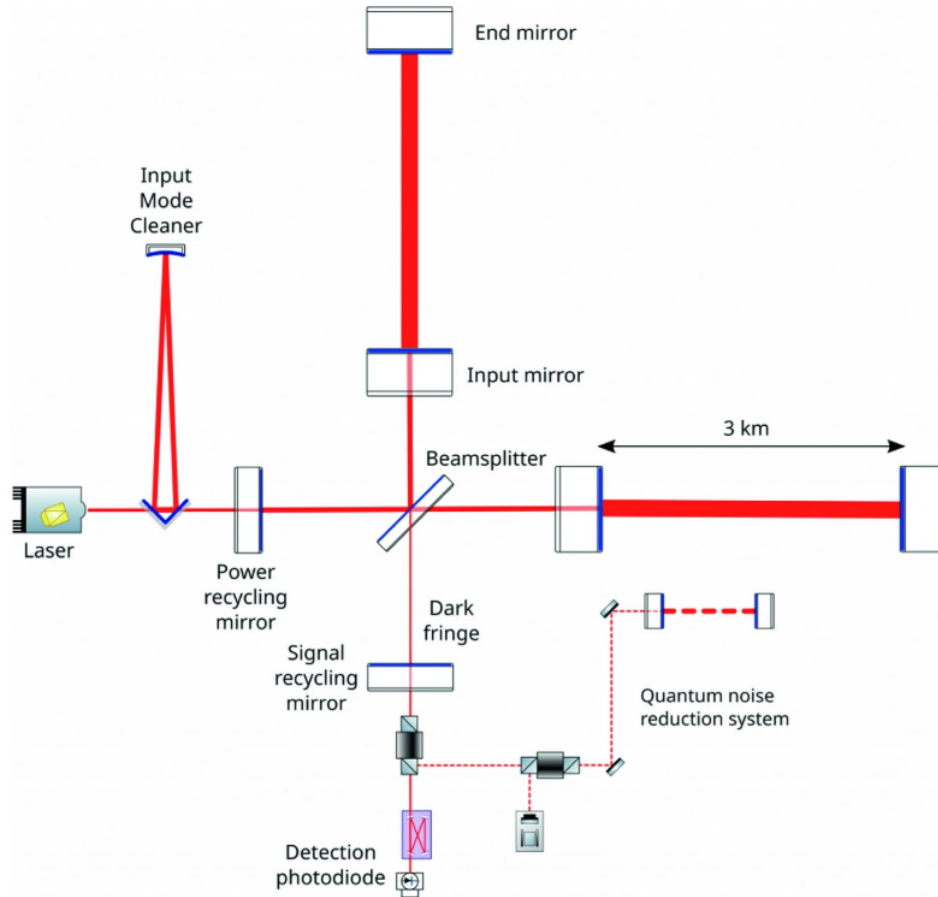


Figure 1.2: Simplified schematic of a Michelson interferometer representative of large ground-based detectors such as Virgo (3km arms) and LIGO (4km arms), instrumented with Fabry–Pérot arm cavities. A single laser beam is split by the beam splitter into two perpendicular arms; in each arm the light resonates between two high-reflectivity mirrors forming a Fabry–Pérot cavity. Reflected beams recombine at the beam splitter and are directed to the photodetector, where differential changes in the optical path lengths induced by a passing gravitational wave produce measurable phase shifts. Image reproduced from [15]

The Laser Interferometer Gravitational-Wave Observatory (LIGO) and Virgo are large-scale instruments designed for the direct detection of gravitational waves [16]. Both adopt the Michelson interferometer configuration with resonant Fabry–Pérot arm cavities, schematically illustrated in Figure 1.2. A

coherent laser beam is split into two orthogonal arms, each several kilometers long and terminated by highly reflective mirrors acting as test masses. The Fabry–Pérot cavities are formed by the Input Test Mirror (ITM), located near the beam splitter and partially transmitting the incoming light, and the End Test Mirror (ETM), placed at the far end of each arm and highly reflective. When the beams are recombined at the beam splitter, they produce an interference pattern whose modulation reveals minute differential changes in the arm lengths caused by a passing gravitational wave. LIGO operates two detectors with 4 km arms located at Hanford (Washington) and Livingston (Louisiana), while Virgo, near Pisa, employs 3 km arms. Sensitivity is enhanced by Fabry–Pérot cavities, which increase the effective optical path length through multiple reflections. Additional improvements arise from power recycling, which reinjects the reflected light to boost intracavity power, and signal recycling, which uses an output cavity to tailor the interferometer response in selected frequency bands [16]. Several additional subsystems are essential to the overall architecture. The Input Mode Cleaner stabilizes the incoming laser beam both spatially and temporally. At the output port, a detection photodiode measures the interference pattern and converts optical variations into electrical signals. To reduce quantum fluctuations, techniques such as the injection of squeezed light are employed, improving the signal-to-noise ratio [17]. High-stability Nd:YAG lasers, operating at 1064 nm with active frequency and amplitude control, provide the coherent source [18]. To suppress seismic and environmental noise, the End Test Mirrors (ETM) are suspended from multi-stage isolation systems, implemented as Virgo’s superattenuator (Appendix A.1) and LIGO’s Seismic Isolation System (SIS) [19]. These mirrors are fabricated from ultra-pure fused silica, chosen for its low mechanical and optical losses, and coated with dielectric multilayers to minimize thermal noise [20]. Precision beam splitters ensure accurate division and recombination of the laser beam, while ultra-high-vacuum beam tubes guarantee undisturbed propagation along the arms [21]. Thanks to the combined action of high-power stabilized lasers, low-noise mirror coatings, advanced seismic-isolation systems, and ultra-high-vacuum infrastructures, the Advanced LIGO and Advanced Virgo interferometers have achieved strain sensitivities at the level of $h \sim 10^{-23} \text{ Hz}^{-1/2}$ and $h \sim 10^{-22} \text{ Hz}^{-1/2}$ around 100 Hz, respectively, as demonstrated in their recent observing runs [22, 23].

1.3.1 Fundamental Principles of Interferometric Detection

An interferometric detector is designed to convert the infinitesimal differential variations in arm length, produced by a passing gravitational wave, into a measurable optical signal. In the absence of a gravitational signal, the interferometer operates at a working point defined by the optical path difference between the two arms, expressed as [24]

$$\Delta\phi_0 = \frac{2\pi}{\lambda_{\text{laser}}}(L_N - L_W). \quad (1.8)$$

In interferometric gravitational-wave detectors, it is customary to assume that the two arm lengths are equal in the absence of a signal, i.e. $L_N = L_W = L$. When a gravitational wave passes, it induces differential variations in the lengths of the two interferometer arms. The measurable strain is defined as

$$h(t) = \frac{\Delta L}{L} \quad (1.9)$$

where

$$\Delta L = \delta L_N - \delta L_W, \quad (1.10)$$

with δL_N and δL_W denoting the length variations of the North and West interferometer arms, respectively. The resulting phase shift is given by [3]

$$\Delta\phi(t) = \frac{4\pi L}{\lambda_{\text{laser}}} h(t) \text{sinc}\left(\frac{\omega_{\text{gw}} L}{c}\right), \quad (1.11)$$

with $\omega_{\text{gw}} = 2\pi f_{\text{gw}}$ the gravitational-wave angular frequency. The sinc factor accounts for the reduced response when the arm length becomes comparable to the gravitational wavelength. The relevant time argument is the photon propagation time along one arm, $t = L/c$, since this is the interval over which the perturbation modulates the optical path. To enhance the sensitivity of the detector, each arm is equipped with a Fabry–Pérot cavity of finesse F , which increases the photon storage time and amplifies the effective phase shift according to

$$\frac{\Delta\phi_{\text{FP}}}{\Delta\phi} = \frac{2F}{\pi}. \quad (1.12)$$

The overall frequency response of the interferometer, for gravitational waves in the long-wavelength limit, is then described (to a good approximation) by the transfer function from strain to phase, which follows directly from the

phase-shift expression derived by¹ [2]:

$$T_{h \rightarrow \phi}(f) \simeq \frac{8FL}{\lambda_{\text{laser}}} \frac{1}{\sqrt{1 + (f_{\text{gw}}/f_p)^2}}, \quad (1.13)$$

where $f_p \simeq c/(4FL)$ is the storage frequency² of the cavity, setting the bandwidth of the detector. From an experimental point of view, the detector measures a phase variation $\delta\phi(t)$ at the output port. To characterise the response of the interferometer to a gravitational wave, it is most convenient to express the measured quantities in the frequency domain. In this representation, the signal takes the form

$$\tilde{\phi}(f) = T_{h \rightarrow \phi}(f) \tilde{h}(f) + \tilde{N}_\phi(f), \quad (1.14)$$

where $T_{h \rightarrow \phi}(f) \tilde{h}(f)$ describes the phase response of the interferometer to a gravitational wave, with $T_{h \rightarrow \phi}(f)$ acting as the strain-to-phase transfer function and $\tilde{h}(f)$ the gravitational-wave. The term $\tilde{N}_\phi(f)$ instead denotes the phase noise at the output port. The equivalent strain is defined by inverting the transfer function,

$$h_{\text{eq}}(f) = \frac{\tilde{\phi}(f)}{T_{h \rightarrow \phi}(f)}, \quad (1.15)$$

which expresses the strain that would produce the same measured phase variation at frequency f . For a given phase noise $\tilde{N}_\phi(f)$, a larger transfer function corresponds to a smaller strain noise and therefore to a better strain sensitivity.

1.3.2 Sensitivity and Dominant Noise Contributions

The same relation 1.15 applies to noise fluctuations. Since any phase variation at the interferometer output is indistinguishable from that produced by a gravitational wave, it is convenient to express phase noise in terms of an *equivalent strain noise* [3],

$$\tilde{N}_h(f) = \frac{\tilde{N}_\phi(f)}{T_{h \rightarrow \phi}(f)}. \quad (1.16)$$

¹Starting from $|\Delta\phi_{\text{FP}}(f_{\text{gw}})| \simeq h(f_{\text{gw}}) \frac{8FL}{\lambda_{\text{laser}}} [1 + (f_{\text{gw}}/f_p)^2]^{-1/2}$, the transfer function is obtained by defining $T_{h \rightarrow \phi}(f_{\text{gw}}) \equiv \Delta\phi_{\text{FP}}(f_{\text{gw}})/h(f_{\text{gw}})$, which directly leads to Eq. 1.13.

²The storage frequency f_p is the characteristic frequency of the Fabry–Pérot arm cavities, defined by the photon lifetime inside the cavity. It sets the detector bandwidth: below f_p the cavity efficiently stores light and converts gravitational-wave strain into phase modulation, while above f_p photons escape too quickly, reducing the interferometer response.

which corresponds to the strain level that would generate a phase perturbation identical to that produced by the noise. This reformulation allows all noise sources to be treated in the same way as an effective gravitational-wave signal. For a stationary stochastic process³, the equivalent strain noise is fully characterized by its Power Spectral Density (PSD), defined as [25]

$$S_h(f) \delta(f - f_0) = \langle \tilde{N}_h(f) \tilde{N}_h(f_0) \rangle, \quad (1.17)$$

where $S_h(f)$ quantifies the contribution to the mean-square strain noise per unit bandwidth. The quantity directly compared to gravitational-wave signals is the *Amplitude Spectral Density (ASD)*, also referred to as the detector *strain sensitivity* [3],

$$h_{\text{sens}}(f) = \sqrt{S_h(f)}, \quad (1.18)$$

which represents the minimum resolvable strain per unit bandwidth. This relation makes explicit that the detector's sensitivity is governed not only by its optical response but also by the level of noise superimposed on the gravitational-wave signal.

³A stochastic process describes noise whose values fluctuate randomly in time, while stationary means that its statistical properties are invariant under time translations.

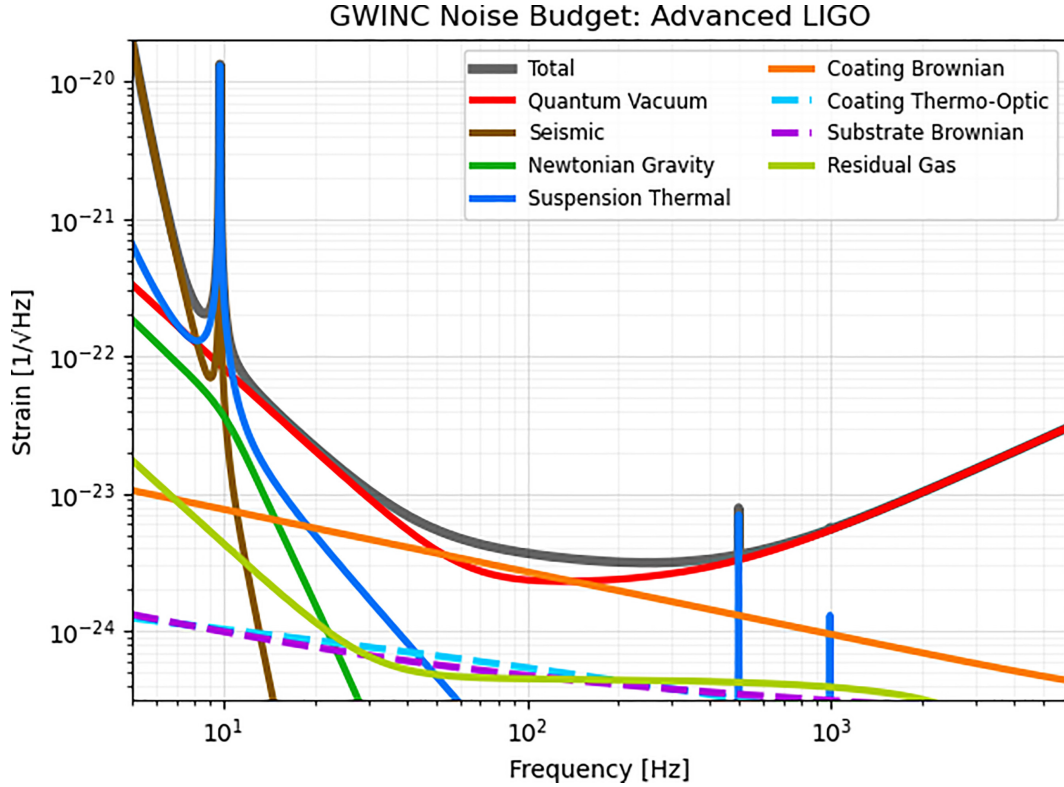


Figure 1.3: Advanced LIGO reference strain sensitivity curve (black), showing the overall noise envelope together with the contributions from individual noise sources. The plot highlights the three fundamental limitations to detector sensitivity: seismic noise (brown), which dominates at low frequencies (below ~ 50 Hz); thermal noise, arising from suspension thermal motion (blue), coating Brownian noise (orange), coating thermo-optic noise (light blue), and substrate Brownian noise (purple), which provides the leading contribution in the intermediate band; and quantum noise (red), manifesting as radiation pressure at intermediate frequencies and as shot noise at high frequencies (above ~ 500 Hz), which sets the ultimate high-frequency boundary. Frequency is plotted on a logarithmic scale in Hertz, and strain sensitivity is expressed in $\text{Hz}^{-1/2}$. Image reproduced from [26]

In Figure 1.3, the reference strain sensitivity curve of Advanced LIGO is presented, showing the overall noise envelope together with the contributions from the main noise sources. Among these, three categories are regarded as fundamental, as they set the theoretical limits of sensitivity across different frequency bands. Consistently with the ranges reported in the LIGO O4 observation study [27], and noting that the corresponding limits for Virgo are broadly similar:

- *Seismic noise* (Appendix A.1), arising from ground vibrations, which

dominates at low frequencies (< 50 Hz) and determines the lower bound of the observable band;

- *Quantum noise* (Appendix A.2), associated with the discrete nature of laser light, which manifests as radiation pressure at low and intermediate frequencies and as shot noise at high frequencies. In particular, shot noise dominates above 500 Hz, thereby setting the high-frequency upper limit of the measurement band;
- *Thermal noise* (Section 1.3.3), generated by the microscopic agitation of materials, particularly in the mirror substrates and optical coatings, which represents the dominant contribution in the intermediate band (50–500 Hz), coinciding with the region of greatest astrophysical interest. Only Brownian noise is treated in the main body of this thesis, as it is the most relevant for the results presented here, while the other contributions are discussed in Appendix A.3.

1.3.3 Thermal Noise in the Test Masses

Thermal noise represents one of the fundamental sources of disturbance that limits the sensitivity of gravitational-wave interferometers in the intermediate frequency band (around 200 Hz [28, 27]), and is particularly significant for astrophysical observations. It can be decomposed into several components, depending on the underlying physical mechanisms:

- Brownian noise (Paragraph 1.3.3), arising from internal friction within the materials of the substrate, the coating, and the mirror suspensions (Paragraph A.3);
- Thermorefractive noise (Appendix A.3.2), associated with variations of the refractive index in the coating layers due to thermal fluctuations;
- Thermoelastic noise (Appendix A.3.3), generated by temperature fluctuations that induce thermal expansions both in the substrate and in the coating;
- Photothermal noise (Appendix A.3.4), a manifestation of thermoelastic and thermorefractive processes, induced by the absorption of laser radiation within the coating;

- Thermoradiation noise (Appendix A.3.4), associated with temperature fluctuations originating from both the emission and absorption of thermal radiation, representing an intrinsic radiative process.

Among these components, the dominant contributions in the Virgo and LIGO interferometers (see Figure 1.4) are the substrate and coating Brownian noise, the coating thermoelastic noise, and the coating thermorefractive noise, which together define the fundamental sensitivity limit of the instruments in the intermediate frequency band.

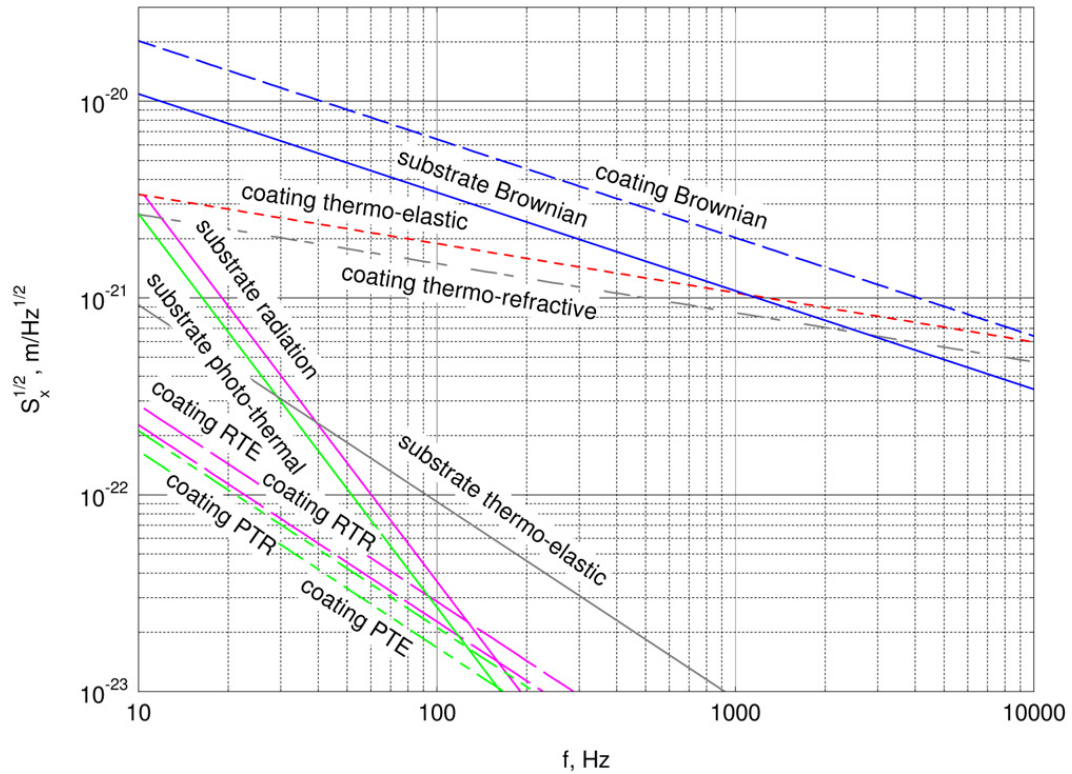


Figure 1.4: Amplitude spectral density $S_x^{1/2}$ (in $\text{m}/\text{Hz}^{1/2}$) as a function of frequency. The curves illustrate the principal contributions of thermal noise in precision optical systems. Brownian, thermoelastic, and thermorefractive noise emerge as the dominant sources in the intermediate band. Image reproduced from [29]

Brownian Noise: The Main Thermal Noise Source Fluctuations arising from dissipation mechanisms due to internal friction in substrates and optical coatings - the latter being predominant, with the dominant contribution originating from the high-refractive-index material [30] - can be described by the following expression for the Amplitude Spectral Density (ASD) of the surface displacement [29]:

$$S_{x,\text{BR}}^{1/2}(f) = \sqrt{\frac{2k_B T}{\pi^{3/2} w f} \frac{1 - \sigma_s^2}{Y_s} \phi(f)}, \quad (1.19)$$

where:

- w : Gaussian beam radius defined at the $1/e^2$ intensity level
- Y_s : Young's modulus of the substrate
- σ_s : Poisson's ratio of the substrate
- $\phi(f)$: loss angle

This expression applies to both the substrate and the coating by substituting the appropriate loss angle ϕ_s for the substrate and the effective loss angle ϕ_c for the coating. The elastic parameters Y_s and σ_s in Eq. (1.19) are, in all cases, those of the substrate. In particular, ϕ_c is given by [29]:

$$\begin{aligned} \phi_c \simeq \frac{d_{\text{tot}}(1 - 2\sigma_s)}{\sqrt{\pi} w (1 - \sigma_s)(1 - \sigma_{\parallel})} & \left[\frac{Y_{\perp}(1 - \sigma_{\parallel}) - 2\sigma_{\perp}^2 Y_{\parallel}}{Y_{\perp}^2(1 + \sigma_s)(1 - 2\sigma_s)} Y_s \phi_{\perp} \right. \\ & \left. + \frac{Y_{\parallel} \sigma_{\perp}(\phi_{\parallel} - \phi_{\perp})}{Y_{\perp}} + \frac{Y_{\parallel}(1 + \sigma_s)(1 - 2\sigma_s)\phi_{\parallel}}{Y_s(1 + \sigma_{\parallel})} \right] \end{aligned} \quad (1.20)$$

where:

- d_{tot} : total coating thickness, defined as $d_{\text{tot}} = N(d_l + d_h)$
 - N : number of layer pairs
 - d_l : thickness of the low-index layer
 - d_h : thickness of the high-index layer
- $Y_{\parallel}, Y_{\perp}$: effective Young's moduli of the coating for parallel and perpendicular deformations
- $\sigma_{\parallel}, \sigma_{\perp}$: effective Poisson's ratios of the coating for parallel and perpendicular deformations
- $\phi_{\parallel}, \phi_{\perp}$: loss angles associated with parallel and perpendicular deformations.

Note: these effective parameters are obtained via volume averaging over the multilayer coating materials.

According to equations 1.19 and 1.20, the reduction of *Coating Thermal Noise* (CTN) can be pursued by acting on several key parameters [20]:

- *Coating temperature:* the dependence on T allows thermal noise to be reduced by operating at cryogenic temperatures. Cryogenic operation (at temperatures around 22 K), as implemented in the 2.5-generation KA-GRA detector [11] and planned for third-generation observatories such as ET, enables a significant suppression of coating thermal noise [31, 20]. However, cooling large test masses poses significant technological challenges, since mechanical losses as well as optical and structural properties are temperature dependent. For example, $\text{TiO}_2 : \text{Ta}_2\text{O}_5$ and SiO_2 exhibit a loss angle at cryogenic temperatures that can be 4–10 times larger than at room temperature [32, 33]. For this reason, a fundamental change in technology is required to operate GWDs at low temperatures.
- *Elastic parameters:* CTN is minimized when the Young’s modulus of the coating matches that of the substrate ($Y_s \simeq Y_{\parallel}, Y_{\perp}$). As the elastic properties of available materials are relatively similar, the impact of this parameter on CTN reduction is marginal compared to other contributions [20].
- *Laser beam radius:* the $1/w$ dependence indicates that increasing the beam diameter leads to a substantial reduction in CTN. For instance, in *Advanced Virgo Plus*, the beam size will be increased by approximately 65% [23]. Similarly, ET and CE plan to employ significantly larger beam sizes to further suppress CTN [20].
- *Coating thickness:* the direct proportionality to d_{tot} implies that CTN can be mitigated by minimizing the physical thickness of the most dissipative layers. This is primarily achieved through the engineering optimization of Bragg reflectors, deviating from the standard quarter-wavelength design to reduce the physical thickness of the high-index (and high-loss) material [34, 35].
- *Coating loss angle:* the dependence on ϕ (intrinsic material dissipation) implies that CTN reduction is strongly driven by lowering the mechanical

loss of the layers. This is achieved through post-deposition thermal treatments (annealing), which structurally relax the amorphous network and drastically reduce internal friction, or by developing new coating mixtures characterized by intrinsically lower mechanical dissipation [36, 20].

The considerations outlined above underscore that thermal noise represents a fundamental limitation to the design sensitivity of current and future gravitational-wave interferometers. Given that this noise is intrinsically linked to the mirror properties, the following chapter (Chap. 2) focuses on the mirrors used in gravitational-wave interferometers, with a particular emphasis on their multilayer coatings, the materials from which they are fabricated, and the strategies developed to meet the stringent performance requirements imposed by advanced detectors.

Chapter 2

Advanced Mirror Technologies for Ground-Based Gravitational Wave Interferometers

This section presents an analysis of the highly reflective mirrors used in gravitational-wave detectors, with particular emphasis on those installed in the Virgo interferometer. This focus is motivated by the fact that a substantial portion of the present doctoral work has been conducted in collaboration with the Virgo Coating R&D project [37], which investigates the optical coatings of Virgo’s mirrors. Otherwise, the results obtained are broadly applicable and hold significant relevance for other detectors, most notably LIGO.

The structure of this chapter is organized as follows:

- Section 2.1: discussion of the two principal mirrors, the Input Test Mass (ITM) and the End Test Mass (ETM), with particular emphasis on the ETM.
- Section 2.2: analysis of the highly reflective coatings of the ETMs and the properties required to meet their stringent performance demands.
- Section 2.3: discussion of the state of the art in coating materials, highlighting their limitations, strengths, and the most promising future candidate materials.
- Section 2.4: brief outline of how the work presented in this thesis fits within the broader context introduced above.

2.1 Core Optics: Input Test Mass (ITM) and End Test Mass (ETM)

In each arm of the interferometer, the Fabry–Pérot cavity is defined by two mirrors with distinct optical functions: the Input Test Mirror (ITM) and the End Test Mirror (ETM). The ITM, located near the beam splitter, is partially transmissive ($T \approx 1.4\%$ [38, 10]) and regulates the coupling of the laser field into the arm cavity. In contrast, the ETM, positioned at the far end of the arm, is designed to be nearly perfectly reflective to close the cavity, enabling multiple round trips of the light. Simultaneously, it serves as the principal test mass whose displacement encodes the differential arm length variations induced by gravitational waves [38, 10]. In the context of this thesis, the focus will be placed on the ETM.

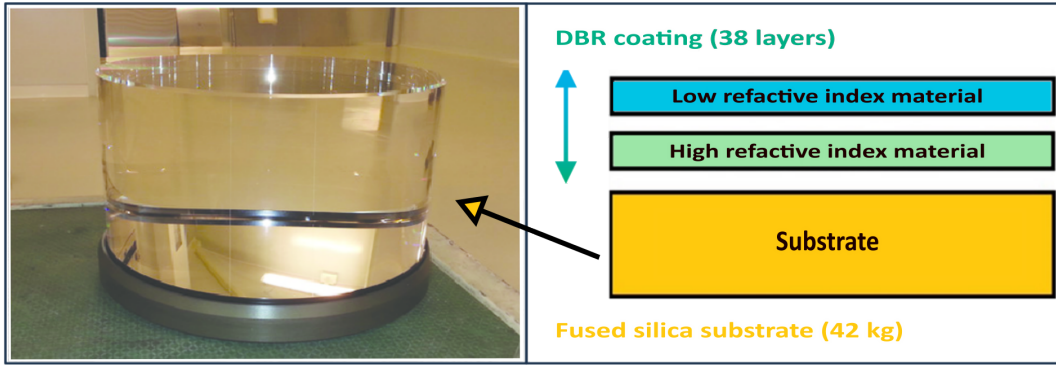


Figure 2.1: Left: Photograph of the mirror substrate used in the Virgo gravitational-wave interferometer, prior to the deposition of the high-reflectivity coating. Image cropped from [10]. Right: Schematic representation of the mirror structure, consisting of a 42 kg ultra-pure fused silica substrate coated with a Distributed Bragg Reflector (DBR). The DBR comprises 19 pairs (38 layers) of alternating high- and low-refractive-index materials [28], each typically designed with an optical thickness of one quarter of the 1064 nm laser wavelength to maximize reflectivity through constructive interference. The total coating thickness is approximately $5.9\mu\text{m}$ [39]. .

Figure 2.1 illustrates one of the two ETMs currently in use in the Virgo interferometer: the left panel shows the bare mirror substrate while the right panel provides a schematic representation of the reflective coating, consisting of a Distributed Bragg Reflector (DBR). The current generation of mirrors¹

¹Earlier upgrade plans for *Advanced Virgo+* proposed larger test masses (from 35 cm to

exhibit a cylindrical geometry with a diameter of 35 cm, a thickness of 20 cm, and a mass of about 42 kg [42, 23]. They are fabricated from a Suprasil 312 substrate [10], a fused silica variant that provides slightly inferior optical properties compared to Suprasil 3002 - used for the ITM - yet still ensures excellent performance. This choice is motivated by the distinct functional roles of the mirrors: while the ITMs must transmit high laser powers and therefore require substrates with extremely low optical absorption (typical values are $0.25 \text{ ppm}\cdot\text{cm}^{-1}$ at 1064 nm [43]), the ETMs are designed to reflect nearly all incident light [10]). Consequently, optical absorption becomes less critical, and the primary parameter of interest shifts to the mechanical quality factor, which is essential for reducing thermal noise arising from Brownian coating losses [44]. To meet the required reflectivity, both ETMs and ITMs are coated with a thin and uniform dielectric multilayer forming a Distributed Bragg Reflector (DBR). The difference lies in the number of layers: ETMs employ a thicker stack to achieve their extreme reflectivity, while ITMs use fewer layers [10, 28].

2.2 Highly Reflective Coatings

The high-reflectivity coating employed in End Test Mirrors (ETMs) is realized as a DBR structure, consisting of alternating layers of high- and low-refractive-index materials. The conventional DBR² operates according to the quarter-wave principle: each layer is designed with an optical thickness of $\lambda/4$, so that reflections from all interfaces add in phase [45]. This constructive interference maximizes the reflected field, thereby enhancing the overall reflectivity of the multilayer stack [46]. Consequently, the reflectivity of a DBR depends on both the number of low-high index pairs N and the refractive-index contrast between the constituent materials, defined as $\Delta n = n_1 - n_2$. Since the total number of layers can be either even or odd, two distinct formulations are required. Equation 2.1 applies when the stack contains an even number of

55 cm in diameter and from 42 kg to nearly 100 kg) [40]. More recent updates, however, indicate that the next replacement will keep the current dimensions and mass, focusing instead on improved optical quality and reduced coating noise [41].

²As discussed in Section 1.3.3, the layer thicknesses of a DBR can intentionally deviate from the ideal $\lambda/4$ condition to reduce coating thermal noise. This is achieved by redistributing the optical thickness among the high- and low-index materials, thereby lowering the contribution of the mechanically dissipative layers.

layers [46]:

$$R = \left(\frac{\frac{n_1^2}{n_0 n_{\text{sub}}} \left(\frac{n_1}{n_2} \right)^{2N} - 1}{\frac{n_1^2}{n_0 n_{\text{sub}}} \left(\frac{n_1}{n_2} \right)^{2N} + 1} \right)^2 \quad (2.1)$$

In contrast, Equation 2.2 corresponds to the case of an odd number of layers:

$$R = \left(\frac{\frac{n_{\text{sub}}}{n_0} \left(\frac{n_1}{n_2} \right)^{2N} - 1}{\frac{n_{\text{sub}}}{n_0} \left(\frac{n_1}{n_2} \right)^{2N} + 1} \right)^2 \quad (2.2)$$

In both cases, increasing N and enhancing the refractive index contrast drive the reflectivity towards unity, thereby ensuring the optical performance required for precision interferometry. However, to achieve the strain sensitivity of $3.5 \cdot 10^{-24} / \sqrt{\text{Hz}}$ required for Advanced Virgo [47], further extremely stringent constraints on the coating specifications must be imposed.

Mechanical losses, primarily arising from the high-index material within the coating [30], must remain below $2.3 \cdot 10^{-4}$, in order to suppress coating Brownian thermal noise (see Paragraph 1.3.3), which would otherwise dominate the mid-frequency sensitivity band of the interferometer. Regarding absorption, the specified values are less than 1 ppm, while actual coatings exhibit measured absorption in the range of 0.2–0.4 ppm [48]; low absorption is essential to minimize thermorefractive and photothermal noise (see Appendix A.3). Scattering losses must be constrained below 5 ppm [49], as any stray light may recombine with the main beam after interacting with surrounding structures, thereby reducing the interferometer’s sensitivity. To ensure that scattering remains within this limit, the residual surface roughness must exhibit a root mean square (RMS) deviation below 0.1 nm [50], a requirement that is met through state-of-the-art polishing techniques [10]. A summary of the mirror specifications is presented in Table 2.1.

These considerations lead naturally to a closer examination of the coating materials themselves, whose intrinsic mechanical and optical properties ultimately determine the achievable performance.

End Test Mirror (ETM) Parameters	
Substrate	
Material	Suprasil 312
Thickness [mm]	200
Diameter [mm]	350
Mass [kg]	42
Absorption [ppm/cm]	< 3
Coating	
HRI Material	Ti-doped Ta ₂ O ₅
LRI Material	SiO ₂
Coating diameter [mm]	340
Transmission [ppm]	< 1
Absorption [ppm]	< 1
Reflectivity [-]	> 0.9999
Surface Quality	
Roughness [nm]	< 0.1
Flatness_RMS [nm]	0.5
Losses per Surface [ppm]	37.5
Scattering [ppm]	< 10

Table 2.1: Technical specifications for the End Test Mirror (ETM) used in the arm cavities of Advanced Virgo, including reflectivity and scattering constraints. The values are extracted from [47].

2.3 Coating Materials: State of the Art

As introduced in Section 1.3.3 and 2.2, the dominant contribution to thermal noise in optical coatings arises primarily from the high-refractive-index layers [30, 51]. By contrast, silica (SiO₂), employed as the low-index material, is considerably less problematic for detectors operating at ambient temperature³. In current optical coatings, the main source of dissipation is the high-index titania–tantala oxide mixture: extensive experimental studies have shown that the

³SiO₂ exhibits a loss angle at cryogenic temperatures that is 4–10 times larger than that measured at room temperature [20], making it a problematic material for next-generation interferometers such as the Einstein Telescope.

excess mechanical loss originates specifically from the Ta_2O_5 component, while the addition of TiO_2 serves to reduce this loss by stabilizing the amorphous structure of the film [30, 51, 28]. Given this limitation, current research is primarily focused on identifying alternative materials that provide an adequate refractive-index contrast to preserve DBR reflectivity, while simultaneously reducing coating thermal noise [52, 53]. The use of amorphous oxide mixtures presently represents the only technologically viable solution for large-scale interferometers, as these materials are highly isotropic, exhibit extremely low optical absorption, and can be deposited via Ion Beam Sputtering (IBS), which is the only technique capable of producing optical coatings with the uniformity and optical quality required over the large surface areas of gravitational-wave detector mirrors [49]. These coatings are fabricated using the Grand Coater at the Laboratoire des Matériaux Avancés (<http://lma.in2p3.fr/>) [20]. Within this framework, $\text{TiO}_2\text{:Ta}_2\text{O}_5$ ⁴ [54, 55] (currently the standard [56, 7]) and $\text{TiO}_2\text{:GeO}_2$ [53, 57] (the most promising candidate [58]) constitute the two primary coating materials investigated in this thesis. Other potentially interesting amorphous oxide mixtures include $\text{Nb}_2\text{O}_5\text{:TiO}_2$ [59], $\text{ZrO}_2\text{:Ta}_2\text{O}_5$ [60], $\text{SiO}_2\text{:HfO}_2$ [61], and $\text{TiO}_2\text{:SiO}_2$ [62, 63]. Special attention is also given to $\text{HfO}_2\text{:Ta}_2\text{O}_5$ [61, 64, 65, 66].

These materials offer high refractive indices, but their performance is ultimately constrained by issues such as crystallization, IBS-induced intrinsic stress, and mechanical losses [20, 67]. In addition to amorphous oxides, other approaches are under investigation but are not yet applicable on a large scale [20]. Building on these general considerations, the following subsections focus on the two most relevant amorphous oxide mixtures: $\text{TiO}_2\text{:Ta}_2\text{O}_5$ (Subsection 2.3.1) and $\text{TiO}_2\text{:GeO}_2$ (Subsection 2.3.2), as well as the broader impact of annealing on their optical, structural, and mechanical properties (Section 2.3.3).

⁴In this work, the binary oxide materials investigated span a broad range of compositions, some of which fall clearly within doped-oxide regimes, others within mixed-oxide regimes, and several lying close to the compositional boundary between the two (typically around 20%–30% of the secondary oxide). For this reason, and to avoid imposing an *a priori* structural or compositional classification, we adopt a deliberately neutral notation and use both the hyphen (–) (e.g., $\text{TiO}_2\text{–Ta}_2\text{O}_5$, $\text{HfO}_2\text{–Ta}_2\text{O}_5$) and colon (:) (e.g., $\text{TiO}_2\text{:Ta}_2\text{O}_5$, $\text{HfO}_2\text{:Ta}_2\text{O}_5$) forms interchangeably.

2.3.1 Currently Adopted High-Index Material: $\text{TiO}_2\text{--Ta}_2\text{O}_5$

Tantala's amorphous network consists of distorted octahedral and bipyramidal units with a high density of edge- and face-sharing connections, a structural feature empirically correlated with increased internal friction at room temperature [68, 69, 57] (see Appendix B.3.1). Despite this intrinsic mechanical dissipation, tantala was initially adopted because of its very low optical absorption at the interferometer operating wavelength (1064 nm), amounting to about 0.6 ppm for the full multilayer stack [49]. Unless otherwise specified, all refractive-index values reported in this section refer to this same wavelength. Pure tantala has a refractive index of about 2.07 in the *as-deposited* state, decreasing slightly to ~ 2.05 after annealing at 500°C for 10 hours [56]. Titania exhibits a significantly higher refractive index, ranging from 2.3 to 2.45 in the *as-deposited* state [70], so titania–tantala mixtures naturally show values above those of pure tantala. Structurally, when introduced into the tantala matrix, titanium cations preferentially adopt five- and six-fold coordination states rather than four-fold configurations [68]. Because of this complex structural integration, the optical and mechanical properties of the mixture are not a simple weighted average of the two oxides: recent studies show that both the Urbach energy and the mechanical losses vary nonlinearly with stoichiometry [54]. For a mixture containing 27% titania, which corresponds to a minimum mechanical loss of 3.04×10^{-4} at room temperature and 1 kHz, the refractive index is 2.11 in the *as-deposited* state and 2.09 after annealing [56, 71]. The presence of two cationic species disrupts the crystalline order and inhibits crystallization, maintaining an amorphous structure that allows for higher-temperature annealing [72]. Both the structural modification induced by cation mixing and the subsequent thermal relaxation can significantly reduce the high compressive stress typically associated with ion-beam sputtering deposition [73, 20, 74].

2.3.2 Emerging High-Index Materials for Next-Generation Mirrors: $\text{TiO}_2\text{--GeO}_2$

In titania–germania films, germania improves the mechanical properties of the material system by reducing the loss angle: the amorphous germania network is predominantly composed of corner-sharing tetrahedral units (see

Appendix B.3.2), a structural feature that has been empirically shown to minimize internal friction at room temperature [57]. Conversely, titanium cations within this matrix act as both network formers and modifiers, altering the overall organization through the introduction of four-, five-, and six-fold coordinated polyhedra that integrate into the glass through mixed Ti–O–Ge linkages [75]. Although pure germania films exhibit a refractive index that is too low at 1064 nm (around 1.60 [53]), combining germania with titania increases the refractive index to values approaching 1.88 [58] and yields mechanical losses of approximately 1×10^{-4} [58], making the mixture highly promising for high-index coating applications. Because $\text{TiO}_2 : \text{GeO}_2$ has a lower refractive index than the conventional $\text{TiO}_2 : \text{Ta}_2\text{O}_5$ mixture, achieving the required end-mirror reflectivity demands a larger number of layer pairs. In the study by Fazio *et al.* [52], the coating stack consisted of 27 doublets (54 layers), while current Advanced LIGO and Virgo ETMs employ only ~ 19 doublets (38 layers), based on alternating layers of SiO_2 and $\text{TiO}_2 : \text{Ta}_2\text{O}_5$ [28]. The total optical absorption remains exceptionally low, below 1 ppm and the achieved reflectivity is remarkably high, reaching 99.9995% [52].

2.3.3 Role of Thermal Treatments in Coating Optimization

Annealing plays a crucial role for the amorphous materials used in the optical coatings of gravitational-wave detector mirrors. Deposition processes, particularly ion-beam sputtering (IBS), typically produce out-of-equilibrium coatings characterized by high residual stress [76, 77, 78, 79, 80]. For this reason, post-deposition annealing is a mandatory procedure for GWD mirrors [56]. More generally, in amorphous oxide coatings it enables structural relaxation and enhances optical and mechanical properties [54, 20], for example increasing transmittance [81, 82] and reducing absorption [45, 52]. Annealing also promotes the desorption of argon, an undesired byproduct incorporated during deposition through IBS [83, 84].

From a structural perspective, while short-range order remains largely unaffected, annealing modifies the medium-range order [85, 86, 87], reducing the fraction of polyhedra connected via faces or edges and increasing those sharing corners [69]. This rearrangement leads to a decrease in thermal noise and mechanical loss angle. Furthermore, the reduction of Urbach tails [88] - which

originate from a combination of thermal and structural disorder [89], with the latter dominating in amorphous networks [90] - correlates directly with the decrease in mechanical loss [91], further confirming the role of annealing in enhancing structural organization.

Despite these benefits, certain precautions must be considered: defects such as cracks and blisters should be avoided [92, 93], and crystallization remains a major constraint, as it induces unwanted light scattering [54]. As previously mentioned in Section 2.3, a well-established strategy to mitigate these issues is the use of multi-cation oxide coatings, which suppress crystallization during high-temperature annealing [60].

For many amorphous materials used in the optical coatings of gravitational-wave detector mirrors, however, the effects of annealing on structural and optical properties remain only partially understood. In the specific case of *titania-tantala*, much of the fundamental knowledge comes from ex-post characterizations performed not on the mixture itself, but on its two pure constituents [82, 83, 94, 95]. Further studies directly addressing the *titania-tantala* mixture [91, 54, 56] remain limited to ex-post annealing analyses. These measurements provide information only on the initial and final state of the film and do not resolve how the material evolves during the thermal cycle, leaving considerable room for optimization [74]. A similar picture emerges for $\text{TiO}_2\text{:GeO}_2$ coatings. Only a few recent studies have carried out ex-post annealing tests [58, 52, 93]. As with *titania-tantala*, these investigations probe only the initial and final state of the film and remain confined to a narrow subset of possible annealing conditions, providing no insight into the physicochemical processes occurring during the thermal cycle. This lack of in-situ information, combined with the intrinsic complexity of mixed $\text{TiO}_2\text{-GeO}_2$ networks, further underscores the scarcity of systematic studies and the presence of a significant knowledge gap.

2.4 Thesis Aim and Contribution to Existing Research Gaps

Building on the considerations outlined above, thermal noise (see 1.3.3) is intrinsically linked to the mechanical and optical properties of mirror coatings through the fluctuation-dissipation theorem (see A.3.1). Among the relevant

parameters, coating thermal noise is primarily determined by the mechanical loss angle of the constituent materials and by the total coating thickness, which for quarter-wave DBR designs is given by the sum of the physical thicknesses of all layers. Furthermore, the reflectivity of the ETM is determined by the refractive-index contrast between the high- and low-index materials forming the DBR stack (see 2.2). Photothermal noise (see A.3.4) is primarily associated with absorption phenomena. Finally, as detailed above (see 2.3.3), annealing plays a central role in improving the optical and mechanical properties of amorphous coatings and in mitigating coating thermal noise, while requiring careful control to avoid undesirable effects such as crystallization. Despite its importance, the behavior of the materials used in these coatings remains only partially understood, as most available information comes from ex-post measurements that reveal only the final state of the film and offer no insight into its evolution during the thermal cycle. To address these challenges, the present thesis advances the state of the art by enabling systematic, in-situ, real-time monitoring of coating evolution during the annealing process. The characterization method developed here provides real-time access to both optical parameters, such as refractive index, dielectric constant, and optical gap, and structural quantities, such as layer thickness and Urbach energy, offering a comprehensive picture of how annealing conditions influence coating properties. This versatile approach has enabled the investigation of materials across a wide spectrum — from well-established compounds to exotic systems scarcely documented in the literature — under elevated-temperature conditions, thereby providing valuable insights into their intrinsic behavior. The results reveal a complex material response to annealing, showing that even minor adjustments in the thermal cycle can lead to markedly different outcomes. Together, these observations underscore both the sensitivity of these systems and the importance of precise process control.

These considerations naturally lead to the experimental methodology at the heart of this thesis. The following chapter introduces ellipsometry and the theoretical principles that underpin its use in quantifying material evolution under thermal treatment.

Chapter 3

Core Technique: Ellipsometry

For most of the results presented in this thesis, ellipsometry was the primary experimental technique. The following sections outline the theoretical framework required to understand the work carried out in this study. In particular:

- *Theoretical Foundations of Ellipsometric Measurements (Section 3.1)*
Subsection 3.1.1 derives the reflection coefficients for a three-layer optical system, which serves as the reference model for describing the optical behavior of the majority of the samples examined in this work. Subsection 3.1.2 then establishes the connection between these coefficients and the ellipsometric parameters Ψ , Δ , and ρ . Subsection 3.1.3 concludes the section with a brief discussion on the choice of the angle of incidence.
- *Analytical Models and Key Physical Parameters (Section 3.2)*
Subsection 3.2.1 presents the optical models used to interpret the experimental data. Subsection 3.2.2 then outlines the main physical parameters extracted from the modeling.

3.1 Theoretical Foundations of Ellipsometry

Ellipsometry is an optical technique that measures changes in the polarization state of light upon reflection from a material surface. These polarization changes are highly sensitive to the optical properties and thickness of thin films, making ellipsometry a powerful and non-destructive characterization technique [96, 97]. By analyzing the relative amplitude and phase of the s- and p-polarized components of the reflected beam, the technique provides access to

the complex dielectric function and other key material parameters. The interpretation of ellipsometric data relies on comparing experimental measurements with optical models that describe the multilayer system under investigation. Owing to its precision and versatility, ellipsometry is widely employed in the study of thin films, coatings, and nanostructured materials [96, 98, 99]. The goal of this section is to describe the interaction between a polarized light beam and a representative sample from our temperature-dependent study, hereafter referred to as the *standard sample*. A broader and more comprehensive treatment is discussed in Appendix C.1, where the reader can find a detailed derivation of the Fresnel coefficients starting from Maxwell’s equations (together with the associated definitions of p- and s-polarized light) followed by the derivation of reflection and transmission coefficients for single- and multi-interface systems.

3.1.1 Light–Matter Interaction: Reflection Coefficients in a Three-Interface System

Our standard sample can be represented as a three-interface system, which is isotropic, homogeneous, and characterized by low surface roughness. Bottom to top, the system consists of a Single-side polished¹ silicon substrate (layer 3); a very thin native oxide layer (SiO_2 , ~ 2 nm; layer 2); a thin surface-deposited film (coating, ~ 500 nm; layer 1); and air (layer 0).

¹Single-side polishing suppresses unwanted backside reflections, as the rough unpolished bottom surface scatters the transmitted light away from the detector, avoiding the secondary reflections typically encountered in double-side polished substrates [100].

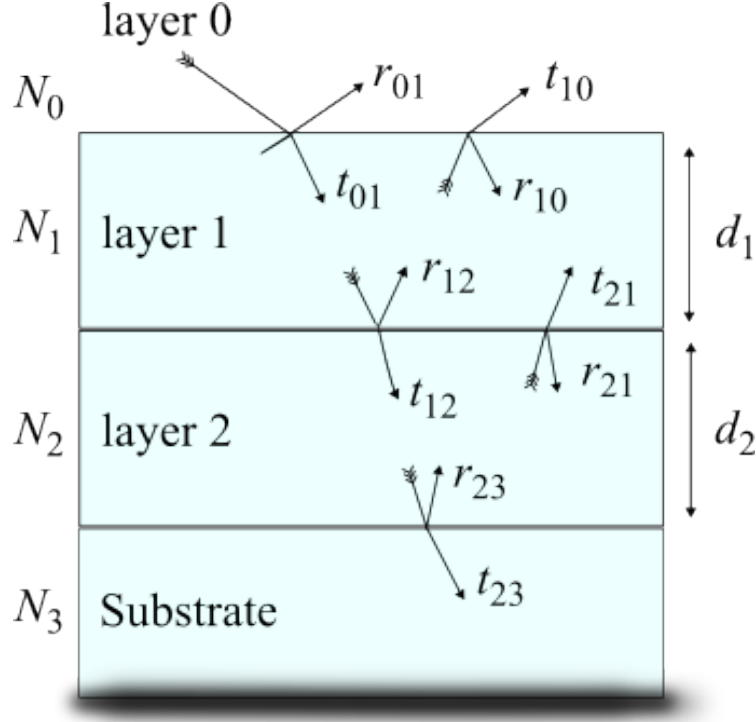


Figure 3.1: Multilayer system with three interfaces: air (layer 0) / coating (layer 1); coating / native oxide (layer 2); native oxide / single-side polished substrate (layer 3). Back-reflection is suppressed by the single-side polishing of the substrate. Image adapted from [101].

This three-interface system is illustrated in Figure 3.1. We begin by reducing it to an equivalent two-interface system. This is achieved by grouping the substrate and the second layer into an effective medium and calculating their combined reflection and transmission coefficients, r_{123} and t_{123} . In this way, we obtain Eqs. (3.1) and (3.2):

$$r_{123} = \frac{r_{12} + r_{23}e^{-i2\beta_2}}{1 + r_{12}r_{23}e^{-i2\beta_2}} \quad (3.1)$$

$$t_{123} = \frac{t_{12}t_{23}\exp(-i\beta_2)}{1 + r_{12}r_{23}\exp(-i2\beta_2)} \quad (3.2)$$

with β_2 being the phase shift caused by the 2nd layer (native oxide):

$$\beta_2 = \frac{2\pi d_2 N_2 \cos \theta_2}{\lambda} \quad (3.3)$$

and:

- r_{ij} : reflection coefficient between medium i and medium j ;

- d_2 : thickness of the second layer;
- N_2 : complex refractive index of the second layer;
- θ_2 : angle of light propagation in the second layer;
- λ : wavelength of light in vacuum.

Once r_{123} and t_{123} are known, we substitute them into the conventional two-interface equation described in Appendix C.1.3 and obtain

$$r_{0123} = \frac{r_{01} + r_{123}e^{-i2\beta_1}}{1 + r_{01}r_{123}e^{-i2\beta_1}} \quad (3.4)$$

$$t_{0123} = \frac{t_{01}t_{123}\exp(-i\beta_1)}{1 + r_{01}r_{123}\exp(-i2\beta_1)} \quad (3.5)$$

with β_1 being the phase shift caused by the 1st layer (coating).

By substituting the expressions for r_{123} (3.1) and t_{123} (3.2) into the equations for r_{0123} (3.4) and t_{0123} (3.5), we obtain an explicit form that shows how multiple reflections and interferences across all layers contribute to the total reflection and transmission coefficients:

$$r_{0123} = \frac{r_{01} + r_{12}\exp(-i2\beta_1) + [r_{01}r_{12} + \exp(-i2\beta_1)]r_{23}\exp(-i2\beta_2)}{1 + r_{01}r_{12}\exp(-i2\beta_1) + [r_{12} + r_{01}\exp(-i2\beta_1)]r_{23}\exp(-i2\beta_2)} \quad (3.6)$$

$$t_{0123} = \frac{t_{01}t_{12}t_{23}\exp[-i(\beta_1 + \beta_2)]}{1 + r_{01}r_{12}\exp(-i2\beta_1) + [r_{12} + r_{01}\exp(-i2\beta_1)]r_{23}\exp(-i2\beta_2)} \quad (3.7)$$

While these coefficients themselves do not explicitly depend on polarization, they can be adapted for either *s*- or *p*-polarization by substituting the appropriate Fresnel coefficients for r_{ij} and t_{ij} .

All equations presented above are taken from Ref. [101].

3.1.2 Ellipsometric Parameters (Ψ , Δ , ρ) and their Relation to Reflection Coefficients

The reflection coefficients previously derived for the three-layer standard sample are precisely the quantities that ellipsometry allows us to measure experimentally.

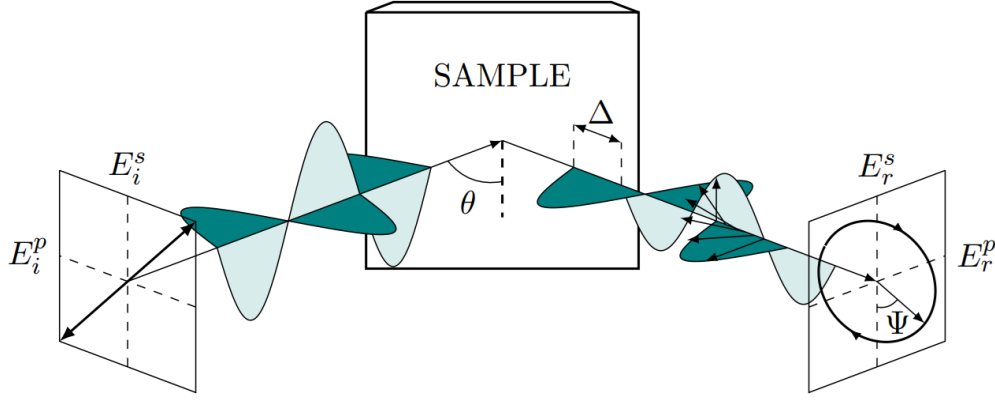


Figure 3.2: Measurement principle of ellipsometry. A linearly polarized beam impinges on the sample at an angle θ and is decomposed into its incident p- and s-polarized components: E_i^p and E_i^s . The resulting modification of the reflected components E_r^p and E_r^s defines the polarization state, which is quantified by the ellipsometric parameters Ψ and Δ , encoding the amplitude ratio and phase difference between the reflected p- and s-components. Image reproduced from [3].

Specifically, as schematized in Figure 3.2, ellipsometry measures the complex ratio between the reflection coefficients of the overall optical system for p- and s-polarized light [101, 102]. This complex reflectance ratio, denoted as ρ , is expressed in terms of the measurable ellipsometric parameters Ψ and Δ [101]:

$$\rho \equiv \tan \Psi e^{i\Delta} \equiv \frac{r_p}{r_s} \equiv \left(\frac{E_{rp}}{E_{ip}} \right) / \left(\frac{E_{rs}}{E_{is}} \right) \quad (3.8)$$

where:

- ρ is the complex reflectance ratio, describing the global change in polarization upon reflection;
- r_p and r_s are the complex amplitude reflection coefficients for p- and s-polarized light, respectively;
- E_{rp} and E_{rs} are the reflected electric field components for p- and s-polarization;
- E_{ip} and E_{is} are the incident electric field components for p- and s-polarization;

- Ψ is the amplitude ratio angle, defined through $\Psi = \arctan\left(\left|\frac{r_p}{r_s}\right|\right)$, representing the amplitude ratio of the reflection coefficients;
- Δ is the relative phase shift between the p- and s-polarized components induced upon reflection.

These measured values, Ψ and Δ (or equivalently ρ), as will be explained in Section 3.2, can subsequently be compared with theoretical predictions generated by optical models through a fitting procedure.

3.1.3 Selecting the Experimental Angle of Incidence: Brewster and Pseudo-Brewster Angles

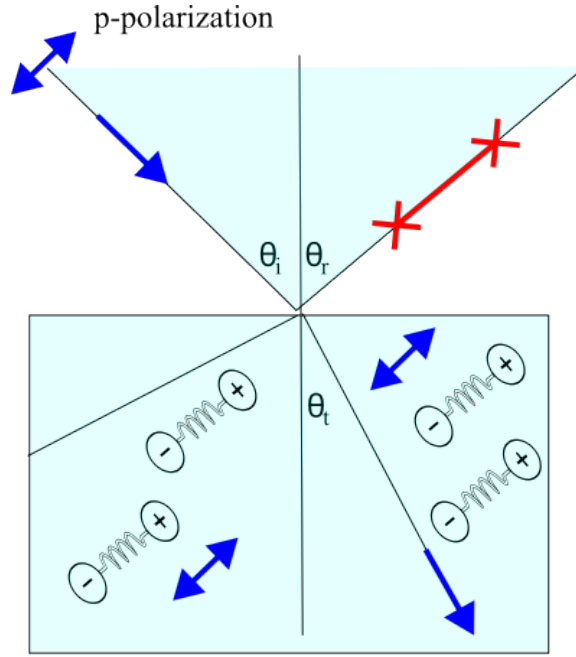
To enhance the sensitivity of the measurement, it is advantageous to operate near the *Brewster angle* (θ_B), where the difference between the reflectance of s- and p-polarized light is maximized. This increased contrast in the optical response increases the ellipsometric signal and improves the accuracy of the measurement [101]. The Brewster angle depends on the refractive indices of the media and, for an interface between two transparent media, follows Brewster's Law [103, 104]:

$$\tan \theta_B = \frac{n_t}{n_i} \quad (3.9)$$

where:

- θ_B is the Brewster angle,
- n_i is the real refractive index of the incident medium (e.g. air),
- n_t is the real refractive index of the transmitting (or refracted) medium (e.g. coating).

It should be noted that when dealing with absorbing media (where the extinction coefficient $k > 0$), or in complex multilayer systems, the situation changes. Because the Fresnel reflection coefficients become complex numbers, the p-polarized reflectance R_p never drops exactly to zero [103]. Instead, one identifies a *pseudo-Brewster angle* (θ'_B) corresponding to the angle of incidence where the overall R_p reaches a minimum [104].



At the Brewster angle, **p-polarized light** undergoes **zero reflection**.

Figure 3.3: Physical interpretation of the Brewster angle using the dipole-radiation model. When p-polarized light is incident on the interface at the Brewster angle, the induced dipoles in the material oscillate in a direction that prevents them from reradiating energy along the reflection direction. As a consequence, the reflected p-polarized component is suppressed, while the transmitted beam continues into the second medium. Image adapted from [101].

From a conceptual point of view, this behavior can be intuitively understood by considering electric dipole radiation (see Fig. 3.3). When the angle of incidence θ_i is slightly below θ_B , the reflected p-polarized component is still present, but reduced. As θ_i approaches θ_B , the direction of the reflected beam becomes increasingly aligned with the oscillation axis of the dipoles induced in the material. At exactly $\theta_i = \theta_B$, these dipoles do not radiate in the reflection direction for p-polarized light, leading to zero (or to a minimum, in absorbing media) of R_p . In contrast, s-polarized light, whose dipole oscillations are perpendicular to the plane of incidence, continues to reflect with non-zero intensity. For our standard temperature-dependent measurements, the experimental apparatus was designed to operate with a fixed incidence angle of 70° . This value is a suitable choice for a wide range of semiconductor and dielectric characterizations, as their Brewster (or pseudo-Brewster) angles typically fall within the 70° – 80° range. For instance, silica has a Brewster angle of about

56° , while crystalline silicon exhibits a pseudo-Brewster value of $\sim 74^\circ$ [101], and tantalum exhibits a value of $\sim 64^\circ$ [56].

3.2 Analytical Models and Physical Parameters

Once the angle of incidence has been set and the measurement procedure completed - yielding the experimental values of Ψ and Δ as a function of wavelength (in our case, a full set of $\Psi(\lambda)$ and $\Delta(\lambda)$ for each temperature) - the next and most critical step [101] is to construct an optical model capable of accurately describing the sample's structure and optical properties. Specifically, an optical model is a theoretical representation of the sample's layered structure. For each individual layer, the model must specify two main categories of parameters. The first category includes the optical properties, characterized by the complex refractive index ($N = n - ik$) or, equivalently, the complex dielectric function ($\varepsilon = \varepsilon_1 - i\varepsilon_2$) [101, 103]. Since these functions are often unknown across the entire spectral range, they are described using specific mathematical expressions known as *dielectric function models*. Common examples include the Cauchy or Sellmeier equations for transparent materials, the Drude model for free-carrier absorption, and Lorentz-type oscillators such as the Tauc-Lorentz models for describing interband transitions. The second category involves structural and morphological parameters, primarily the physical thickness (d) of each layer. To achieve high accuracy, realistic models must also account for non-ideal features such as interfacial layers and surface roughness. Interfacial regions are typically described using the Effective Medium Approximation (EMA), which treats the interface as a homogeneous layer composed of a physical mixture of the two adjacent materials in appropriate volume fractions. Surface roughness is handled in an analogous way: the rough top layer is modeled as an EMA mixture of the underlying bulk material and voids (air) [103, 101]. In addition, the software used in this work (WVASE) allows the user to include further non-idealities such as thickness non-uniformity², angle spread³, and spectral bandwidth⁴.

²A variation of the film thickness across the sample.

³A small angular divergence of the incident beam, so that the measurement is effectively performed over a narrow range of incidence angles rather than a single one.

⁴The finite wavelength interval over which each spectral point is measured, due to the non-zero bandwidth of the light source or monochromator.

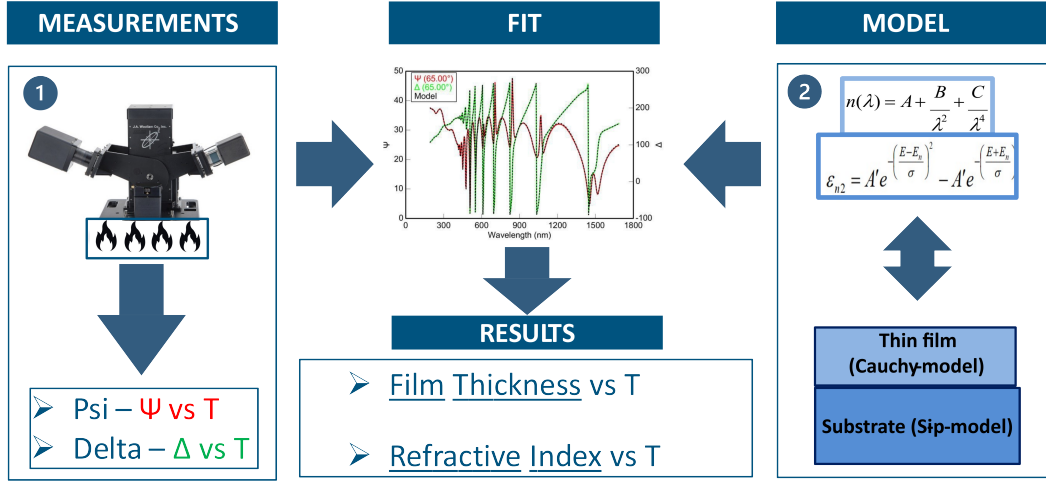


Figure 3.4: Schematic overview of a standardized optical characterization process.

1) The experimental measurement begins: the sample is heated and ellipsometric spectra are acquired in situ during the annealing process. 2) Optical models are constructed to describe the sample structure. 3) A regression procedure is performed to fit the simulated data to the experimental Ψ and Δ values. 4) Key physical parameters are extracted, such as the coating thickness and the refractive index. Image adapted from [105].

To construct the model, we begin by assigning an initial guess to the properties of each layer in the sample. These initial values are typically based on literature data or prior expertise [97]. Based on this initial configuration, the theoretical values of Ψ and Δ are calculated and compared with the experimental measurements. A linear regression analysis (LRA) is then performed, during which the model parameters are iteratively adjusted so that the simulated Ψ and Δ progressively converge toward the experimental data [106, 103, 101]. The quality of the fit is monitored using a metric known as the *Mean Squared Error (MSE)* [107, p. 61], defined as:

$$\text{MSE} = \sqrt{\frac{1}{2N - M} \sum_{i=1}^N \left[\left(\frac{\Psi_i^{\text{mod}} - \Psi_i^{\text{exp}}}{\sigma_{\Psi_i}} \right)^2 + \left(\frac{\Delta_i^{\text{mod}} - \Delta_i^{\text{exp}}}{\sigma_{\Delta_i}} \right)^2 \right]} \quad (3.10)$$

where:

- MSE: Mean Squared Error, the metric minimized during the fitting process.
- N : Number of measured data points, i.e., pairs (Ψ, Δ) .

- M : Total number of real-valued fitting parameters.
- Ψ_i^{exp} : Experimental value of Ψ at point i .
- Ψ_i^{mod} : Modeled (simulated) value of Ψ at point i .
- σ_{Ψ_i} : Standard deviation (uncertainty) associated with Ψ_i^{exp} .
- Δ_i^{exp} : Experimental value of Δ at point i .
- Δ_i^{mod} : Modeled (simulated) value of Δ at point i .
- σ_{Δ_i} : Standard deviation (uncertainty) associated with Δ_i^{exp} .

Through this iterative procedure, the model ultimately yields the key physical and optical parameters of the sample, such as layer thicknesses and refractive indices.

3.2.1 Key Models for Data Analysis

All the functional forms used to construct the dielectric function of our samples, with the exception of the Pole and Cauchy models, are *Kramers–Kronig* (KK) consistent. KK consistency ensures that the real and imaginary parts of the *complex dielectric function* and *refractive index* are physically linked through causality, meaning that the material’s optical response obeys fundamental physical principles [108]. This relationship is mathematically expressed through the Kramers–Kronig integral relations, as shown in the following equations [96]:

$$\epsilon_1(E) - 1 = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{E' \epsilon_2(E')}{E'^2 - E^2} dE', \quad (3.11)$$

$$n(E) - 1 = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{E' k(E')}{E'^2 - E^2} dE', \quad (3.12)$$

Where:

- $n(E)$: the real part of the complex refractive index at energy E .
- $k(E)$: the imaginary part of the complex refractive index (also known as the extinction coefficient).
- $\epsilon_1(E)$: the real part of the complex dielectric function.

- $\epsilon_2(E)$: the imaginary part of the complex dielectric function.
- E : photon energy at which the function is evaluated.
- E' : integration variable representing photon energy.
- $\mathcal{P}$: the Cauchy principal value.

It is important to note that, although the *Cauchy model* is not KK-consistent, this does not imply that it lacks physical meaning. It remains widely used for transparent, non-absorbing materials in spectral regions where absorption is negligible [101]. In such cases, the lack of KK consistency is not critical, and the model can still yield accurate and reliable refractive index values. However, its use requires caution, particularly when extrapolating beyond the measured spectral range or when absorption becomes non-negligible, as it may lead to non-physical dispersion behavior [96].

Recalling that our standard sample consists of a silicon substrate (0.5 mm), a thin native silica layer (~ 2 nm), and a thin coating (~ 500 nm), and considering that the aim is to investigate the effect of annealing on the optical properties of the sample, it is important to note that each model must incorporate the temperature dependence of the optical properties of the individual layers. We therefore describe the optical response of each layer as follows, from bottom to top:

- The silicon substrate was modeled using a *multiparametric dielectric function model* developed by J. A. Woollam Co., Inc. [108]. In particular, among the multiple nominally identical silicon samples subjected to different annealing cycles, the most reliable dataset was selected, and a set of standard models was constructed, each corresponding to a specific temperature from room temperature up to 600°C in 5°C increments. These models, obtained directly from experimental data, were used as reference (see Section 5.1). Since the temperature-induced changes in the optical properties of crystalline silicon [109], are fully reversible within the investigated temperature range [101, 103], the same models were applied during both the heating and cooling phases.
- The native silica layer was modeled using a library approach, i.e., with fixed optical constants characteristic of the material. Experimental measurements on silica (see Section 5.2) confirm that, in the standard sam-

ple, this layer remains optically stable and is accurately reproduced by the library model up to 600 °C, as both its refractive index and thickness remain essentially unchanged [101]. Conversely, for deposited silica (e.g., a 500 nm layer grown on top of the substrate), the refractive index remains essentially constant, while the thickness increases with temperature. This macroscopic expansion is primarily driven by structural relaxation and the release of internal stress within the amorphous network, rather than by oxygen diffusion and the associated additional oxidation [110, 20].

- The coating was modeled using the *general oscillator (GenOsc)* approach, which models the dielectric function as a superposition of analytical oscillators, each characterized by a specific number of parameters. In the transparent spectral range (900–1600 nm), a *Cauchy* model, optionally complemented by a *Pole–Oscillator* term, was employed to determine the film thickness and refractive index. Once the thickness was established, a *Cody–Lorentz* model, again optionally including a *Pole* term, was applied to the full spectral range, yielding parameters such as the optical gap and the Urbach energy. This two-step procedure is a well-established strategy for ellipsometric data analysis [101, 3], and was consistently adopted for all samples at each temperature.

All these models — GenOsc, Cauchy, Cody–Lorentz, and Pole oscillators — together with the introductory modeling framework, are described in greater detail in Appendix C.2. The key physical parameters extracted from them, such as the optical gap and the Urbach energy, are discussed in Section 3.2.2.

3.2.2 Key Physical Parameters

The key parameters considered in this study, extracted through the modeling procedure, are as follows:

- *Coating Thickness*: Owing to the high sensitivity of ellipsometry to thickness variations, this technique enables highly precise measurements [101]. Thickness represents a valuable indicator of the material’s structural evolution during annealing, since in amorphous materials structural rear-

rangements are often accompanied by measurable changes in thickness. In addition, the deposition process via IBS can introduce internal stresses within the film, which are progressively relaxed during annealing: another factor contributing to thickness variation [28, 74, 111]. Thermal expansion or contraction induced by temperature changes also directly affects the physical thickness of the coating [112], although this effect represents a marginal contribution, as discussed in Appendix D.1.. For these reasons, monitoring thickness evolution throughout the annealing process is crucial both for understanding the material's behavior and for optimizing thermal treatment protocols.

- *Refractive Index* (n and k): The refractive index is a complex quantity defined as [101, p. 22]⁵:

$$\tilde{n} = n - ik. \quad (3.13)$$

The real part n is defined as [113, p. 3].:

$$n = \frac{c}{v}, \quad (3.14)$$

where c is the speed of light in vacuum and v is the phase velocity of light in the medium. The imaginary part k is the extinction coefficient, which is directly related to the absorption coefficient α by [101, p. 23]:

$$\alpha = \frac{4\pi k}{\lambda}, \quad (3.15)$$

where λ is the wavelength of light in vacuum. This coefficient quantifies the attenuation of light as it propagates through a medium according to Beer's law:

$$I(z) = I_0 e^{-\alpha z}, \quad (3.16)$$

where I_0 is the incident intensity, $I(z)$ is the transmitted intensity, and z is the propagation distance [113, p. 3]. The complex refractive index is related to the complex (relative) dielectric function $\tilde{\varepsilon}$ through [101, p. 29]:

$$\tilde{n} = \sqrt{\tilde{\varepsilon}} = \sqrt{\varepsilon_1 - i\varepsilon_2}, \quad (3.17)$$

where ε_1 and ε_2 are the real and imaginary parts of the dielectric function, respectively. Both n , k , ε_1 , and ε_2 are wavelength-dependent and provide critical insight into the optical behavior of a material.

⁵In this formula we adopt the so-called “Nebraska convention”, which is the standard reference in ellipsometry and optical modeling [101].

- *Optical Gap* (E_g)⁶: In crystalline solids, the band gap corresponds to the minimum energy required to excite an electron from the valence to the conduction band [114, 113]. In amorphous materials, however, the absence of long-range order blurs the band edges and generates localized states extending into the forbidden gap [103]. In this case, the bandgap is no longer a sharp threshold: the *optical gap* is defined as the empirical energy at which optical transitions between extended states begin [101], and is typically extracted through methods based on the linear extrapolation of the absorption edge in the region dominated by extended states [114]. When the photon energy exceeds the optical gap (E_g), strong interband absorption takes place. The value of E_g therefore also serves as an indicator of the material’s transparency. In applications that demand extremely low optical absorption, such as the coatings of the Virgo interferometer mirrors operating at 1064 nm (corresponding to a photon energy of about 1.16 eV), the behavior of the optical gap and of the sub-gap states becomes critical. Typical room-temperature values for the high-refractive-index amorphous oxides used in these multilayer stacks lie in the range $E_g \approx 3.5\text{--}3.8$ eV [20, 104].
- *Urbach Energy* (E_U): As formally described by Adachi [103], the Urbach tail originates from the structural disorder of the material, which destroys the sharp band edges and causes a tailing of the localized electronic density of states (DOS) directly into the forbidden gap. A lower E_U indicates a more ordered atomic network with fewer defects and improved short- and medium-range structural organization [20], whereas a higher E_U reflects increased disorder and structural inhomogeneity. Moreover, reduced Urbach energies have been empirically correlated with lower mechanical losses [91], which are the dominant source of coating thermal noise in state-of-the-art interferometers. The absorption tail follows the well-known Urbach rule [103]:

$$\alpha(E) = \alpha_0 \exp\left(\frac{E - E_g}{E_U}\right), \quad (3.18)$$

⁶In crystalline semiconductors, the symbol E_g typically denotes the electronic bandgap, whereas in amorphous materials the parameter E_0 is more appropriately used to describe the optical gap. However, the WVASE software adopts the notation E_g as the fitting parameter in its dispersion models. Since this thesis has a strongly application-oriented focus and directly refers to results obtained using WVASE, the notation E_g is retained for consistency.

where α_0 is a material-dependent constant, E is the photon energy, and E_U is the Urbach energy. Annealing-induced structural relaxation typically reduces E_U [74].

Chapter 4

Optimization of the Experimental Setup and Implementation of a Reproducible Optical Characterization Method

This chapter begins with an introductory section entitled *Ellipsometric Experimental Setup* (Section 4.1), which describes the experimental setup employed for the measurements. Starting from this experimental setup, we developed a comprehensive protocol for in-Situ Real-Time Ellipsometry optical characterization, designed to provide reliable, reproducible, and directly comparable results across different samples. The establishment of this protocol required a systematic characterization of the experimental apparatus, the identification and mitigation of potential sources of error, and the full automation of data acquisition during the annealing cycle, analysis, and graphical representation. In this way, the outcome of this work is not only a set of measurements but a robust and standardized methodology applicable to a wide range of materials. A standard full optical characterization involves a cycle of acquisitions comprising thousands of data points collected as a function of temperature and wavelength. For each temperature, an optical model is constructed, and a fitting procedure is performed between the experimental data and the model-generated data, with the goal of minimizing the Mean Squared Error (MSE). Following the fitting process, the extracted optical parameters are interpreted and compared with those obtained from other samples. Given

the complexity and duration of this procedure, it was necessary to standardize the workflow to ensure meaningful and directly comparable results. The standardization process was carried out in three main directions:

1. *Evaluation and Mitigation of Systematic Errors* (Section 4.2): In this section, a thorough analysis was conducted to characterize the experimental setup, identify systematic errors, and, where possible, eliminate or mitigate them.
2. *Choice of the Fitting Protocol* (Section 4.3): This section examines the influence of the fitting strategy on the final results. Defining a consistent modeling and fitting approach was a key step in consolidating the workflow.
3. *Standardization of Data Analysis and Automation* (Section 4.4): This section describes the full automation of the sample-characterization workflow through custom scripts that manage all stages of the measurement process. From scan execution to data acquisition, model generation, fitting, and graphical output, the entire procedure is standardized to ensure consistency, reproducibility, and efficiency. The scripts incorporate the optimized fitting protocols and refined optical models developed in the previous sections and are designed to reduce systematic errors such as beam misalignment, scan-timing variations, and temperature inaccuracies identified during the apparatus characterization.

4.1 Description of the Ellipsometric Experimental Setup

In this work, two spectroscopic ellipsometers from J.A. Woollam Co. were employed, chosen for their complementary characteristics in terms of spectral range and optical configuration:

- *M-2000 (RCE)*: spectral range 245–1680 nm, horizontal sample configuration. This rotating compensator ellipsometer enables very rapid measurements, making it particularly suitable for *in situ* and real-time applications. It served as the primary investigative instrument in this study.

- *VASE (RAE)*: with a spectral range of 190–2500 nm and a vertical sample configuration, this rotating analyzer ellipsometer provides higher sensitivity and a broader spectral range. However, its substantially longer acquisition times make it unsuitable for real-time measurements. It was therefore employed as a complementary instrument to the M-2000 for ex-post analyses.

This section focuses exclusively on the technical details of the main experimental setup employed in this work, namely the M-2000 coupled with the heating stage. A broader discussion of ellipsometer configurations, together with their theoretical description based on the Jones formalism, is presented in Appendix¹ C.3.

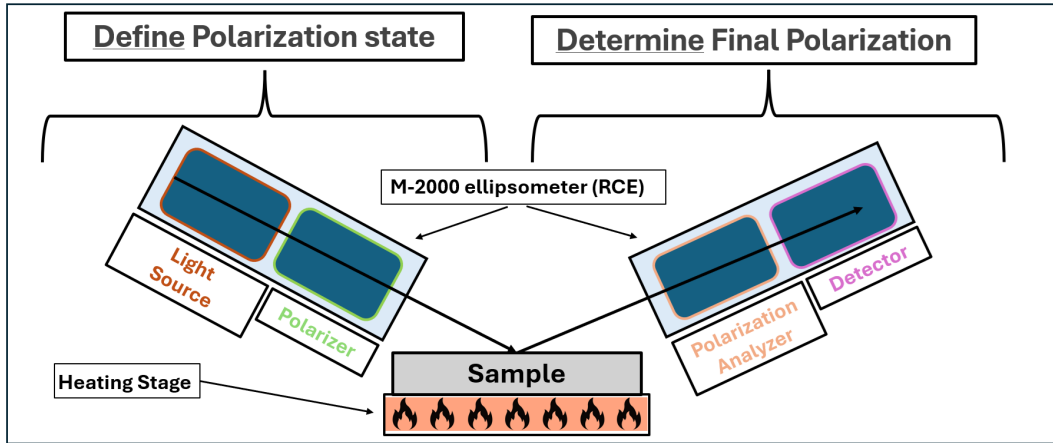


Figure 4.1: Schematic representation of the experimental setup used for real-time ellipsometric measurements, featuring an M-2000 RCE ellipsometer coupled with a Linkam THMS600 heating stage for temperature-controlled analysis. Image adapted from [105].

Figure 4.1 illustrates the experimental setup employed for real-time ellipsometry measurements, comprising an M-2000 ellipsometer coupled with a heating stage. The heating stage is a Linkam THMS600 [115], a high-precision

¹The structure of this manuscript establishes a clear distinction between theoretical and experimental material: Chapter 3 and its corresponding appendix contain the theoretical background relevant to our ellipsometric work, whereas Chapter 4 and its appendix are devoted to the experimental apparatus, measurement procedures, and the evaluation of uncertainties. Although the reference to Appendix C.3 appears in Chapter 4, it refers to material that is mainly theoretical and therefore remains linked to the appendix of Chapter 3 rather than to the appendix accompanying the "experimental" chapter 4.

thermal control stage designed for experiments involving optical microscopy and spectroscopic techniques under *in-situ* conditions. The system enables thermal analysis of samples over a temperature range from -196°C (when equipped with the optional cooling feature) up to 600°C , with thermal stability better than 0.01°C . Heating is provided by a resistive element embedded within a high-thermal-conductivity cylindrical silver block, allowing ramp rates up to $150^{\circ}\text{C min}^{-1}$. Temperature control is managed by a Pt1000 sensor (class 1/10 DIN B), ensuring high measurement accuracy.

Spectroscopic ellipsometry (SE) measurements were carried out using a J.A. Woollam Co., Inc. M2000 ellipsometer [116], which operates across a broad spectral range from 245 to 1685 nm (corresponding to 0.7–5.1 eV or $0.18\text{--}1.22 \times 10^{15}$ Hz). The system provides a spectral resolution of 1.5 nm between 245 and 1000 nm (inclusive), and 3.4 nm from 1000 to 1685 nm. It employs a collimated beam with an approximate diameter of 4 mm. Data acquisition was managed using the WVASE software suite [117]. Spectra were continuously recorded throughout the experimental procedure, with a temporal resolution of less than 3 s per spectrum, ensuring high temporal fidelity in tracking dynamic changes in the sample’s optical properties. The sample, with lateral dimensions of $\sim 1 \times 1 \text{ cm}^2$, was mounted on a temperature-controlled stage enclosed by a top cover equipped with two optical-grade windows. These windows were specifically designed to allow ellipsometric measurements while maintaining a fixed angle of incidence of 70° . All measurements were performed in air, with the chamber atmosphere left unmodified.

4.2 Assessment and Mitigation of Systematic Errors in the Experimental Setup

This section is divided into three parts:

- a) Subsection 4.2.1 examines the impact of introducing the Linkam heating stage into the ellipsometric optical path. In this configuration, the sample is enclosed beneath the stage cover, with the probing beam passing through the windows prior to and following interaction with the surface, which may potentially introduce systematic errors.
- b) Subsection 4.2.2 examines the light-misalignment errors occurring within

the detector arising from temperature-dependent effects, including deformations of the sample holder and the increase in sample thickness.

- c) Subsection 4.2.3 addresses two primary sources of uncertainty: the actual time interval between consecutive ellipsometric scans and the effective temperature of the sample. These sources of error are considered jointly, as they introduce analogous deviations in the experimental data.

4.2.1 Evaluation of Window-Induced Effects

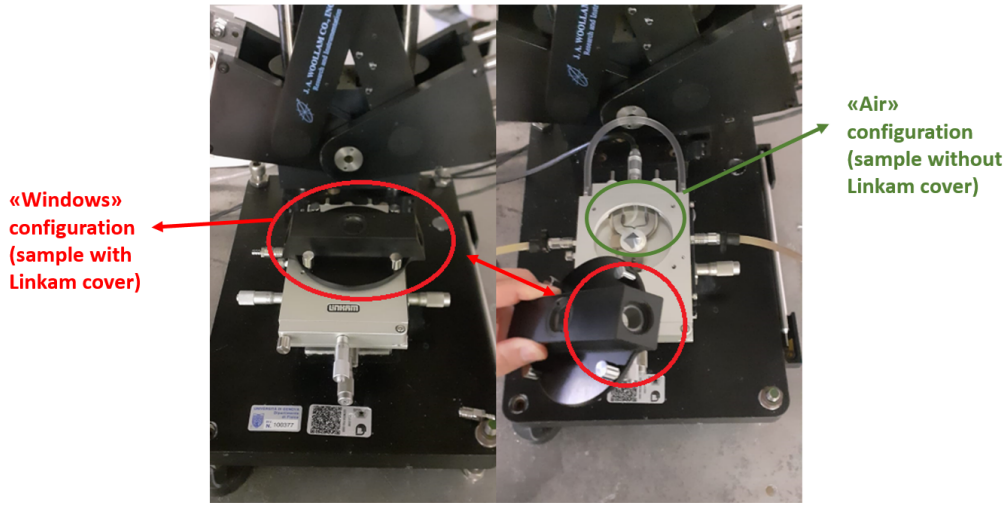


Figure 4.2: Schematic representation of the two configurations of the experimental apparatus (an M-2000 ellipsometer coupled with a Linkam heating stage). The “Air” configuration corresponds to the case in which the sample is exposed to air and the probing beam is directly reflected from its surface, whereas the “Windows” configuration refers to the enclosed setup in which the probing beam passes through a first window, reflects off the sample, and then traverses a second window before reaching the detector. For clarity, we note that in both configurations no inert atmosphere is employed: the annealing is performed in air, fully consistent with the Virgo protocol [74].

Figure 4.2 illustrates the two experimental configurations adopted to assess the influence of the Linkam Heating Stage windows introduced into the ellipsometric setup. In the “Air” configuration, the probing beam is directly reflected by the sample surface. In the “Windows” configuration, used during heating above 200 °C, the beam passes through a first window, reflects off the

sample, and then goes through a second window before reaching the detector. In both cases, the optical path occurs in air, consistent with the standard Virgo annealing procedure [20, 28]. Two batches of samples were analyzed: a) crystalline silicon, used as a reference material and representative of the substrate; b) titania–germania ($\text{TiO}_2\text{--GeO}_2$) films deposited on silicon, corresponding to the samples used for the official measurements. Each sample was measured twice under identical conditions, with and without the Linkam windows, enabling a direct comparison and isolation of window-induced artifacts. All measurements were performed at room temperature, either before or after an annealing cycle.

Window-Induced Effects on Crystalline Silicon Figure 4.3 shows the ellipsometric difference spectra $\delta\Psi$ and $\delta\Delta$ for crystalline silicon, where $\delta\Psi = \Psi_{\text{Windows}} - \Psi_{\text{Air}}$ and $\delta\Delta = \Delta_{\text{Windows}} - \Delta_{\text{Air}}$. The data derive from five independent measurements, each performed after a complete annealing cycle (Table 4.1). After each cycle, the sample was cooled to room temperature, measured in both configurations, and their difference was calculated to isolate the effect of the windows.

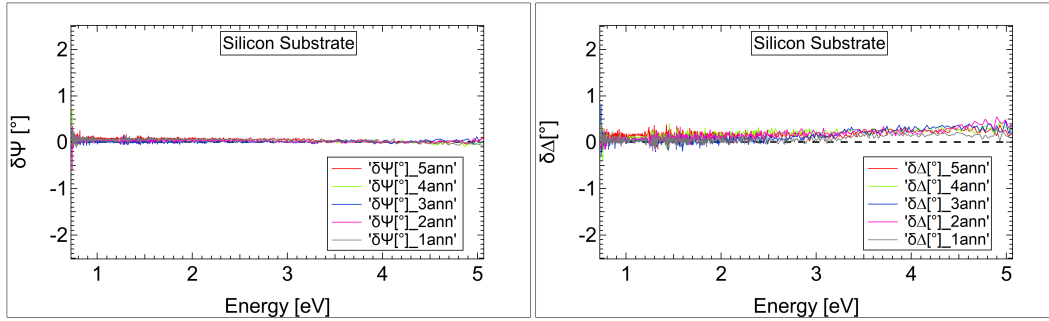


Figure 4.3: Ellipsometric difference spectra $\delta\Psi$ (left) and $\delta\Delta$ (right) for crystalline silicon in the 0.7–5.1 eV range. Each curve represents the difference between measurements acquired with the Linkam windows and those obtained in air, i.e., $\delta\Psi = \Psi_{\text{windows}} - \Psi_{\text{air}}$ and $\delta\Delta = \Delta_{\text{windows}} - \Delta_{\text{air}}$. The five curves correspond to measurements acquired at the end of the annealing cycles listed in Table 4.1.

Table 4.1: Parameters of annealing cycles performed on crystalline silicon substrates. Each cycle was carried out before the ellipsometric measurements. After the sample had cooled back to room temperature, measurements were performed in both the Air and Window configurations.

Ann. Cycle	Ann. Temperature [°C]	Ann. Time [min]	H/C rate [°C/min]
1	300	30	10
2	300	30	10
3	400	30	10
4	500	30	10
5	600	30	10

The average variation between the two configurations is below 0.1° for Ψ and below 0.4° for Δ . The mean value of $\delta\Psi$ remains centered around zero over the entire spectral range, whereas the mean value of $\delta\Delta$ is centered around zero up to approximately 2.5 eV and shifts to about 0.2 from 2.5 eV up to 5 eV. Δ is the parameter most affected by the windows, particularly above 3 eV in the UV–VIS region. Despite the increase observed at higher photon energies, these deviations remain small compared with the typical measurement values (see the next paragraph, Sec. 4.2.1) and do not show any systematic trend across the annealing cycles. This indicates that the windows do not undergo permanent optical modifications during high-temperature operation.

Window-Induced Effects on Titania–Germania Films Figure 4.4 presents the ellipsometric difference spectra of three TiO_2 – GeO_2 samples ((1), (2), (3)).

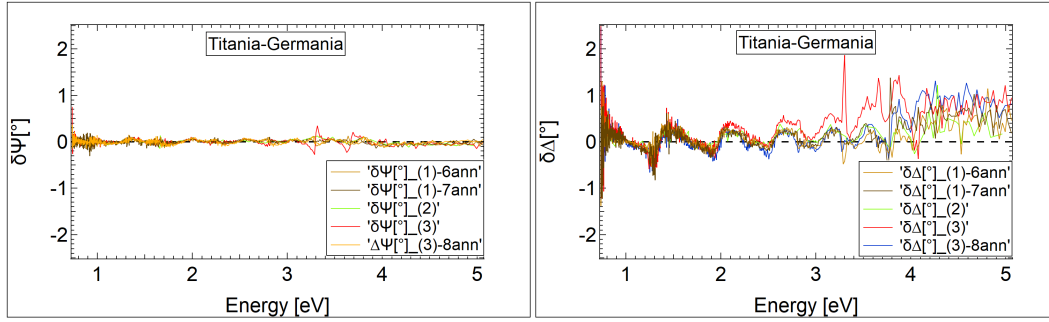


Figure 4.4: Ellipsometric difference spectra $\delta\Psi$ (left) and $\delta\Delta$ (right) for titania-germania ($\text{TiO}_2\text{-GeO}_2$) films deposited on silicon. Each curve represents the difference between measurements acquired with the Linkam windows and those obtained in air, i.e., $\delta\Psi = \Psi_{\text{windows}} - \Psi_{\text{air}}$ and $\delta\Delta = \Delta_{\text{windows}} - \Delta_{\text{air}}$. The curves correspond to measurements performed on three distinct samples, acquired before and/or after the annealing cycles listed in Table 4.2. Sample (1) was measured only after annealing under different conditions; sample (2) was measured only prior to annealing; whereas sample (3) was characterized both before and after annealing.

As in the case of silicon, all measurements were performed in both air and windows configurations at room temperature. For these high-index films, the average variations in Ψ remain below 0.1, while those in Δ stay below 0.8, with the largest deviations occurring above 4 eV. The mean value of $\delta\Psi$ oscillates around zero across the entire spectral range, whereas the mean value of $\delta\Delta$ oscillates around zero (with larger fluctuations than in silicon) up to approximately 3 eV and around 0.5 from 3 eV to 5 eV. Although $\delta\Delta$ can reach amplitudes of about 0.8°, these oscillations remain small when compared to the typical values of Δ in the wavelength range of interest (e.g., $\Delta \approx 170^\circ$ for $\lambda > 600\text{ nm}$; see Fig. 5.1). Importantly, a comparison between Figure 4.3 and Figure 4.4 shows that the oscillations observed below 4 eV are absent in the silicon reference, and therefore cannot be attributed to the windows. Their occurrence solely in the $\text{TiO}_2\text{-GeO}_2$ samples indicates that these features are linked to the film-dependent optical behavior, rather than to any window-related effect, which would otherwise appear consistently in both sample types. Consequently, the contribution of the windows can be regarded as negligible in the overall error budget.

Table 4.2: Parameters of the annealing cycles performed on titania–germania ($\text{TiO}_2\text{--GeO}_2$) samples deposited on crystalline silicon. Measurements were conducted at room temperature, both before and after annealing. The heating rate was set to 50 or 100 °C/h.

Ann. Cycle	Ann. Temperature [°C]	Ann. Time [min]	H/C rate [°C/h]
6	600	600	50
7	600	600	50
8	600	0	100

4.2.2 Temperature-Induced Misalignment

An additional characterization step required for the standardization of the measurement workflow concerns the behavior of optical-beam misalignment at elevated temperatures. In this context, misalignment refers to the situation in which the light reflected from the sample does not strike the center of the four-quadrant photodiode detector. This causes a partial loss of signal and, more importantly, alters the effective angle of incidence measured by the ellipsometer. To address this, the instrument includes a two-axis tilt platform that allows the beam spot to be manually centered on the detector. This mechanical system is coupled to dedicated software that provides the X and Y coordinates. In this convention, X represents the out-of-plane displacement (along the direction normal to the sample surface), whereas Y corresponds to the in-plane displacement (right–left on the detector, parallel to the sample surface). The software also reports the intensity of the light reaching the detector. Under standard room-temperature conditions, alignment is typically performed once prior to data acquisition; however, during high-temperature measurements, alignment becomes a critical parameter and must be continuously monitored. During heating, the system naturally tends to drift out of alignment. This behavior is primarily attributed to the thermal expansion of the mechanical components of the experimental setup as temperature increases. To quantitatively assess the misalignment and evaluate its impact on the measurements, crystalline silicon was selected as the reference material, as it is a well-established standard in ellipsometry and corresponds to the substrate of the samples investigated in this work. Two pieces

cut from the same silicon wafer² were subjected to two nominally identical annealing cycles consisting solely of heating (no plateau or cooling), with a heating rate of 200 °C/h from room temperature to 600 °C. Ellipsometric spectra were acquired every 5 °C, together with the alignment values (X and Y) and the detector intensity. For the first silicon piece, hereafter referred to as Silicon-MIS (misaligned), no realignment was performed during heating. For the second piece, referred to as Silicon-AL (aligned), the operator systematically realigned the beam throughout the entire temperature cycle. Figure 4.5 reports the results of the two heating experiments. The left panels show the alignment values measured from 30 °C to 600 °C, while the right panels display the differences in the ellipsometric parameters Ψ and Δ at three selected temperatures (175, 200, and 230 °C) between Silicon-MIS and Silicon-AL. These comparisons allow us to quantify the potential measurement errors induced by misalignment.

²Two pieces of 1 cm² cut from the same single-side polished silicon wafer from Nanovision S.r.l., with the following characteristics: P-doped, resistivity $\rho < 1 \text{ } \Omega \cdot \text{cm}$, orientation (100) $\pm 0.5^\circ$, and thickness of 0.5 mm.

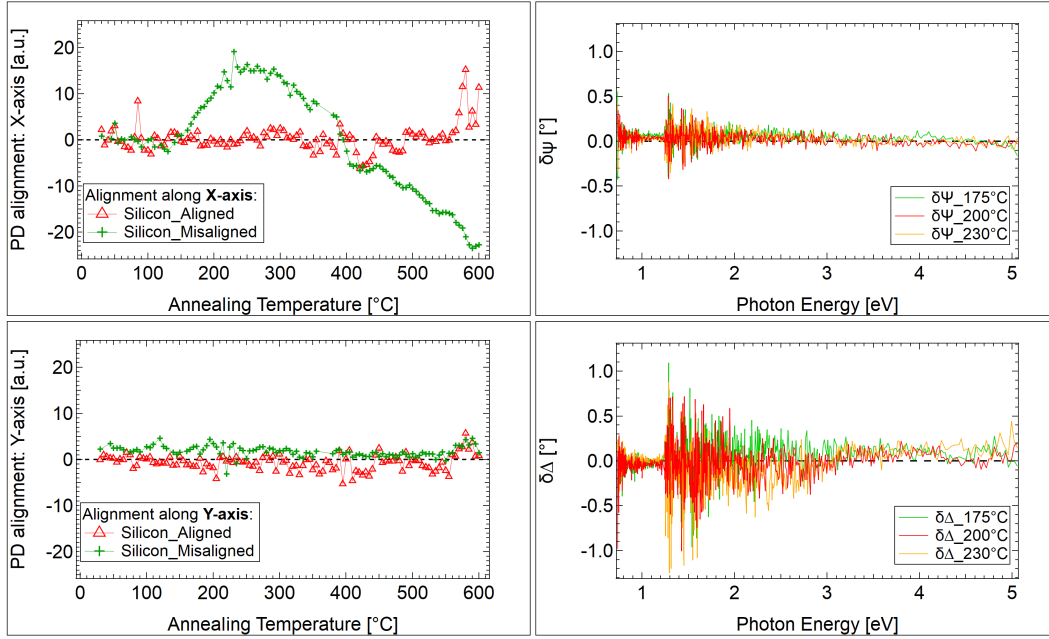


Figure 4.5: Left: Photodiode (PD) alignment signal, expressed in arbitrary units [107], measured along the X-axis (top panel) and Y-axis (bottom panel) as a function of temperature. In this convention, the X-axis corresponds to the out-of-plane direction (normal to the sample surface), whereas the Y-axis corresponds to the in-plane right-left direction on the detector (parallel to the sample surface). The experiment was carried out on a crystalline silicon sample progressively heated from room temperature to 600 °C at a rate of 200 °C/h.

Right: Difference between misaligned and aligned Ψ and Δ , defined as $\delta\Psi = \Psi_{\text{misaligned}} - \Psi_{\text{aligned}}$ and $\delta\Delta = \Delta_{\text{misaligned}} - \Delta_{\text{aligned}}$, measured on the same crystalline silicon sample. The values shown correspond to measurements taken at 175 °C, 200 °C, and 230 °C. For each temperature, the corresponding misalignment values were: $X_1 = 5.9$, $Y_1 = 2.9$ (175 °C); $X_2 = 10.2$, $Y_2 = 3.5$ (200 °C); $X_3 = 19.2$, $Y_3 = 3.5$ (230 °C).

Several considerations emerge from the analysis:

1. The X coordinate is strongly affected by temperature, while the Y coordinate remains essentially constant and can therefore be neglected. This behavior arises because X is directly influenced by the thermal expansion of the system: only marginally by the sample (the substrate provides a minor contribution, while the thin silica layer can be safely neglected) and predominantly by the silver cylinder supporting it, a mechanical component of the Linkam heating stage. The relative thermal expansion of these three elements (see Appendix D.1) contributes to the displace-

ment, with thickness variations in the sample or the cylinder producing a shift along the direction orthogonal to the incidence plane.

2. The largest misalignments occur in the 200–300 °C and 500–600 °C temperature ranges (see Fig. 4.5, top left).
3. For X-misalignment values up to 20, the intensity of the light reaching the detector (not shown here) exhibits no observable correlation with the misalignment. This indicates that the measured intensity is independent of the displacement within this range.
4. The right-hand panels of Figure 4.5 show the differences between the aligned (Silicon-AL) and misaligned (Silicon-MIS) measurements at 175 °C, 200 °C, and 230 °C, corresponding to misalignments of $X_1 = 5.9$, $X_2 = 10.2$, $X_3 = 19.2$ and $Y_1 = 2.9$, $Y_2 = 3.5$, $Y_3 = 3.5$. Even in these cases, misalignment does not introduce deviations in Ψ or Δ that exceed the intrinsic noise level of the measurement.

In summary, temperature-induced misalignment primarily affects the X axis, but for $X < 20$ it does not introduce measurable errors in the ellipsometric data. To further mitigate this issue, the automated acquisition software was designed to record the misalignment value associated with each measurement and to allow the operator to perform continuous, real-time alignment during data acquisition. Thanks to this procedure, misalignment was kept well within acceptable limits. For the measurements discussed in the Results section (5), the X coordinate never exceeded $X = 5$, a value substantially lower than the safety threshold of $X = 20$. When misalignment approaches or exceeds the predefined limit, the system allows rapid identification of the issue through the session log file, enabling the operator to intervene and exclude compromised data points when necessary.

4.2.3 Scan Timing Accuracy and Thermal Response

The experimental setup employed for the ellipsometric measurements consists of two main components: the ellipsometer, responsible for acquiring the optical spectra, and the Linkam heating stage, which controls the sample temperature through a programmable thermal ramp. The two instruments operate independently and do not communicate with each other. The ellipsometer software allows the user to define the temporal interval between successive

scans, while the Linkam controller enables the selection of parameters such as heating or cooling rate, maximum temperature, and plateau time. During the automation of the measurement procedure, it was necessary to verify that the ellipsometric scans were effectively acquired at the intended temperatures. In this context, it is important to distinguish between the temperature measured by the system and the temperature actually reached by the sample. The Linkam stage monitors temperature using a PT-1000 sensor embedded in the silver heating block. In this study, we consider the sample temperature to be effectively equal to that of the heating block. This assumption is physically well-founded: the heated area is significantly larger than the sample, the sample thickness is very small (approximately 0.5 mm), and the applied thermal ramp is slow (approximately $1.5\text{ }^{\circ}\text{C min}^{-1}$). More rigorously, for thin and highly conductive substrates such as crystalline silicon, the thermal equilibration time is extremely short. According to Fourier's law, the characteristic diffusion time is $t \approx L^2/\alpha$, where L is the sample thickness and α its thermal diffusivity. For silicon ($\alpha \approx 9.0 \times 10^{-5}\text{ m}^2/\text{s}$ [118]) and a thickness of 0.5 mm, this yields $t \sim 3\text{ ms}$. Such a nearly instantaneous response indicates that temperature gradients across the sample are practically non-existent under slow heating ramps. Moreover, the deposited coatings have thicknesses of only a few hundred nanometres, i.e., more than three orders of magnitude thinner than the silicon substrate. Their thermal mass and resistance are therefore negligible compared to those of the 0.5 mm silicon wafer.

To verify the temporal accuracy of the ellipsometric acquisition, the actual time interval between successive scans was measured and compared with the nominal value set in the ellipsometer software. Figure 4.6 reports the relative percentage error obtained over 45 ellipsometric scans.

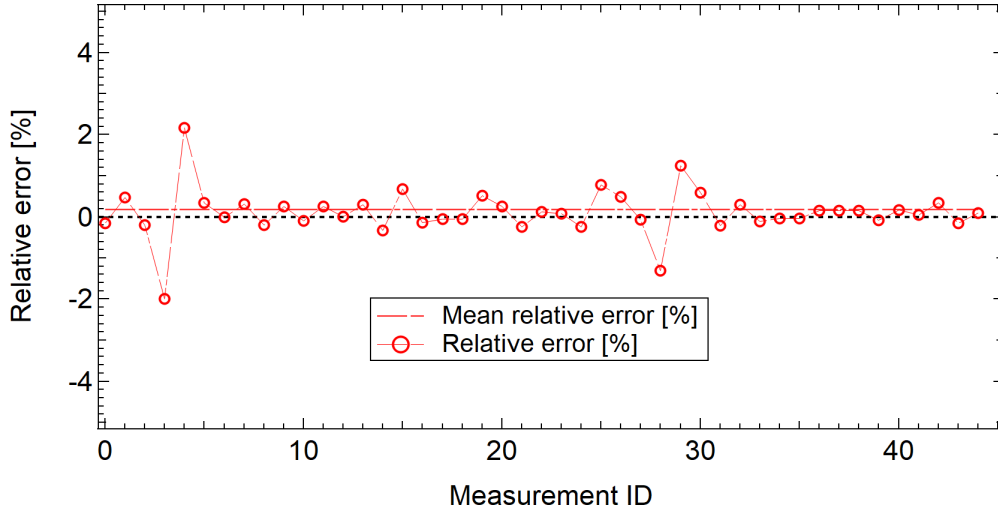


Figure 4.6: Percent relative error of the time interval between consecutive ellipsometric scans across 45 measurements. Each red marker represents the percent relative error (%) computed between the measured interval and the nominal 180 s interval. The red solid line indicates the mean percent relative error, equal to 0.18 %, while the dashed black line marks the zero-error reference.

For each scan, the time elapsed between two consecutive acquisitions was manually recorded and compared with the nominal interval (3 min, i.e. 180 s, in this experiment). The relative error was computed as

$$\frac{t_{\text{nominal}} - t_{\text{measured}}}{t_{\text{nominal}}} \times 100.$$

In order to quantify the impact of the timing uncertainty on the temperature accuracy, we consider the typical operating conditions of our experiments. During a standard measurement run, the nominal sampling interval is 15 min = 900 s. Based on the experimentally determined mean relative timing error of 0.18%, the corresponding absolute uncertainty is

$$\delta t = 900 \text{ s} \times 0.0018 = 1.62 \text{ s}. \quad (4.1)$$

A representative heating rate for our measurements is 100 °C/h. Expressed in SI units, this corresponds to

$$100 \text{ °C/h} = \frac{100}{3600} \text{ °C/s} = 0.02778 \text{ °C/s}. \quad (4.2)$$

The temperature error associated with the timing uncertainty can therefore be estimated as

$$\delta T = (0.02778 \text{ }^\circ\text{C/s}) \cdot 1.62 \text{ s} \approx 0.045 \text{ }^\circ\text{C}. \quad (4.3)$$

Thus, the timing inaccuracy would introduce a temperature deviation on the order of $4.5 \times 10^{-2} \text{ }^\circ\text{C}$ per scan, a potentially cumulative error if not mitigated and one that exceeds the instrumental uncertainty ($< 0.01 \text{ }^\circ\text{C}$ [115]). To reduce this effect, the script (see Appendix D.3) allowed the operator to intervene manually whenever the ellipsometric scan time exceeded a user-defined safety threshold. This procedure ensured that each scan was performed at the intended temperature, keeping the deviation consistently below $\pm 1.5 \text{ }^\circ\text{C}$.

4.3 Choice of the Fitting Protocol

The standard model employed in this work (described in detail in Section 3.2) consists of three layers: a crystalline silicon substrate, a native silica layer, and a coating, the latter represented either by a Cauchy-based dispersion or by a Cody–Lorentz formalism. The Cauchy approach, being a simpler and lower-parameter dispersion model applied in the transparency range, is used to extract the film thickness and refractive index. In contrast, the Cody–Lorentz model is a more complex, multiparameter formulation applied over the full measurement range, enabling the simultaneous determination of thickness, refractive index, optical gap, and Urbach energy. Noting that for each temperature T_x a distinct optical model must be determined, the modelling procedure follows an $(n + 1)$ strategy, in which the optical model extracted at temperature n is used as the initial guess for the subsequent temperature $n + 1$. When the model obtained at temperature n is applied to the experimental data measured at temperature $n + 1$, the parameters are refined through our dedicated fitting protocol (discussed in Subsections 4.3.1 and 4.3.2). Four aspects are particularly critical for ensuring physically meaningful results in the overall analysis, listed here in order of importance:

1. *Data quality.* Regardless of the complexity or accuracy of the model, poor-quality experimental data inevitably lead to unreliable results. Data quality depends primarily on the quality of the sample [107], the measurement apparatus (Section 4.1), and the mitigation of systematic errors (Section 4.2).

2. *Model construction.* “Model construction” refers to the choice of the mathematical functions used to describe the three-layer system. In our case, this choice is based on prior experience and will not be further discussed in this thesis.
3. *Starter model at room temperature.* The quality of the initial model at room temperature influences the results obtained at subsequent temperatures, since the adopted approach is progressive (the $n+1$ method). Consequently, any imperfection in the starter model may propagate through the iterations. A preliminary study (not reported here) showed, however, that this influence is limited. Even when starting from a suboptimal model³, the iterative procedure progressively corrects the initial discrepancies. At iteration n , the resulting variations in refractive index and thickness may reach at most 1%, but these differences steadily decrease as the procedure advances to $n+1$, $n+2$, and subsequent steps. For iteration counts above approximately 10, the model converges to a stable solution and the residual influence of the initial model becomes negligible.
4. *Fitting protocol.* When several parameters must be determined simultaneously, different fitting protocols may be adopted. For three generic parameters A, B, and C, for example, one may fit all parameters at once, fit A and B first and then C, or fit B and C before A. These alternative optimization paths do not compromise the physical validity of the results, but they may lead to different outcomes, both in terms of mean squared error (MSE) and in the final physical quantities.

In this study, a systematic analysis was carried out to evaluate how the adopted fitting protocol affects the quality and consistency of the results. The goal was to identify a standard procedure capable of producing reliable and mutually comparable outcomes. Once defined, this protocol was used to construct all temperature-dependent models for the various samples. To assess the influence of the fitting protocol, a 44% titania–germania sample was heated from room temperature to 490 °C at a rate of 100 °C/h. Two optical models

³Here, “suboptimal model” refers to a model that remains physically meaningful and comparable with values reported in the literature, but whose mean squared error (MSE) is higher than that of other models developed for the same dataset and describing the same physical system.

were constructed, both consisting of the same substrate and silica layer (as detailed in the previous Subsection 3.2), and differing only in the description of the coating layer. In the first case, the coating was modelled using a Cauchy-based dispersion over the transparent spectral range (1000–1500 nm), whereas in the second case it was described using a Cody–Lorentz model over the full ellipsometric range (245–1680 nm). Starting from a defined room-temperature model for both descriptions, all subsequent $(n+1)$ models were generated from room temperature up to 490 °C in 10 °C steps, varying exclusively the fitting protocol. The resulting quantities - namely the thickness, the refractive index at 1064 nm and 1550 nm, the optical gap, the Urbach energy, and the mean squared error (MSE) - were then compared to evaluate the presence of any significant differences.

4.3.1 Cody-Lorentz-Based Model

The Cody-Lorentz model is a multiparametric dispersion model characterized by a large number of free parameters. As a consequence, many different fitting sequences (i.e., fitting protocols) can be defined depending on the order in which these parameters are optimized. Experience accumulated during the preliminary stages of this work indicated that certain parameters - for example, the coating thickness, as well as the amplitude and broadening of the main oscillator - have a substantially stronger influence on the model outcome than others. For this reason, these parameters must be fitted in the early stages of the optimization process, whereas more refined parameters (such as the Urbach energy, pole parameters, or the native silica thickness) should be introduced only at later stages. To construct the room-temperature starter model, several optimization strategies were explored by varying the fitting order of the parameters. Among all the combinations tested, six procedures (A-F; see Table D.8) were selected because they produced sufficiently low MSE values. These six procedures were then applied systematically to build all models at higher temperatures using the progressive $n+1$ approach. By varying exclusively the fitting protocol, the results were compared, as shown in Figures 4.7 and 4.8.

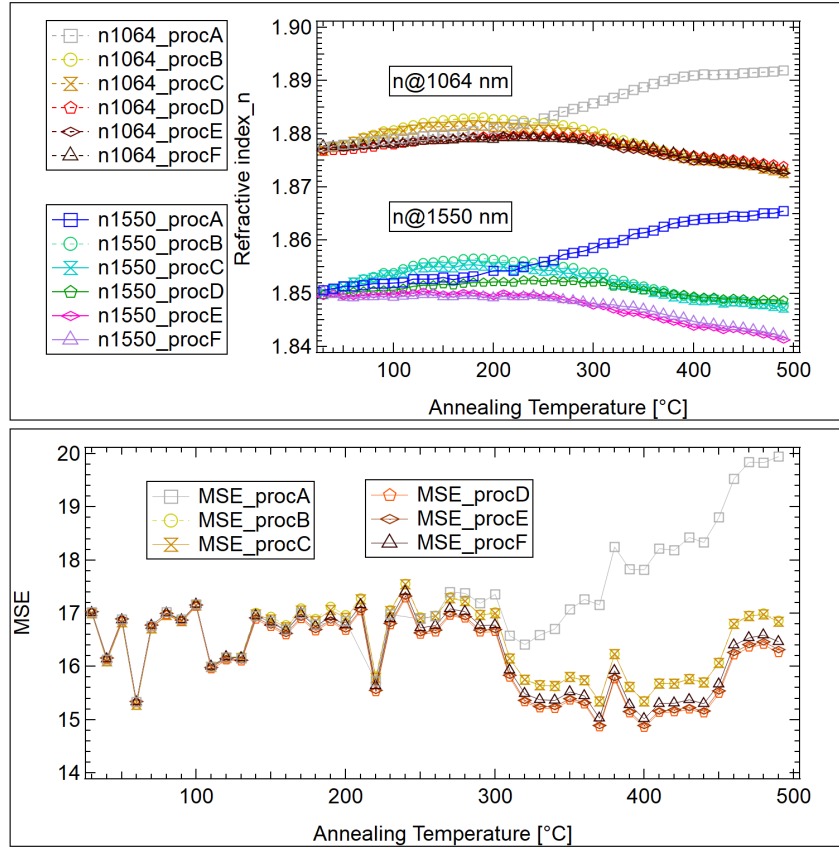


Figure 4.7: Variation of the refractive index at 1064 nm and 1550 nm (top panel) and of the MSE (bottom panel) as a function of temperature, arising solely from the choice of fitting strategy. The dispersion model employed is the Cody–Lorentz-based model. The strategies shown here represent a selected subset of a larger set of tested procedures, chosen because they already yielded fits with satisfactorily low MSE values.

The top panel of Figure 4.7 shows the refractive index at 1064 nm (upper curves) and at 1550 nm (lower curves) for the Ti-Ge sample. Clear discrepancies emerge at higher temperatures, particularly around 200 °C, where the underlying optical and structural modifications of the material make the experimental response increasingly complex to model. Since all curves are evaluated on the same identical sample and originate from the same initial conditions, this growing divergence between the curves does not imply that the material is evolving along different physical paths. Instead, the temperature-induced changes in the data increase the sensitivity of the optimization landscape, causing the specific fitting method used to transition from model n to model $n+1$ to converge toward separate numerical solutions. This numerical instability is further exacerbated by another experimental factor: the data in the near-infrared

region become progressively noisier at high temperatures due to the increasing contribution of background blackbody thermal radiation [119, 113]. This loss in signal-to-noise ratio can increase the uncertainty of the optimization, leading different fitting routines to converge toward slightly separate numerical solutions, especially at longer wavelengths. Method A is the most critical case, showing at 500 °C the maximum discrepancy, with refractive-index deviations reaching up to approximately 1% at both wavelengths compared with the other approaches. In contrast, methods B–F yield mutually consistent results within the experimental uncertainty. This behavior aligns, as previously mentioned, with the fact that these procedures always fit the most influential parameters - namely thickness (tick.2), oscillator amplitude (Amp1), optical gap (Eg.1), and broadening (Br.1) - in the initial steps. Conversely, Method A does not follow this priority order, leaving it more vulnerable to numerical instability at higher temperatures.

The bottom panel of Figure 4.7 shows the Mean Squared Error (MSE) for each fitting protocol. For temperatures below approximately 300 °C, the choice of fitting protocol does not significantly influence the MSE, whose behavior is governed by the intrinsic characteristics of the experimental data. At higher temperatures, however, the differences between the methods become increasingly evident and grow with temperature. Method A once again departs markedly from the others methods.

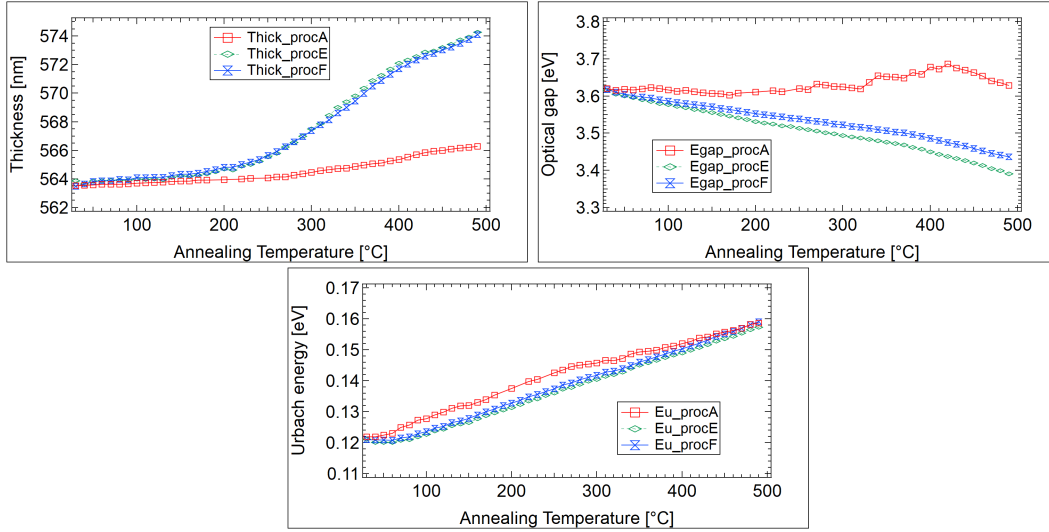


Figure 4.8: Extracted values of the film thickness (top-left panel), the optical gap E_{gap} (top-right panel), and the Urbach energy E_{u} (bottom panel) as a function of temperature. The differences observed in these quantities arise solely from the choice of fitting protocol, namely procedures A, E, and F.

Figure 4.8 reports the extracted coating thickness (top-left), optical gap (top-right), and Urbach energy (bottom). For clarity, only three procedures (A, E, and F) are shown, since methods B-E do not exhibit appreciable differences at the level of detail relevant for this analysis. Once again, the influence of the fitting protocol becomes significant above 200 °C and increases with temperature. Method A introduces maximum deviations of up to 6% in the optical gap and 1.7% in the thickness when compared with the other fitting approaches. In contrast, the Urbach energy does not exhibit an increased divergence among fitting protocols above 200 °C, although it remains moderately sensitive to the fitting procedure, with a maximum deviation of 4.4%. This behavior suggests that E_{U} is particularly affected by the quality of the fit and by the handling of refinement parameters.

Method A was ultimately discarded for two main reasons: (1) its MSE shows the largest divergence among the methods at 500 °C, with deviations reaching up to 24% relative to the other approaches; (2) the trends of thickness and refractive index are inconsistent with those obtained using the Cauchy-based model, which, as discussed later, is independent of the fitting protocol and can therefore serve as a reliable reference.

4.3.2 Cauchy-Based Model

A similar analysis was carried out for the Cauchy-based models. Seven different fitting protocols (see Table D.8) were considered, selected on the basis of a preliminary empirical evaluation. All seven methods already provided satisfactory results in terms of MSE and model stability; a systematic comparison was therefore performed to identify the most robust among them. In this comparison, the MSE as a function of temperature, as well as the refractive index at 1064 nm and 1550 nm and the coating thickness, were evaluated for each fitting protocol (results not shown). The overall analysis shows that, for relatively simple models such as those based on Cauchy dispersion, the choice of fitting protocol has only a marginal effect on the MSE and does not significantly affect the extracted physical parameters. The maximum discrepancy observed across the methods is consistently under 1%. Consequently, the Cauchy model is essentially insensitive to the choice of fitting protocol, which is why it was used as a reference to validate the results obtained with the Cody–Lorentz model, the latter being more sensitive to the fitting protocols. In particular, the thickness and refractive index obtained from the Cauchy model were compared with those extracted using the various Cody–Lorentz fitting protocols. This comparison enabled the identification of the procedure that yields the most physically consistent results for the baseline Cody–Lorentz model, namely *protocol E*. Although minor adjustments may be required when transitioning between different sample types, *protocol E* remains the primary reference approach.

4.4 Towards Fully Automated Real-Time Optical Characterization

In the second year of the PhD, significant progress enabled the transition from traditional in-situ ellipsometry — where data were manually analyzed after acquisition — to a real-time in-situ ellipsometry approach. This advancement allowed the full optical analysis to be performed directly during the annealing process. In this research, the measurement process is divided into two main phases: a relatively short data acquisition phase and a longer, more complex phase of data analysis and interpretation.

- A) *Data acquisition*: During thermal treatment (annealing), typically lasting about 20 hours, ellipsometric spectra are collected at regular intervals. This phase yields raw data, specifically the parameters Ψ and Δ as a function of temperature. To extract meaningful physical insights, these data must be processed through the construction and fitting of optical models.
- B) *Data analysis and interpretation*: This second phase is considerably more demanding in terms of time and effort. Each measurement cycle requires the construction and fitting of a dedicated optical model for every temperature point. Without automation, all these models had to be generated and fitted manually, resulting in a very large number of individual operations and a substantial overall workload.

The introduction of automated scripts made it possible to acquire data at one-minute intervals, increasing the number of points (and models) by a factor of 60⁴ and enabling real-time processing. This automation was essential to the research, as it allowed systematic investigation of annealing effects on optical properties and made it feasible to explore multiple cycles on the same material within the timeframe of the PhD project. A script⁵ now manages the entire measurement process automatically, including data collection, model construction and fitting, and visualization of the results. The detailed operation of the script, together with the full source code, is presented in Appendix D.3.

⁴In the first silicon measurements, a new optical model was generated every 100 °C, which corresponds to one model per hour given the 100 °C/h heating rate. With the automated workflow, a model can now be generated every minute. At the same heating rate, this corresponds to a temperature step of approximately 1.67 °C, yielding an improvement by a factor of about 60 in model density. In practice, however, temperature resolutions of 5, 10, or 15 °C are sufficient for most experiments, as they already capture the relevant variations of the sample.

⁵The script was developed mainly within the WVASE software [117], an ellipsometric analysis tool by J.A. Woollam Co., used for modeling and interpreting the optical properties of materials.

Chapter 5

Real-Time Optical Characterization of Materials for GWD Mirror Coatings During Annealing

Building upon the optical characterization protocol described in the previous chapter 4, a series of samples have been systematically investigated. In particular, this section focuses on the real-time optical characterization of materials that are, or may potentially be, employed as coating layers for the mirrors of the current and next generation of gravitational wave detectors (GWDs). The chapter is organized as follows:

- *Crystalline silicon* (Section 5.1): As the substrate of our reference samples, crystalline silicon is fundamental for interpreting the optical response observed during the annealing process.
- *Low-index material* (Section 5.2): Silica is examined both as the low-index material currently employed in gravitational-wave detector mirror coatings (deposited on crystalline silicon via ion-beam sputtering) and as the native oxide that naturally grows on silicon substrates, the latter forming the interface on which the coatings are deposited.
- *High-index materials* (Section 5.3): This section discusses the high-index material presently in use (titania–tantala) as well as emerging candidates for next-generation coatings, including hafnia–tantala and titania–germania.

All measurements were performed in air, with the Linkam chamber atmosphere left unmodified.

5.1 Crystalline Silicon Substrate

This section presents the optical characterization of the crystalline-silicon bare substrate used as the reference for all samples investigated in this work. The analysis is organized into two subsections. Subsection 5.1.1 provides a systematic characterization of the specific bare substrate supplied by the coating manufacturer (LMA, <http://lma.in2p3.fr/>). Its optical response is measured from room temperature up to 600°C, and the corresponding dispersion models required for subsequent coating analysis are constructed. Subsection 5.1.2 examines how variations among different crystalline-silicon bare substrates (although all originating from the same supplier) affect the coating properties retrieved from optical measurements. Using a hafnia–tantala coating deposited on crystalline silicon as a case study, this subsection quantifies the errors that arise when a model derived from one bare substrate is applied to coatings deposited on other substrates of the same material. This analysis directly addresses a central question of the study: whether a single, standardized substrate model is sufficient for all standard samples (i.e., coatings deposited on crystalline silicon), or whether accurate and reliable coating analysis instead requires individual substrate characterization.

5.1.1 High-Temperature Optical Properties of Crystalline Silicon

Since most of the samples analyzed in this work were deposited on crystalline silicon substrates, the initial phase of the PhD research focused on studying the optical properties of silicon. Several bare Si wafers were characterized using both ex-situ and real-time spectroscopic ellipsometry, covering the full temperature range relevant to our coatings (30 °C - 600 °C) with a 5 °C step.

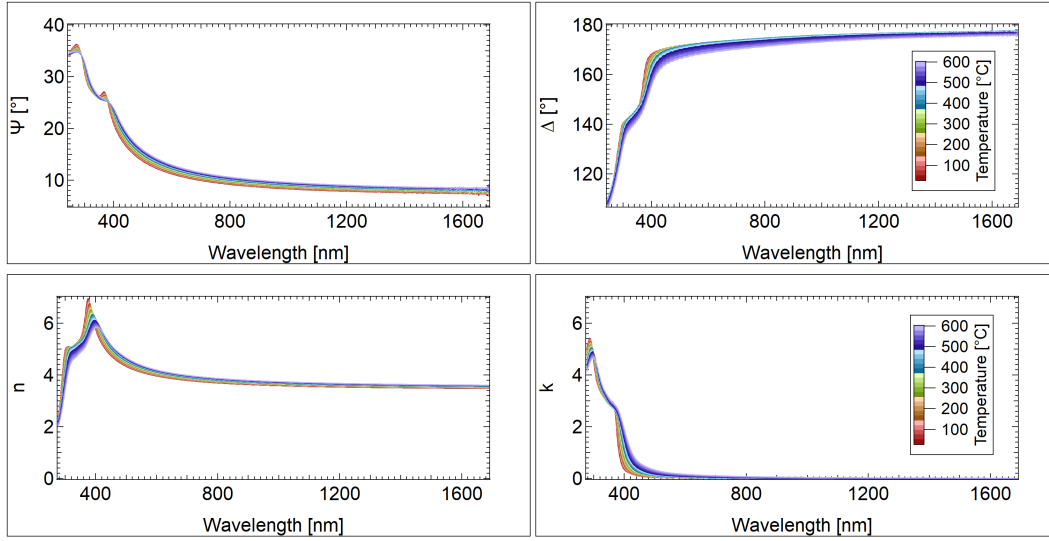


Figure 5.1: Temperature-dependent spectroscopic ellipsometry results for the Si substrate used for the deposition of our standard samples (Substrate 4; see Subsection 5.1.2). The top-left and top-right panels show the ellipsometric parameters Ψ and Δ , respectively, measured from room temperature up to 600 °C. The corresponding refractive index n and extinction coefficient k , obtained through modeling, are shown in the bottom-left and bottom-right panels, respectively, highlighting the evolution of the optical constants as the temperature increases. The color legend indicating the temperature of each curve is shown only in the right-hand plots, but it applies to all panels.

Figure 5.1 shows an example of a thermal annealing cycle performed on a bare silicon substrate, with a heating and cooling rate of 100 °C/h. The upper panels display Ψ and Δ , while the lower panels report the corresponding refractive index n and extinction coefficient k extracted through modeling. Only the heating phase is shown, as the optical response of crystalline silicon in this temperature range is well known to be fully reversible: as widely documented in the ellipsometric literature, the intrinsic thermally-induced modifications of the crystalline silicon band structure up to approximately 600 °C, driven by physical mechanisms such as lattice thermal expansion and electron–phonon interactions [120], are fully reversible upon cooling. Standard experimental protocols systematically confirm this reversibility by comparing room-temperature spectra acquired before and after the heating cycles [119, 121, 122]. When thermal treatments are performed under completely inert conditions, the initial optical properties of the silicon substrate are entirely recovered [121]. Conversely, during annealing in standard or mildly oxidizing environments, any permanent

variation observed in the Ψ and Δ parameters at room temperature is exclusively attributable to the irreversible growth of the surface native oxide layer (SiO_2) [119, 122]. This reversibility is confirmed in Figure 5.2, which compares the ellipsometric response before and after annealing. The negligible change in Ψ and the $\sim 2^\circ$ shift observed in Δ are fully explained by the irreversible growth of the native silica layer, as silicon itself returns to its original optical state after the thermal cycle.

Although the behavior of silicon and the evolution of the native silica layer are well established, the measurements presented in Sections 5.1.2 and 5.2 were nevertheless required to construct substrate and oxide models specifically tailored to our samples. These models were then used as the optical reference for the analysis of the high-index materials.

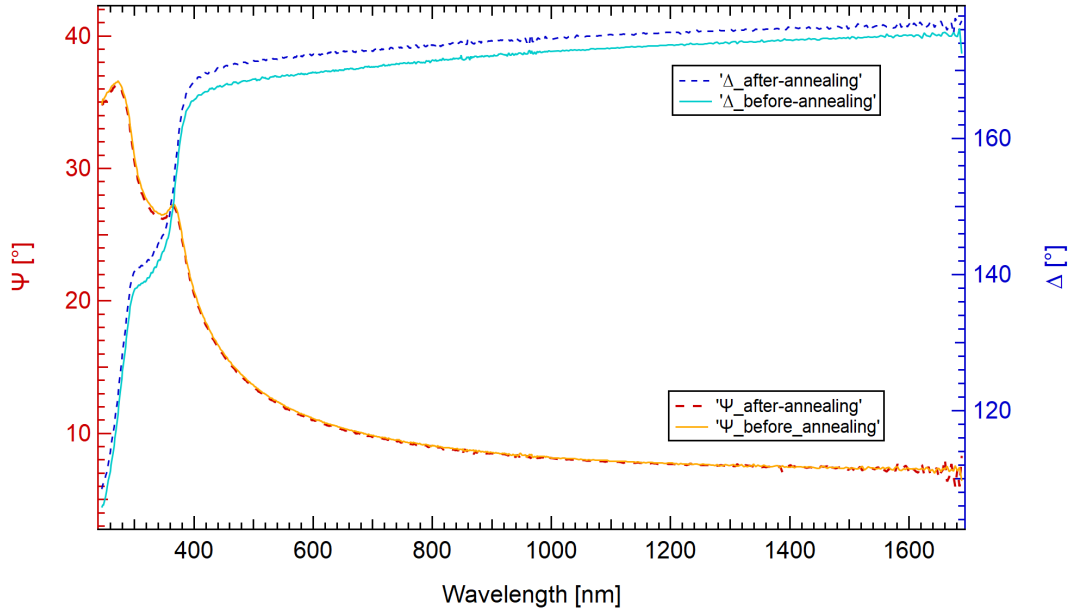


Figure 5.2: Ψ (red and orange curves) and Δ (blue and light-blue curves) for a silicon substrate before and after annealing. The observed change in Δ is consistent with an increase in the thickness of the native silica layer.

5.1.2 Impact of Substrate Choice on Temperature-Dependent Optical Models of the Coated-Sample

In the early stage of this work, representative silicon substrates used for the investigated coatings were characterised, with their structural properties detailed in Appendix B.1. These silicon samples were then subjected

to controlled annealing cycles to assess the stability of their optical response. The measurements confirmed that crystalline silicon exhibits fully reversible optical behaviour within the investigated temperature range, and that variations in the heating rate up to $300^{\circ}\text{C h}^{-1}$ do not induce any significant effect. While this might suggest that a single substrate - and the corresponding temperature-dependent model derived from it - could be sufficient to represent the generic substrate behavior of all samples, this assumption requires verification. In fact, small but non-negligible differences among substrates may persist and could influence the extracted coating properties. To quantify the impact of substrate variability, each silicon wafer was independently annealed and modelled, yielding a set of temperature-specific substrate models. These models were then used in the analysis of the hafnia–tantala reference sample (nominal thickness 500 nm). Hafnia–tantala was selected because it exhibits optical characteristics qualitatively comparable to those of various high-refractive-index coatings, including titania–tantala. The sample was modelled as a three-layer structure consisting of the silicon substrate, a native silica layer (*silica.jaw*), and the hafnia–tantala film, whose dispersion was described using a *Cauchy* function (Figure 5.3). Within this framework, the only element that varies between analyses is the substrate model, enabling us to isolate and quantify how substrate variability propagates into the extracted coating properties.

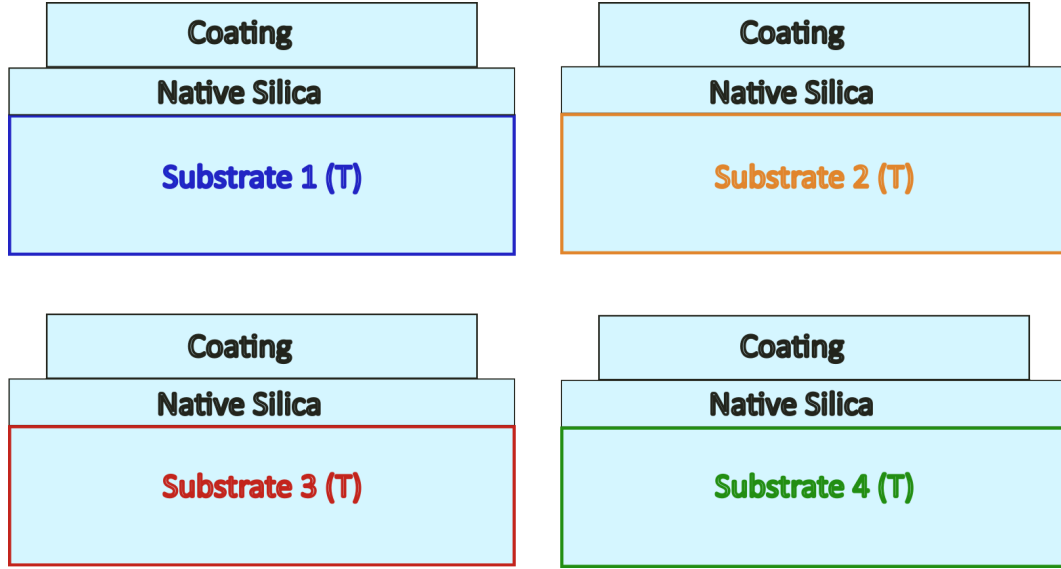


Figure 5.3: Schematic representation of the multilayer models used to extract the refractive index and thickness of hafnia-tantala. All layers exhibit temperature-dependent optical properties; however, they are treated differently in the analysis. For the hafnia-tantala coating layer, the model is re-fitted at each temperature point to match the experimental data. In contrast, the silicon substrate and the native silica¹ are not re-fitted during the annealing cycle. For the substrate in particular, a set of fixed substrate models - one for each temperature - was prepared in advance from experimental measurements performed on four crystalline silicon wafers supplied by the same manufacturer as the samples. During the analysis, the appropriate pre-computed substrate model is used as a temperature-specific library element.

Figure 5.4 reports the evolution of the refractive index and thickness of a hafnia-tantala coating during a 10-hour annealing cycle at 600 °C, performed with a heating/cooling rate of 100 °C h⁻¹.

¹For the latter, i.e., the silica layer, only negligible (<1 nm) thickness fine-tuning was allowed, introduced solely to improve the MSE of the overall three-layer model; such sub-nanometric adjustments are too small to carry any physical significance.

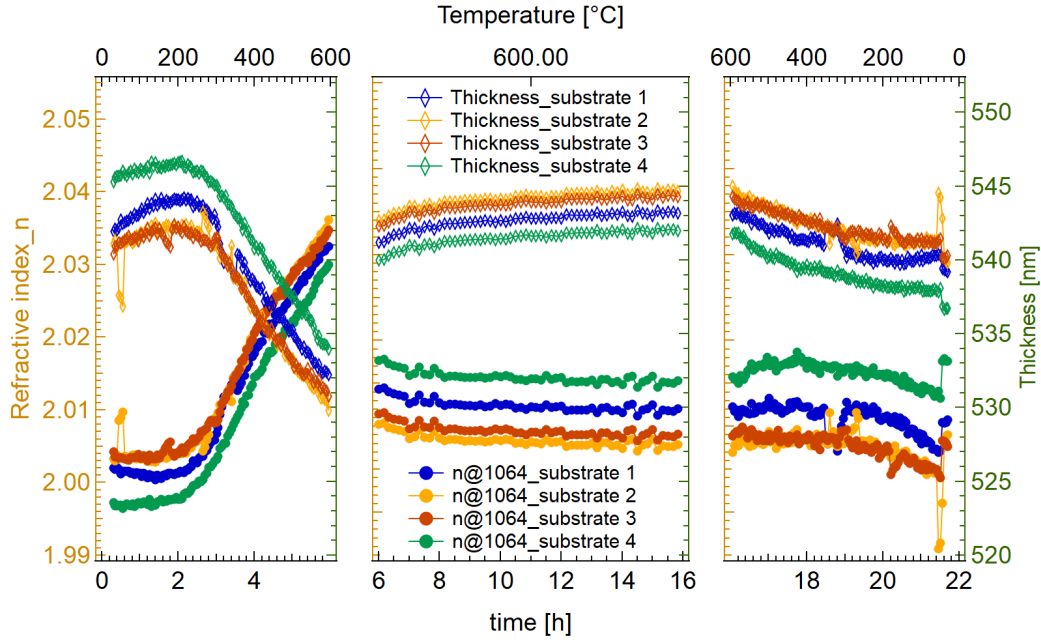


Figure 5.4: Effect of different substrate models on the refractive index and thickness of a hafnia–tantala coating. The coating was subjected to a thermal cycle comprising heating from 30 to 600 °C at 100 °C/h, a 10 h isothermal hold at 600 °C, and cooling back to 30 °C at the same rate. The use of different substrate models (Substrate 1 (blue), Substrate 2 (orange), Substrate 3 (red), Substrate 4 (green)) results mainly in a vertical shift of the refractive index and the thickness, with an error well below 1%. The deviations at the end of the cooling phase (~ 21 h) stem mainly from random uncertainties in the hafnia–tantala measurements, rather than from the substrate models.

The left panel shows the heating phase (from 30 °C to 600 °C), the central panel the 10-hour isothermal plateau, and the right panel the subsequent cooling phase. Among the various crystalline silicon substrates tested under identical thermal conditions, four substrates provided by the coating manufacturer (hereafter Substrate 1, Substrate 2, Substrate 3, and Substrate 4) were selected for detailed modeling. For each substrate, ellipsometric scans were collected every 5 °C during the heating ramp, and an optical model was generated at each temperature point starting from the *si_parametrized* base model (see Appendix C.2.2). The models were fitted to the experimental data through MSE minimization following the procedure summarised in Table 5.1, using a stepwise approach in which the model at temperature n served as the initial guess for the fit at temperature $n + 1$.

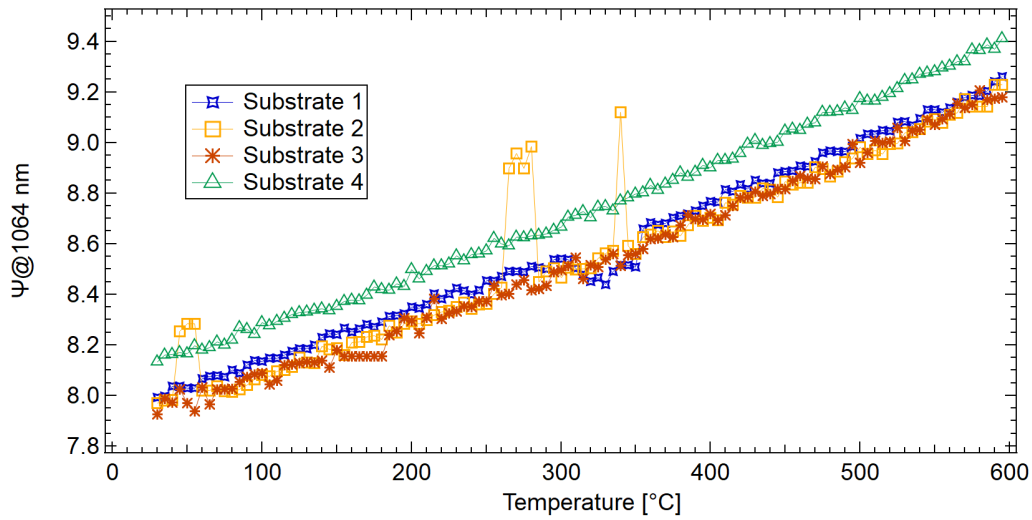


Figure 5.5: Temperature dependence of the ellipsometric parameter Ψ at 1064 nm for the substrates employed in the hafnia–tantala coating model (see Fig. 5.4). The measurements were performed during heating from 30°C to 600°C at 100 °C/h. The four curves correspond to Substrate 1 (blue), Substrate 2 (orange), Substrate 3 (red), and Substrate 4 (green). The silicon models used to describe the coating behaviour were derived from these experimental substrate measurements and applied consistently across all three phases, as crystalline silicon shows reversible optical properties over the investigated temperature range (see Subsec. 5.1.1). Random experimental uncertainties in the substrate measurements propagate into the corresponding coating properties.

This analysis highlights the relative influence of three key factors on the extracted coating properties:

- the quality of the experimental data² for the hafnia–tantala coating deposited on crystalline silicon;
- the quality of the bare-substrate experimental data (Substrates 1–4);
- the accuracy of the optical models used for both the silicon substrate and the hafnia–tantala coating³ (the native silica layer is kept constant; see Section 5.2).

²Here, “data quality” refers to the absence of spikes or outliers, stable optical alignment kept within the required thresholds, absence of operator-induced random errors, and temperature control within ± 1 °C during acquisition. The early issues observed in the very first silicon measurements were later mitigated in the subsequent official-substrate, low-index, and high-index material measurement campaigns, as discussed in Section 4.2.

³In this specific analysis, the quality of the hafnia–tantala model does not affect the

At a first qualitative inspection, the choice of substrate model has only a minor influence on the retrieved coating parameters, leading mainly to a small vertical offset in the curves and deviations well below 1 % in both refractive index and thickness. A closer examination, however, highlights a clear distinction between the behaviour observed during the heating/cooling ramps and that occurring in the subsequent isothermal plateau. In this regime, the curves produced by the four models are essentially indistinguishable. The only residual discrepancy is the initial vertical offset, which originates from the different silicon–substrate models employed and reflects the behaviour already observed during the heating phase. Since each silicon model is subsequently held at a constant temperature, this offset remains unchanged throughout the plateau. Given that the experimental coating data are identical for all cases and that the fitting protocol between point n and point $n + 1$ is fully standardised, the resulting curves exhibit the same evolution. In contrast, during the heating and cooling ramps the curves remain qualitatively identical across all substrates within 1 %, while the point-to-point variations differ slightly. These small fluctuations simply reflect the random experimental uncertainties in the bare-substrate measurements used to construct the relative substrate models, whereas the coating data and the fitting protocol remain identical across all analyses. By the end of the cooling phase (~ 21 h), all four curves exhibit the same anomalous features in both thickness and refractive index, confirming that these behaviours reflect mainly the experimental uncertainties in the hafnia–tantala coating data rather than artifacts arising from the substrate models or from the measurements themselves. Finally, the comparison between the individual substrates highlights how localized, non-physical irregularities in a specific bare-substrate dataset can directly propagate into the extracted coating properties. This effect is particularly evident in Figures 5.4 and 5.5 for Substrate 2 (yellow curve), where small irregularities in the substrate data translate into corresponding fluctuations in the retrieved coating parameters, underscoring the critical importance of high-quality substrate measurements for reliable optical modeling.

To mitigate these issues and establish a solid baseline, a systematic evaluation

comparison of the results, as both the model and the fitting protocol were fixed and applied identically to all curves. In general, however, the choice of the optical model and of the fitting strategy is crucial for accurately describing the coating behaviour and obtaining physically meaningful results.

was performed across all available substrates over the 30–600 °C range. Following this screening, the silicon wafer labeled “Substrate 4” was ultimately selected as the reference for all the samples studied in this work. This choice was motivated by its superior model quality (lowest MSE) and by the complete absence of spikes or irregularities in its experimental data.

Table 5.1: Steps of the fitting procedure for the $si_parametrized$ multi-oscillator model from J. A. Woollam used to describe the silicon substrates. Parameter notation: Am_i , Br_i , En_i refer to the amplitude, broadening, and energy of the i -th oscillator; $PoleMag$ and $PolePos$ denote the magnitude and position of the pole term; $Thick.1$ indicates the thickness of the native SiO_2 layer.

Fitting Protocol for Silicon Substrates

Step	Parameters
1	$Am1 + Br1$
2	$Am2 + Br2$
3	$Am3 + Br3$
4	$Am4 + Br4$
5	$Am5 + Br5$
6	$Am6 + Br6$
7	$En1$
8	$En2$
9	$En3$
10	$En4$
11	$En5$
12	$En6$
13	$Am1 + Br1 + En1$
14	$Am2 + Br2 + En2$
15	$Am3 + Br3 + En3$
16	$Am4 + Br4 + En4$
17	$Am5 + Br5 + En5$
18	$Am6 + Br6 + En6$
19	$En1 + En2 + En3 + En4 + En5 + En6$
20	$Am1 + Am2 + Am3 + Am4 + Am5 + Am6$

	+ Br1 + Br2 + Br3 + Br4 + Br5 + Br6
21	PoleMag
22	PolePos
23	Thick.1

5.2 Low Refractive Index Material: SiO₂

The characterization of silica (SiO₂) films deposited by Ion Beam Sputtering (IBS) on crystalline silicon substrates was performed through ellipsometric measurements as a function of the annealing temperature. A dedicated publication⁴ has recently been published [110]. This section pursues two complementary objectives. First, it aims to elucidate the structural and optical evolution of the IBS-deposited silica films under thermal treatment. Second, it seeks to validate the substrate + native silica optical model at elevated temperatures, thereby enabling its integration into the standard multilayer framework used for the characterization of our samples. An extended discussion of the structural and optical properties of silica, together with the distinction between deposited and native silica, is presented in Appendix B.2. Several batches of IBS-deposited silica films on crystalline silicon substrates were analysed. The coatings exhibited nominal thicknesses of 500 nm, 700 nm, 1000 nm, or 2500 nm. Each sample was subjected to an annealing cycle, and its optical properties were measured *ex situ*, i.e. before and after annealing at room temperature. Table 5.3 presents a selection of representative samples with a nominal thickness of 700 nm from two different batches, while Figure 5.6 shows the corresponding optical analysis results.

⁴In that publication, the ellipsometric measurements presented here constitute a part of a broader experimental study on deposition-induced anisotropy in IBS silica coatings. The full investigation combines complementary techniques to probe structural, optical, and elastic inhomogeneities, and to assess how thermal treatments can restore isotropy and improve the performance of future mirror coatings.

Table 5.3: Silica samples. Optical and thickness data after thermal treatment

Sample ID	n_{1064}	Thickness (nm)	Thickness variation (%)	n variation (%)
Blue1 as-dep	1.483 ± 0.005	718 ± 1	–	–
Blue2 (10h at 500°C)	1.472 ± 0.005	730 ± 1	1.6	-0.74
Blue3 (10h at 800°C)	1.460 ± 0.005	752 ± 1	4.7	-1.55
Blue4 (10h at 900°C)	1.458 ± 0.005	770 ± 1	7.2	-1.68
Red1 as-dep	1.480 ± 0.005	722 ± 1	–	–
Red2 (10h at 500°C)	1.463 ± 0.005	737 ± 1	2.1	-1.15
Red3 (10h at 900°C)	1.454 ± 0.005	774 ± 1	7.2	-1.76

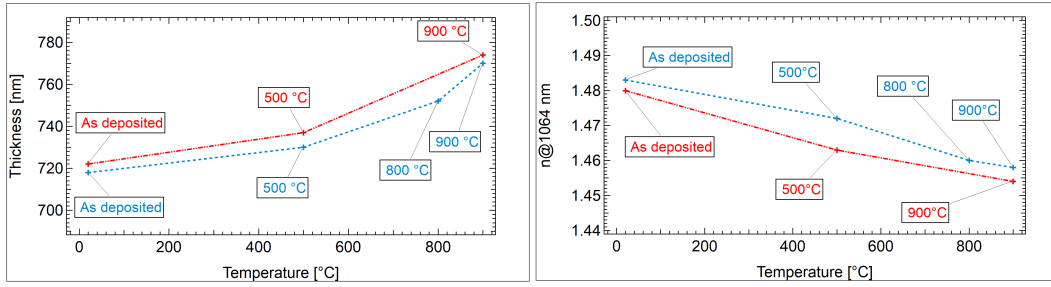


Figure 5.6: Left panel: Thickness of the silica layer deposited by IBS on crystalline silicon, shown as a function of the annealing temperature for a 10-hour thermal treatment. Data from two different deposition batches (blue batch and red batch) are reported. Right panel: Refractive index at 1064 nm (Virgo laser wavelength) of the same IBS-deposited silica layers, plotted as a function of annealing temperature for the two batches.

Figure 5.6 illustrates the evolution of both the film thickness and the refractive index at 1064 nm for the two deposition batches, here referred to as the *blue batch* and *red batch*. The samples were analyzed in the as-deposited condition and after annealing at 500 °C, 800 °C, and 900 °C. As shown in the *left panel*, the thickness increases progressively with annealing temperature, with a particularly significant expansion at 900 °C. For the blue batch, the thickness increases by approximately 1.6%, 4.7%, and 7.2% at 500 °C, 800 °C, and 900 °C, respectively, while the red batch shows variations of 2.1% and 7.2% at 500 °C and 900 °C. These percentages represent the relative increase in thickness with respect to the as-deposited value. The observed behavior is mainly driven by the volumetric expansion associated with the structural relaxation of the highly compressed amorphous film [123, 20]. Upon annealing, the amorphous network undergoes a substantial reorganization that lowers the internal stress and reduces the film density, leading to a measurable thickness

increase. In contrast, additional oxidation at the Si/SiO₂ interface is negligible under the present conditions. According to the Deal–Grove model [124], oxide growth at 900 °C would be appreciable for thin overlayers, but in this case it is effectively suppressed because the large film thickness (approximately 700 nm) acts as an efficient diffusion barrier that severely limits oxygen transport to the interface. The *right panel* of Figure 5.6 shows the corresponding evolution of the refractive index at 1064 nm. A monotonic decrease with increasing annealing temperature is observed: the refractive index decreases by about −0.74%, −1.55%, and −1.68% for the blue batch at 500 °C, 800 °C, and 900 °C, respectively, and by −1.15% and −1.76% for the red batch at 500 °C and 900 °C. These percentages quantify the relative decrease in refractive index with respect to the as-deposited value. According to full-atomistic simulations of IBS silica by Grigoriev *et al.* [123], structural relaxation at an annealing temperature of 1300 K can induce a refractive-index reduction of up to 2% (0.03), corresponding to a macroscopic density decrease of about 3.3% (0.15 g/cm³). In this regime, annealing drives the amorphous network toward a more ordered yet significantly less dense configuration, which in turn lowers the optical density. The experimental data presented here, together with additional full annealing cycles performed on IBS silica deposited on crystalline silicon (not shown here), allowed us to test the Woollam model `Si02.jaw`, based on the tabulated values reported by Herzinger *et al.* [108], and to validate it across the entire temperature range up to 600 °C. Once validated, this model was subsequently employed to describe the *native silica* layer naturally present between the silicon substrate and the coating in the standard samples. Since native silica has an average initial thickness of approximately 2 nm, any absolute thickness variation due to structural relaxation (on the order of a few percent) is practically negligible within the temperature range 30–600 °C. Consequently, in our standard samples the native silica layer is described using the validated Woollam model, with its thickness fitted at room temperature and then kept constant throughout the annealing process.

5.3 High Refractive Index Materials: $\text{TiO}_2\text{--Ta}_2\text{O}_5$, $\text{HfO}_2\text{--Ta}_2\text{O}_5$, and $\text{TiO}_2\text{--GeO}_2$

In the previous sections, the necessary preliminary characterizations were presented. Since the coatings investigated in this work are deposited on crystalline silicon substrates with a native silica layer, a detailed assessment of the substrate–silica system was required to ensure meaningful comparison across all samples. This characterization also enables the optical response of the full stack to be properly decomposed, distinguishing the contributions of the substrate and native silica from those of the coating itself. With this foundation established, the thesis now turns to the core measurements on high-refractive-index materials that are employed, or considered promising candidates, for mirror coatings in gravitational-wave detectors. The following subsections therefore examine each coating system individually: titania–tantala (Subsection 5.3.1), hafnia–tantala (Subsection 5.3.2), and titania–germania (Subsection 5.3.3).

5.3.1 Titania–Tantala ($\text{TiO}_2\text{--Ta}_2\text{O}_5$)

Titania–Tantala ($\text{TiO}_2\text{:Ta}_2\text{O}_5$) is an amorphous high-refractive-index material produced by co-depositing titanium dioxide and tantalum pentoxide [51], whose structural properties are detailed in Appendix B.3.1. Its unique combination of elevated refractive index and low mechanical loss makes it the current high-index material used in dielectric mirror coatings for gravitational-wave detectors [51, 39]. Achieving such low mechanical loss requires subjecting the material to an annealing treatment, which relieves internal stresses and promotes structural relaxation within the amorphous network. However, the annealing temperature must remain below the crystallization threshold, since the formation of grain boundaries would increase light scattering and mechanical dissipation, ultimately degrading the material performance [28, 20]. For this reason, the sample was annealed at 500 °C, a temperature high enough to reduce mechanical loss while safely avoiding the onset of crystalline phases. The treatment followed the standard Virgo procedure, employing heating and cooling rates of 100 °C h^{−1} and a plateau time of 10 h at the maximum temperature [39, 20]. In this work, the evolution of the optical properties during annealing was monitored in real time, enabling a direct observation of the ma-

terial's relaxation dynamics. The analysis presented in this section is based on the dedicated study reported in Ref. [74].

Experimental Data Observation For a general introduction to the interpretation of raw experimental data, see Appendix E.1.

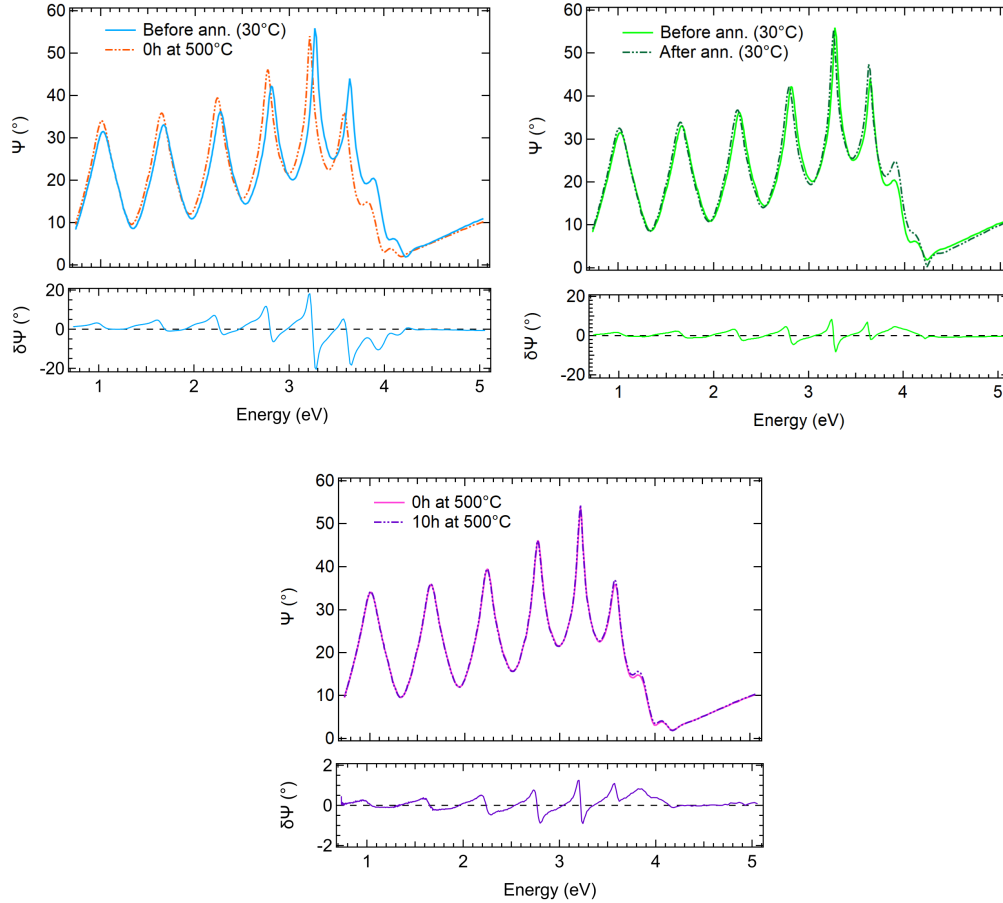


Figure 5.7: Top left: Ellipsometric data Ψ before annealing (light blue, solid) and at 500 °C (orange, dotted). Top right: Ψ before annealing (light green, solid) and after annealing (dark green, dotted). Bottom: Ψ at 500 °C at the beginning (pink, solid) and at the end (purple, dotted) of the 10-hour high-temperature plateau. Below each panel, the corresponding difference spectrum is shown. Note that the vertical scale of the difference spectrum in the bottom panel is ten times smaller than in the upper panels. This figure is reproduced from the author's publication [74].

Figure 5.7 presents a detailed comparison of ellipsometric Ψ spectra recorded at key stages of the annealing cycle. The figure is composed of three panels, each displaying the Ψ spectra in the upper plot and the corresponding difference spectrum directly below.

- (a) *Top left* panel compares Ψ at 500 °C, corresponding to the beginning of the 0 h plateau, with the value measured prior to annealing at room temperature. The leftward shift of the interference fringes indicates an increase in optical path length, consistent with a thicker coating (Appendix E.1). Changes in oscillation amplitude reveal a modification of the refractive-index contrast between film and substrate. This contrast increases due to two concurrent effects: a $\sim 4.4\%$ relative rise in the refractive index of silicon at 1064 nm (Figure 5.1) and a $\sim 0.7\%$ relative decrease in that of the titania–tantala coating (Figure 5.9). Because both materials change their optical properties during heating, the variation observed in the raw data cannot be attributed to the coating alone.
- (b) *Top right* panel compares Ψ before and after annealing, both measured at room temperature. Since crystalline silicon exhibits reversible optical behavior, the observed differences arise exclusively from irreversible transformations in the coating, involving both thickness and refractive-index changes.
- (c) *Bottom* panel compares Ψ at 500 °C after 10 h with its initial value at the beginning of the plateau. This isolates the behavior of the coating at high temperature: the substrate is already thermally stable at 500 °C, so the differences reflect only the coating’s evolution. Compared with panel (a), the variations occurring during the plateau are significantly smaller.

Taken together, these results show that the main trends (film expansion and refractive-index variation) are already visible in the raw Ψ data, while optical modeling serves to quantify them.

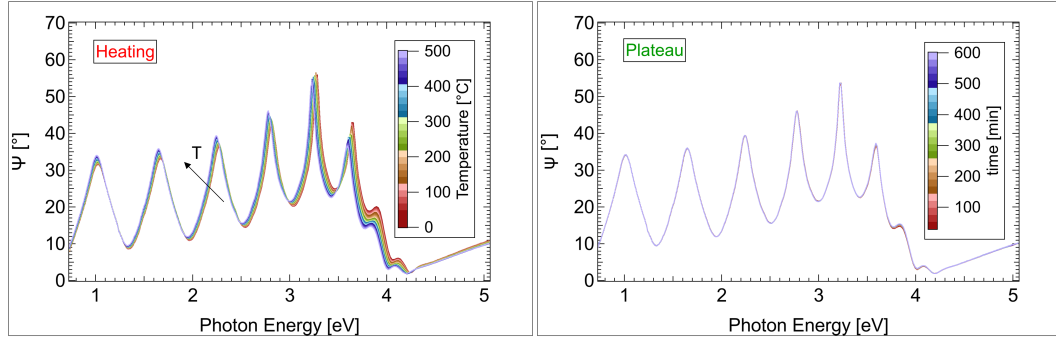


Figure 5.8: Ellipsometric data (Ψ) for a titania–tantala sample deposited on crystalline silicon and subjected to Virgo’s standard annealing protocol. Left: Ψ as a function of temperature during the heating phase, from 30 °C to 500 °C (ramp rate: 100 °C/h). Right: evolution of Ψ during the 10-hour isothermal plateau at 500 °C.

Complementary information is provided by Figure 5.8, which shows the continuous evolution of Ψ during the heating and plateau phases of the thermal cycle. The left panel displays Ψ as a function of temperature from 30 °C to 500 °C. In the transparent region (< 3 eV), the interference fringes shift toward lower photon energies and the oscillation amplitude increases, consistent with the trends identified in Figure 5.7. These variations reflect the combined temperature-dependent rise in the refractive index of silicon (Section 5.1) and the likely decrease in that of the coating (Paragraph 5.3.1). The right panel of Figure 5.8 shows the evolution of Ψ during the 10-hour isothermal plateau at 500 °C. Here, the changes are more subtle: a slight additional left-shift and a modest increase in amplitude indicate that the coating is still undergoing structural and optical modifications. Taken together, Figures 5.7 and 5.8 provide a coherent picture of the coating’s evolution: the most pronounced changes occur during heating, whereas the plateau phase leads to smaller yet non-negligible modifications.

Temperature and Time-Dependent Changes in Refractive Index and Thickness Figure 5.9 presents the results of the modeling procedure applied to the experimental data described in the previous section. The coating thickness of the titania–tantala film is shown in green, while the refractive indices at 1064 nm (triangles) and 1550 nm (squares) are displayed in yellow during the heating phase (0 h to 5 h), the plateau phase (5 h to 15 h), and the cooling phase (15 h to 20 h).

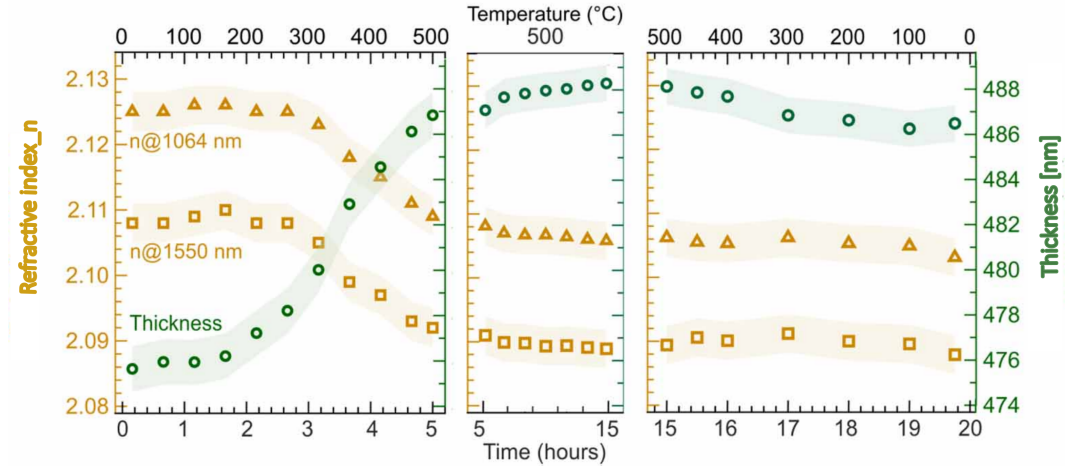


Figure 5.9: Refractive index (left axes) and thickness (right axes) of the titania–tantala thin film measured during the heating phase (left panel), the 500 °C plateau (middle panel), and the cooling phase (right panel). Colored bands around the data points represent the associated error bars. This figure is based on the author’s publication [74].

The first significant changes in coating thickness and refractive index emerge between 200 °C and 300 °C during the heating phase, with the fastest variations occurring near 350 °C. These changes begin once the coating temperature exceeds the deposition temperature. After the sample reaches the peak temperature of 500 °C, additional but comparatively small modifications continue throughout the 10 h high-temperature plateau. Even at the end of this plateau, the coating properties are still evolving, suggesting that the current annealing protocol does not fully exhaust the possible structural rearrangements. Extending the plateau duration may therefore enable further modifications. During cooling from 500 °C to RT, the observed decrease in thickness and refractive index is attributed to reversible temperature-induced effects in the titania–tantala coating [112, 125]. Overall, the physical thickness increases by approximately 2.3%, while the refractive index decreases by about 1%. This behavior is consistent with previous ex-post annealing studies [95, 126, 77].

The measured variations arise from a complex interplay of physicochemical processes associated with the relaxation of compressive stress introduced during ion-beam sputtering deposition [77, 127]. These processes affect both the optical and mechanical responses of amorphous transition-metal oxides and are best understood at the atomistic level. Amorphous titania–tantala consists of Ti- and Ta-centred oxygen-sharing polyhedra [128, 129, 130] (see Ap-

pendix B.3.1), which may connect through corners, edges, or faces [68]. Annealing can modify this network through several mechanisms, including:

- Structural rearrangements: For example, in zirconia-tantala mixtures, annealing increases the ratio of corner-sharing to edge-sharing polyhedra and modifies the local Ta coordination environments [69, 131].
- Rearrangement of interstitial nanovoids: modifications occur in the geometry and spatial distribution of nanovoids [69, 131].
- Enhancement of medium-range order: thermal annealing increases structural ordering on intermediate length scales in amorphous tantala-based films [85, 86, 132].
- Reduction of oxygen deficiency: annealing in air may remove a slight oxygen deficiency present in as-deposited films [133].
- *Release of trapped argon*: Argon incorporated during IBS deposition may be expelled during annealing. In materials such as Ta_2O_5 , $\text{TiO}_2 : \text{Ta}_2\text{O}_5$, and SiO_2 , this effect is strongly reduced under atmospheric conditions, and the gas can remain trapped within the layer even at very high temperatures due to the low atomic mobility [84, 83, 111]. As we will discuss later in Paragraph 5.3.3, this behavior does not apply to $\text{TiO}_2 : \text{GeO}_2$ coatings, where the proximity of the annealing temperature to the glass transition of germania leads to enhanced atomic mobility and a massive release of the trapped gas [111].

Additional insight is provided by the Urbach energy, whose reduction is associated with increased medium-range order in amorphous structures [91]. The Urbach energy depends on both structural and compositional order and on thermal disorder [134]. Its evolution during the heating ramp reflects a combination of structural changes and increasing temperature, and isolating the structural contribution would require dedicated experiments. Variations observed during the constant-temperature plateau reflect changes in structural and compositional order. In this study, the Urbach energy decreased by 4 ± 1 meV during the high-temperature plateau, whereas previous measurements reported a reduction of about 45 meV after the full annealing cycle [54]. These results indicate that the dominant part of the structural evolution takes place during the

heating ramp, while also demonstrating that the plateau contributes in a non-negligible manner. The in-situ real-time measurements therefore suggest that the current annealing protocol for gravitational-wave detector mirrors could be further refined. In particular, extending the 500 °C plateau (and monitoring the Urbach energy under isothermal conditions) may promote additional structural relaxation and ultimately lead to improved coating performance.

5.3.2 Hafnia–Tantala ($\text{HfO}_2\text{--Ta}_2\text{O}_5$)

Hafnium oxide (HfO_2) is a high-index dielectric material, with a refractive index of about 1.9 at 1064 nm [135, 136, 64]. Pure HfO_2 exhibits a relatively high Young’s modulus, significantly larger than that of SiO_2 , and a tendency to partially crystallize during deposition or upon annealing [61, 128]. Since crystallization affects both mechanical loss and optical uniformity, understanding how HfO_2 evolves with temperature is essential for assessing its applicability in low-noise coatings. Recent measurements on amorphous HfO_2 films deposited by plasma-assisted e-beam evaporation and ion-assisted deposition have reported room-temperature loss angles in the low- 10^{-4} range [65, 66], motivating a more systematic investigation of its thermal stability. Mixing hafnia with other oxides has been shown to raise the crystallization temperature by several hundred degrees Celsius [128], enabling high-temperature annealing without inducing structural degradation [137]. These results suggest that the temperature-dependent behavior of hafnia, both in its pure form and within mixed-oxide systems, plays an important role in assessing its suitability for next-generation low-noise optical coatings for GWD mirrors.

Temperature and Time-Dependent Changes in Refractive Index and Thickness The annealing response of the $\text{HfO}_2\text{--Ta}_2\text{O}_5$ film system, with a nominal cation composition of 41% Hf/(Hf+Ta), appears to follow trends similar to those observed in $\text{TiO}_2\text{--Ta}_2\text{O}_5$ coatings. This resemblance may be related to the neighboring positions of hafnium ($Z = 72$, atomic weight = 178.49 u) and tantalum ($Z = 73$, atomic weight = 180.90 u) in the periodic table, which are associated with comparable electronic structures and ionic radii. Consequently, the oxides might exhibit partially comparable bonding characteristics, dielectric behavior, and thermomechanical responses [138, 139], potentially contributing to the similar annealing trends observed in the two

systems.

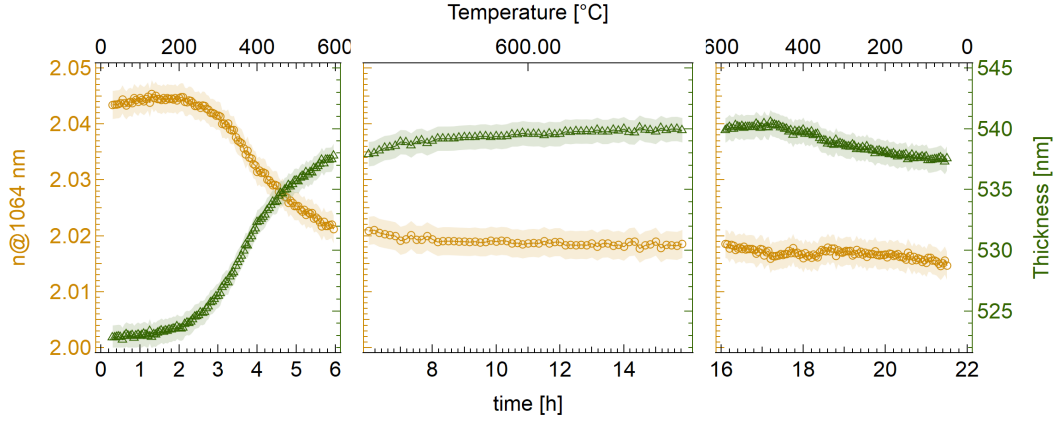


Figure 5.10: Refractive index at 1064 nm (left axis) and thickness (right axis) of the hafnia–tantala thin film deposited on crystalline silicon, measured during the heating phase (left panel), the 600 °C plateau (middle panel), and the cooling phase (right panel). Colored bands around the markers represent the associated error bars. The bottom panel shows the thermal profile of the annealing cycle to which the sample was subjected.

Figure 5.10 illustrates the evolution of the refractive index at 1064 nm and the film thickness of hafnia–tantala during its annealing cycle. For comparison, Figure 5.9 shows the refractive indices at 1064 nm and 1550 nm alongside the thickness changes for Titania–Tantala. The only variation between the two procedures is the peak temperature: both use a heating rate of 100 °C/h, but hafnia–tantala samples were ramped to 600 °C and held for 10 h, whereas Titania–Tantala samples reached a maximum of 500 °C. Despite this difference in maximum temperature, both materials exhibit nearly identical qualitative trends. In the left panel, corresponding to the heating ramp from room temperature (RT) to 600 °C, the first detectable changes emerge around 200 °C, close to the original deposition temperature. Between 350 °C and 600 °C, the variations in both thickness and refractive index appear to reach their maximum magnitude. Specifically, for the $\text{HfO}_2\text{--Ta}_2\text{O}_5$ coating, the refractive index decreases by 1.1% and the thickness increases by 2.9% over the 30 °C–600 °C ramp at 100 °C h^{-1} . In the middle panel, during the 10 h plateau at 600 °C, the changes are markedly smaller yet persistent compared to the heating ramp. The nonzero derivatives of both refractive index and thickness after 10 h suggest that the sample continues to evolve and that extending the plateau time at 600 °C would lead to additional transformations.

Upon completion of the full annealing cycle, the sample exhibits irreversible changes: an overall refractive-index reduction of 1.2% and a thickness increase of 2.5%.

5.3.3 Titania–Germania (TiO_2 – GeO_2)

As anticipated in the previous chapter, the Titania–Germania system, whose structural properties are detailed in Appendix B.3.2, is presented separately from the other high-index materials. As will become evident, TiO_2 – GeO_2 displays a remarkably distinctive behavior, unlike anything observed in any of the coating materials studied so far. Its unexpected response to thermal treatment posed significant challenges throughout this work. Indeed, a substantial portion of this thesis has been devoted to characterizing this material and to examining how various annealing parameters affect its optical and structural properties. A recent dedicated study authored by our group, covering all these aspects, is presented in ref. [111].

Titania–Germania stands out as one of the most promising candidates for next-generation coatings on gravitational-wave detector (GWD) mirrors. Its implementation is expected to yield a substantial improvement in detector sensitivity [58]. Unlike titania and other transition metal oxides used in GWDs coating Germania is a strong glass former with a glass-transition temperature near 500 °C [140, 141]. Consequently, trends established for other coating systems may not translate to this material, and recent studies have therefore focused on understanding its underlying mechanisms [93, 52, 75, 57, 53]. To this end, multiple annealing cycles were performed on titania–germania samples, and in this thesis only the most relevant cycles are presented, as summarised in Table 5.4. All samples share the optimized composition of 44% TiO_2 – 56% GeO_2 , a ratio selected not merely to minimize mechanical loss—which is intrinsically lower in pure germania—but to provide the optimal compromise between a sufficiently high refractive index and exceptionally low mechanical dissipation, ultimately yielding the lowest expected coating thermal noise [58]. Furthermore, recent structural analyses have revealed that at this exact concentration the amorphous network achieves a particular topological balance between Ti–O–Ge (42%) and Ge–O–Ge (44%) linkages, which is believed to play a decisive role in suppressing internal friction [75].

Cycle #	Heating rate (°C/h)	Cooling rate (°C/h)	T plateau (°C)	Time at max. T (h)
1	100	100	500	10.0
2	100	100	550	10.0
3	100	100	600	10.0
4a [†]	50	50	600	10.0
4b [†]	50	50	600	10.0
5	100	600 [§]	600	0.0
6	100	1200	600	1.4 [‡]

Table 5.4: Overview of the annealing protocols applied to the $\text{TiO}_2\text{--GeO}_2$ coatings investigated in this thesis. All samples were diced from the same coated wafer and therefore shared identical as-deposited conditions. [†]Cycles #4a and #4b were performed consecutively on the same sample to assess the effect of a second thermal annealing. [§]Cycle #5 features a cooling ramp of 1200 °C/h down to 400 °C, followed by 600 °C/h down to room temperature. [‡]Cycle #6 corresponds to an isothermal plateau lasting 85 min.

Experimental Data Observation We begin by examining the experimental data. This allows us to demonstrate that the trends observed in the refractive index and thickness as a function of temperature are not artifacts introduced by the modeling procedure, but instead emerge directly from the measurements. In Figure 5.11, three panels are shown. The *top-left panel* shows the evolution of Ψ as a function of photon energy and temperature. The data were acquired during the heating of a representative titania–germania sample from room temperature (RT) to 600 °C, at a heating rate of 100 °C/h. The *top-right panel* provides a zoomed view of the Ψ maximum at 1.6 eV, which primarily reflects changes in the coating during heating [142]. The *bottom panel*, composed of three sub-images, presents the plateau phase (10 h at the annealing temperature) of the titania–germania sample at 500 °C (left), 550 °C (center), and 600 °C (right). At the 500 °C plateau, only small variations are observed, qualitatively similar to those seen during heating; that is, with increasing time a slight increase in amplitude occurs, but no appreciable spectral shift is detected. At the 600 °C plateau, the evolution follows an opposite trend with respect to heating: the interference features shift in the reverse direction, indicating (see Appendix E.1) a decrease in thickness. Most of this change occurs within the first two hours of the plateau (light-purple lines). The behavior at 550 °C lies between these two limiting cases, showing an intermediate evolution of both spectral position and amplitude.

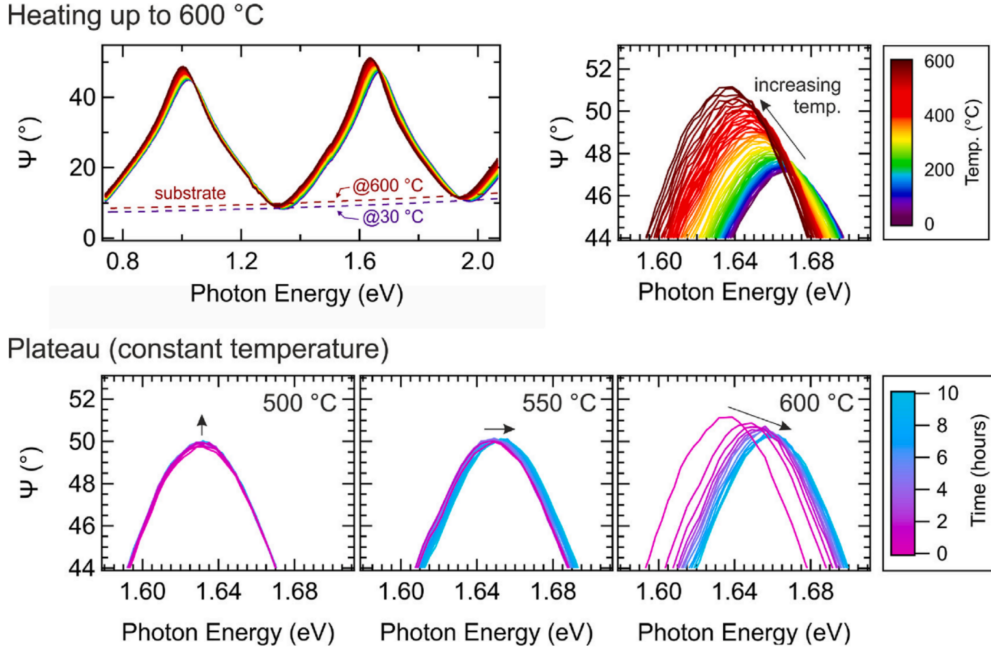


Figure 5.11: Top left panel: Ψ spectra measured during the heating ramp from room temperature up to 600 °C (continuous lines), together with measurements on the bare substrate at room temperature and at 600 °C (violet and dark red dotted lines, respectively). Top right panel: zoom on one of the maxima in the Ψ spectra shown in the top left panel. Bottom panels: zoom on one of the Ψ maxima recorded during the plateau at 500 °C (left), 550 °C (center), and 600 °C (right). As highlighted by the black arrows, the trends observed as a function of temperature are qualitatively different. This figure is reproduced from the author's publication [111]

Temperature and Time-Dependent Changes in Refractive Index and Thickness A systematic investigation was conducted to determine how the thermal-treatment conditions influence the optical and structural evolution of the coatings. Building on the observations presented in the previous section, the following analysis examines the dependence of the refractive index and thickness on three key parameters: the *annealing temperature*, the *plateau duration* (i.e., the time spent at the maximum temperature), and the *heating rate*. The refractive index and thickness values used in this analysis were extracted by fitting the experimental data with a Cauchy model applied within the transparency window of the coating, specifically in the 1000–1550 nm range. The results are presented in the next subsections, each dedicated to one of these parameters, in order to disentangle their individual contributions to the overall behavior of the TiO₂–GeO₂ coatings.

Annealing Temperature Effect The main results are reported in Figure 5.12, which is composed of two panels. The upper panel displays the percentage variation in the coating thickness during the three phases of the annealing cycle: heating (left), the 10 h plateau (center), and cooling (right). The lower panel shows the corresponding percentage variation of the refractive index at 1064 nm over the same phases.

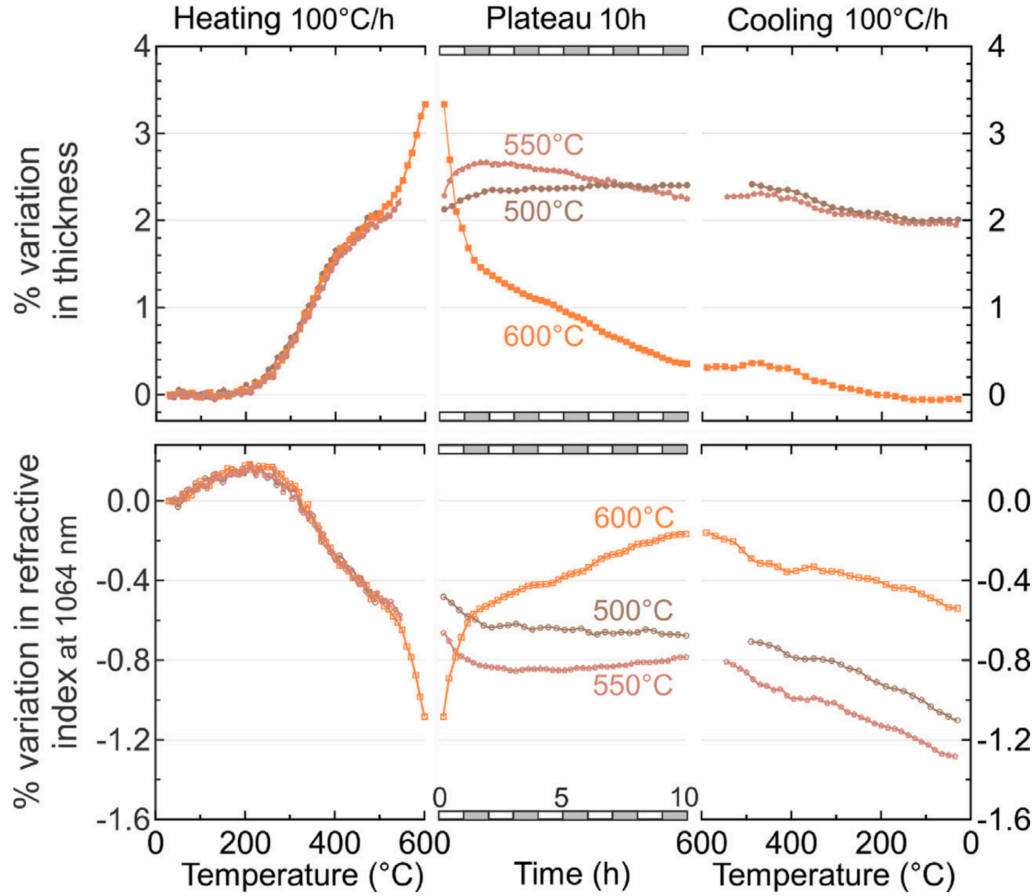


Figure 5.12: Results of the in-situ real-time ellipsometry analysis performed on $\text{TiO}_2\text{-GeO}_2$ coatings annealed at 500 °C, 550 °C, and 600 °C (cycles #1, #2, and #3, respectively; see Table 5.4). The top panels show the percentage variation in thickness, while the bottom panels report the corresponding percentage change in the refractive index at 1064 nm. All variations are expressed relative to the as-deposited state of the coatings. This figure is reproduced from the author’s publication [111].

A first important observation concerns the heating phase. For both thickness and refractive index, the curves of the three cycles overlap up to approximately 500 °C, indicating that the experiments are highly reproducible across different thermal cycles. The heating phase can be divided into four main

regimes:

- Up to $\sim 200^\circ\text{C}$, no significant variations are observed.
- Between $\sim 200^\circ\text{C}$ and $\sim 500^\circ\text{C}$, substantial changes occur, comparable to those previously reported for titania–tantala coatings.
- From 500°C to 550°C , the trend continues smoothly without abrupt transitions.
- Between 550°C and 600°C , a marked acceleration in both refractive index and thickness variations is observed.

Particular attention must be paid to the plateau stage, as it reveals three distinct trends. The sample annealed at 500°C continues its natural evolution (similar to titania–tantala), exhibiting a slight increase in thickness (0.4%) and a small decrease in refractive index (-0.2%). The 550°C sample initially follows a similar trend for the first two hours, after which both curves invert: the thickness begins to decrease slightly, while the refractive index increases over the remaining eight hours. The behavior at 600°C is even more pronounced: the thickness decreases by $\sim 3\%$ (17 nm), and the refractive index increases by $\sim 0.9\%$ throughout the plateau, with a particularly steep variation during the first two hours. This early inversion is examined in more detail in Figure 5.13. During cooling, all three samples undergo thermally induced transformations that result in a reduction of both thickness and refractive index. At the end of this phase, despite the markedly different behaviors observed during the plateau, the final thicknesses of the 500°C and 550°C samples are essentially identical, each showing an overall increase of about 2%. Their refractive indices, by contrast, differ slightly, decreasing by 1.1% and 1.3%, respectively. The sample annealed at 600°C represents a distinct case, as its overall thickness remains unchanged before and after annealing. This implies that ex-situ measurements would detect no thickness variation, even though the film thickened by nearly 3% during heating and subsequently thinned by a comparable amount during the plateau and cooling. The refractive index, instead, shows a net decrease of approximately 0.5%. This demonstrates that, without in-situ ellipsometry, all substantial transformations occurring during the plateau - never previously reported - would have remained completely hidden. It is also worth noting that the temperature-dependent optical properties of titania–germania coatings had received very limited attention prior to this study.

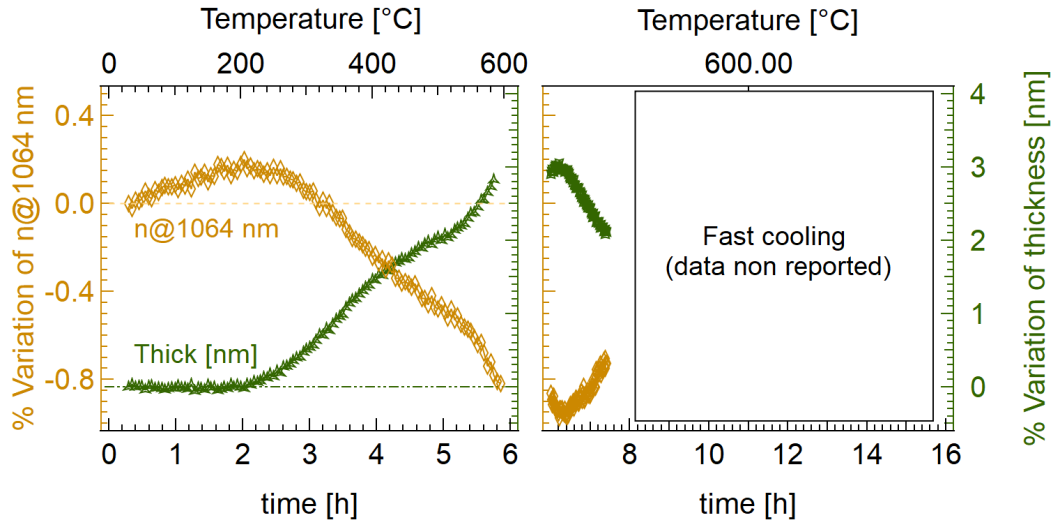


Figure 5.13: Results of the in-situ real-time ellipsometry analysis performed on the $\text{TiO}_2\text{-GeO}_2$ sample annealed at 600 °C for 85 min, with a heating rate of 100 °C/h (cycle #6; see Table 5.4). The analysis was carried out on a sample nominally identical to those shown in Figure 5.12. The goal was to increase the number of ellipsometric scans (one scan per minute during the plateau and one scan every 5 °C during heating) in order to study the inversion point with higher accuracy. Only the heating phase and the plateau are therefore shown.

Annealing Time Effect We now consider annealing cycles #4a and #4b. These two cycles are nominally identical and were performed on the same titania-germania sample. The sample first underwent cycle #4a, consisting of heating at 50 °C/h, a 10 h plateau at 600 °C, and cooling to room temperature at 50 °C/h. Eight days later, the same sample was subjected to the identical cycle #4b.

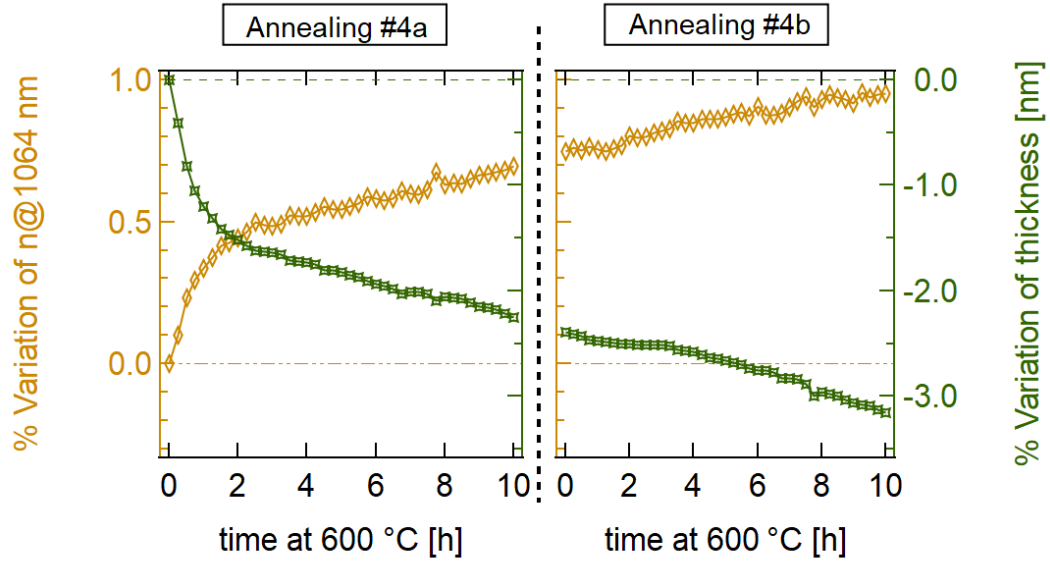


Figure 5.14: Percentage variation in the refractive index at 1064 nm (orange markers) and thickness (green markers) of a $\text{TiO}_2\text{-GeO}_2$ coating during two consecutive plateaus at 600 °C (annealing cycles #4a and #4b; see Table 5.4). Data acquired during the heating and cooling ramps are omitted.

Figure 5.14 shows two adjacent panels. The left panel reports the percentage variation of the refractive index at 1064 nm (yellow markers) and of the thickness (green markers) during the 10 h plateau of the first annealing cycle. The right panel shows the same quantities measured during the second cycle. The behavior observed during the second plateau appears to be a natural continuation of the trend measured during the first plateau, indicating that the transformations occurring during the cooling phase of cycle #4a are reversible. After 10 h of the second cycle (corresponding to 20 h at 600 °C), both the refractive index and the thickness are still evolving (i.e. their temperature derivatives are not zero). This indicates that additional transformations would likely occur if the plateau duration were extended beyond 20 h, or if a third identical cycle were applied to the same sample, further motivating an investigation of longer plateau times, for example up to 100 h [58].

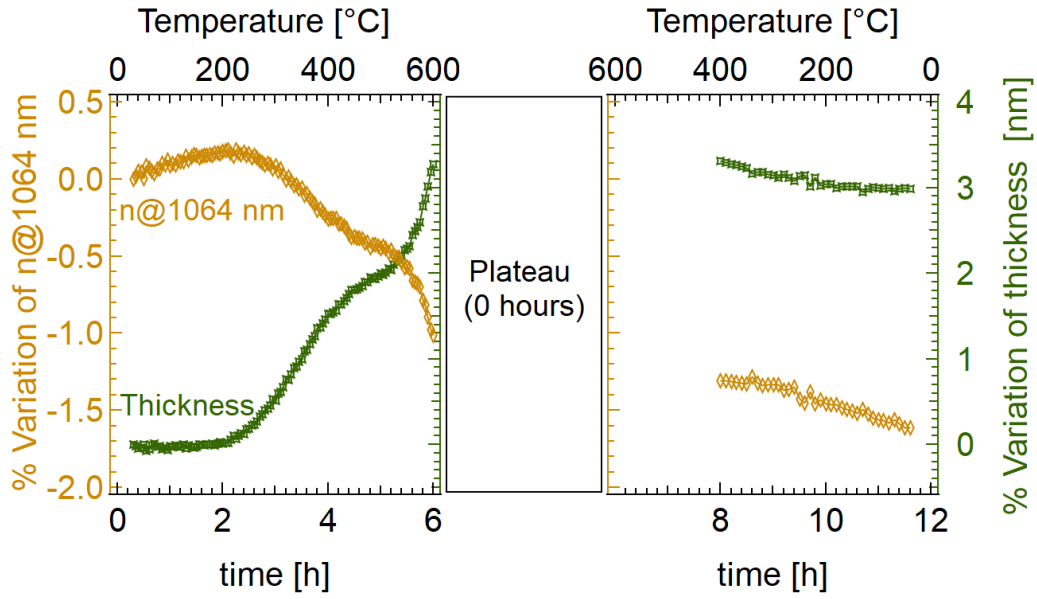


Figure 5.15: Annealing cycle #5 (see Table 5.4): the sample was heated from 30 °C to 600 °C at 100 °C/h and, upon reaching 600 °C, was immediately subjected to rapid cooling without any plateau. Cooling was performed at 1200 °C/h down to 400 °C, and then at 600 °C/h to room temperature; data were collected only below 400 °C. The left panel shows the behaviour during the heating stage, while the right panel corresponds to the cooling stage. The yellow and green curves represent the percentage variation of the refractive index at 1064 nm and of the film thickness, respectively.

A further experiment was carried out during annealing cycle #5. The sample was heated to 600 °C at a rate of 100 °C/h and subsequently subjected to rapid cooling (1200 °C/h from 600 °C to 400 °C, and 600 °C/h from 400 °C to room temperature). The key aspect of this experiment is that the rapid quench froze the material in the metastable configuration achieved at 600 °C. At room temperature, the thickness increased by approximately 3% (about 20 nm), while the refractive index at both 1064 nm and 1550 nm decreased by 1.6%. In the absence of a plateau at 600 °C, neither the thickness inversion nor the decrease in refractive index were observed. This annealing cycle is particularly relevant for the ex-post Raman measurements, as it enables us to assess whether the inversion observed during the plateau at 600 °C is associated with crystallization. By comparing samples subjected to cycle #3 (10 h at 600 °C), cycle #5 (0 h at 600 °C, i.e. before inversion), and cycle #6 (1.5 h at 600 °C, immediately after inversion), it is possible to determine whether crystallization is the driving mechanism behind the observed behavior. The

analysis is presented in Par. 5.3.3.

Heating Rate Effect Figure 5.16 compares annealing cycles #3 and #4a. The only difference between the two cycles is the heating and cooling rate. In cycle #3 (green markers), the rate was $\pm 100^\circ\text{C/h}$, whereas in cycle #4a (blue markers) the rate was $\pm 50^\circ\text{C/h}$. Only the thickness is reported, since the refractive index did not vary within the experimental uncertainty.

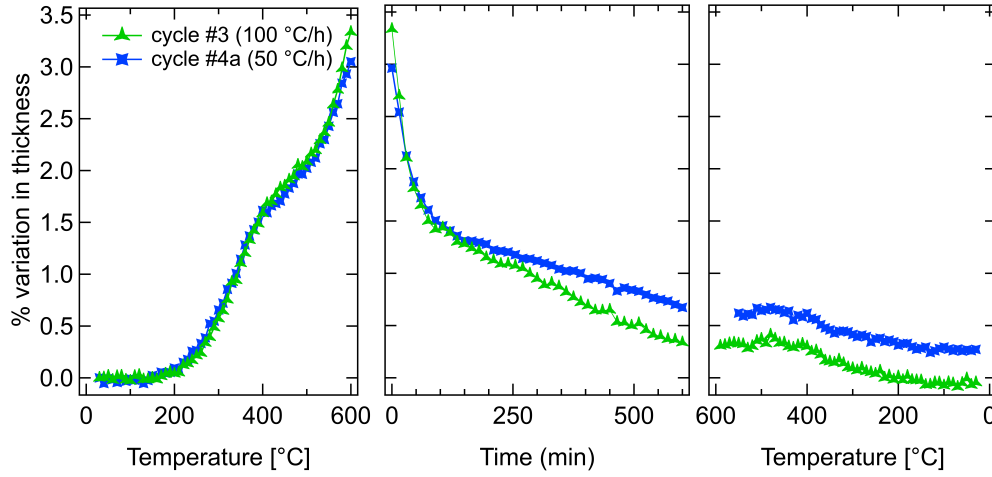


Figure 5.16: Percentage variation in the thickness of $\text{TiO}_2\text{--GeO}_2$ coatings annealed using two different heating and cooling rates: green markers correspond to 100°C/h , and blue markers to 50°C/h (cycles #3, and #4a; see Table 5.4). Differently from the other plots in this work, here the temperature is shown on the lower axes (left: heating, right: cooling), while the central axis reports the time at a fixed 600°C . This choice avoids misleading comparisons, since the two heating rates would otherwise correspond to different absolute times.

A slight divergence between the two curves becomes visible toward the end of the heating ramp, between 550°C and 600°C . At 600°C , the coating heated at 100°C/h is approximately 0.4% thicker than the one heated at 50°C/h . During the plateau the coating annealed at 100°C/h exhibits a steeper and more pronounced thickness reduction. As a result, by the end of the plateau it becomes about 0.4% thinner than the coating annealed at 50°C/h . This difference remains nearly constant throughout the cooling phase, during which both coatings follow a similar trend. The small but measurable difference in thickness between coatings annealed at different rates demonstrates that the heating rate can influence the macroscopic properties of $\text{TiO}_2\text{--GeO}_2$.

coatings. For this reason, studies on the annealing of optical coatings should report not only the maximum annealing temperature and the plateau duration but also the heating rate, in order to ensure reproducibility.

Supplementary Characterization Methods In this paragraph, we present additional complementary analyses beyond the measurements of thickness and refractive index at 1064 nm as a function of temperature. Specifically, we examine the evolution of *the optical gap* to obtain further insight into the relationship between the optical properties of the coating and its underlying structural state. We then perform *ex-post Raman spectroscopy* to directly monitor the possible onset of crystallization in the titania–germania system and to assess whether crystallization is the driving mechanism behind the behaviour observed during the annealing cycles.

Optical Gap as a Function of Temperature Figure 5.17 shows that the evolution of the optical gap (E_g) displays a clear behavior across the three thermal cycles. Cycles #1, #2, and #3 correspond respectively to annealing at 500, 550, and 600 °C, each performed with a heating rate of 100 °C/h, a 10 h isothermal plateau at the target temperature, and a cooling rate of 100 °C/h.

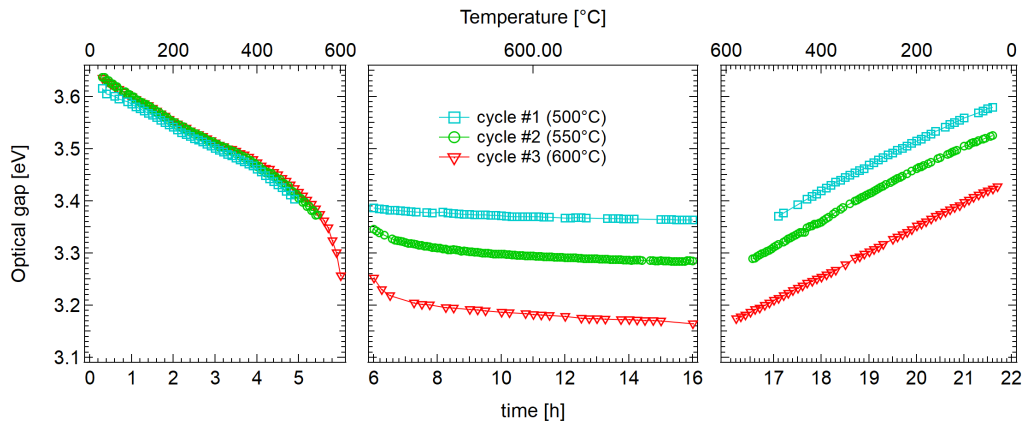


Figure 5.17: Evolution of the optical gap during the annealing process for the three thermal cycles reported in Table 5.4: cycle #1 at 500 °C (cyan), cycle #2 at 550 °C (green), and cycle #3 at 600 °C (red). The three panels correspond respectively to: (left) heating from room temperature to the maximum annealing temperature, (center) the 10 h plateau at constant temperature, and (right) cooling back to room temperature. The optical gap values were extracted from spectroscopic ellipsometry using a Cody–Lorentz dispersion model.

During the initial heating phase, all samples exhibit a monotonic and rapid decrease in E_g , which accounts for the largest portion of the total variation. A reduction in E_g during heating reflects a combination of reversible thermal effects (driven by lattice expansion and electron-phonon interactions [143]) and structural modifications of the continuous random network, leading to possibly irreversible changes⁵. By the end of the heating ramp, the gap is reduced by 5.9% for the 500°C cycle, 6.8% for 550°C, and 9.9% for 600°C, relative to the room-temperature value of ~ 3.61 eV. A similar trend is observed in Fig. 5.12, where, at comparable temperatures, the film thickness increases sharply while the refractive index decreases. This behavior further supports the presence of structural rearrangements occurring within the material. Upon reaching the isothermal plateau, the three curves already appear offset from one another, as a substantial fraction of the total modification has occurred during the heating ramp. Once the temperature stabilizes, all three curves continue to decrease, with a progressively steeper slope as the annealing temperature increases: at 500°C the reduction reaches -7.1% , at 550°C it reaches -9.3% , and at 600°C it reaches -12.5% . During the cooling phase, the trend partially reverses: E_g increases in all cycles as thermal energy is removed, consistent with the reversible reduction of electron-phonon interactions and macroscopic thermal contraction. However, the recovery remains incomplete, revealing a clear hysteretic behavior that becomes progressively more pronounced at higher annealing temperatures. At the end of the cooling stage, a residual deficit persists: -0.7% for 500°C, -2.4% for 550°C, and -5.1% for 600°C. According to the standard theory of amorphous semiconductors, purely thermally induced structural relaxation such as defect annihilation and strain relief, typically leads to an overall *increase* (blueshift) of the optical gap [103]. The anomalous net reduction observed in this system therefore points to the presence of an additional, competing mechanism. As suggested by the evolution of the optical gap, this deficit originates primarily — and most notably for the 550 °C and 600 °C cycles — at the end of the heating ramp and during the first hours of the isothermal plateau. In this regime, approaching and exceeding the glass-transition temperature of germania is expected to enhance

⁵This is particularly evident for annealing cycles reaching 550 °C and 600 °C, where the optical band gap does not fully recover its initial value at the end of the cycle. Part of these irreversible changes may form between the end of the heating ramp and the subsequent plateau, consistent with the variations observed in thickness and refractive index.

atomic mobility, which may underlie the structural changes observed through the thickness evolution (as discussed in Ref. [111] and examined in more detail in Par. 5.3.3). Such thermally driven rearrangements could also affect the optical-gap response, although this remains to be verified and is currently under investigation.

Raman Spectroscopy for Crystallization Detection To better compare the effects of the different annealing treatments, Figure 5.18 shows the first derivative of the Raman intensity for the as-deposited coating (black line) and for the samples annealed at 500 °C (grey), 550 °C (pink), and 600 °C (orange, dark red, blue, and light blue). The four curves at 600 °C correspond to different plateau durations, as listed in Table 5.4.

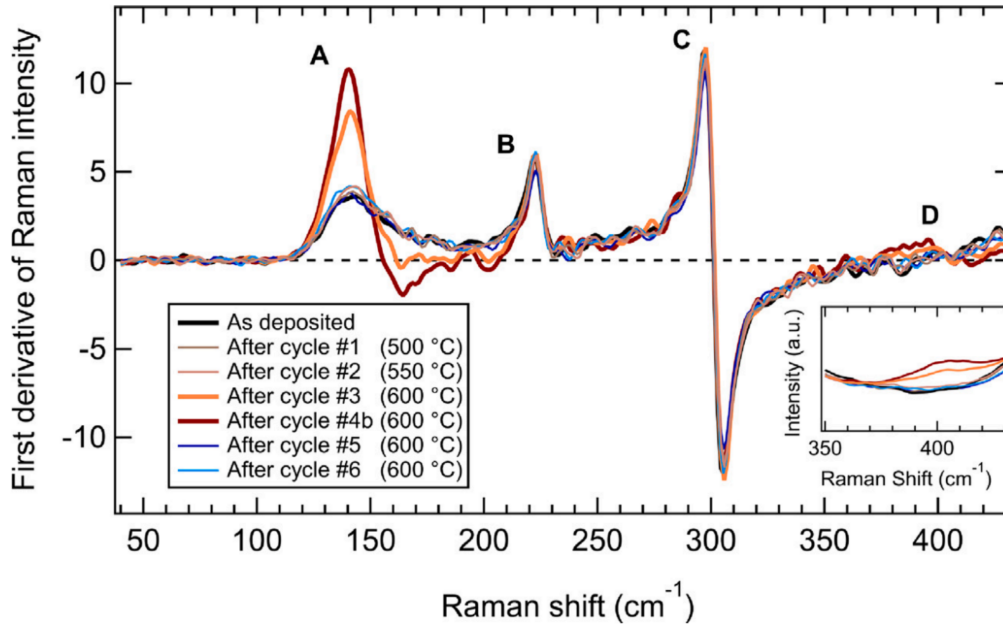


Figure 5.18: First derivative of the Raman intensity for the as-deposited $\text{TiO}_2\text{-GeO}_2$ coating (black line) and for samples annealed at 500 °C (grey), 550 °C (pink), and 600 °C (orange, dark red, blue, and light blue). The four datasets at 600 °C correspond to different plateau durations, as reported in Table 5.4. The inset displays the Raman spectra in the region around 400 cm^{-1} , where the D feature is highlighted; the spectra shown in the inset have been vertically shifted for clarity.

Four spectral features, labelled A, B, C, and D, can be clearly recognised in all datasets. Features B and C remain essentially unchanged and originate from the silicon substrate, corresponding to the TA and 2TA phonon

modes [144]. Features A and D, instead, are associated with the TiO_2 - GeO_2 coating and match the typical anatase TiO_2 Raman peaks near 143 and 395 cm^{-1} [145]. Most spectra closely resemble the as-deposited sample, except for those corresponding to cycles #3 and #4b, which show noticeable differences in the A and D regions. Such deviations, indicative of partial crystallization, will be discussed in detail in the following paragraph.

Final Discussion on the TiO_2 - GeO_2 Results Titania-germania is a complex material system, and this work presents the first in-situ real-time investigation of its optical and structural properties during annealing. In particular, a distinctive inversion in the behavior of both thickness and refractive index has been observed, whereby the two quantities reverse their temperature-dependent trends once the material approaches the 600°C plateau. The inversion of these trends represents a behavior that has not been observed in any of the coatings analysed in this study, nor in those previously examined within the collaboration for gravitational-wave mirror coatings. Based on the combined outcome of multiple dedicated experiments and the limited literature available on the subject, several consistent observations can be made regarding the overall response:

- *Glass transition of germania.* Since such an inversion has not been observed in previous coatings containing titania, where crystallization is instead detected [55], we infer that the glass transition of germania plays a decisive role in the observed behavior. This suggests that a substantial fraction of the effect may be attributed to germania rather than titania. This interpretation is further supported by preliminary measurements on pure germania films, currently under investigation, which exhibit similar trends and reinforce the role of the germania network in governing the observed behaviour.
- *Release of argon.* In a recent study, Lalande *et al.* [93] analysed a TiO_2 - GeO_2 coating similar to the film investigated here. They reported that argon - an undesirable by-product incorporated during the ion-beam sputtering process [83] - is progressively released upon heating, with a thermal desorption peak near 600°C for sub-micron films. Their experimental data show that approximately 65% of the trapped argon is rapidly lost within the first 1000 s (~ 17 min) at 600°C . This rapid ar-

gon release appears consistent with the steep variations in thickness and refractive index observed during the initial stage of the 600 °C plateau (Figure 5.12, central panel). We suggest that the glass-transition temperature of germania may play a key role, as crossing this threshold increases the mobility of the network and thereby allows argon to escape. Consistent with this interpretation, such substantial argon release has not been observed in other amorphous mixed-oxide coatings for GWD applications, including titania–tantala [74].

- *Partial crystallization of titania.* At 600 °C, changes developing over longer time scales (beyond 1–2 h from the start of the plateau) are revealed by Raman spectroscopy, which shows that the TiO₂–GeO₂ coating becomes at least partially crystallised after 10 h at this temperature (cycles #3 and #4b, Figure 5.18). This is indicated by features A and D in Figure 5.18, consistent with the anatase TiO₂ peaks typically observed around 143 and 395 cm⁻¹ [145]. Peaks B and C originate from the silicon substrate and correspond to the TA and 2TA modes [144]. In agreement with previous *in situ* X-ray diffraction studies [146], crystallization is not detected either upon reaching 600 °C (cycle #5, Figure 5.18) or after 1.5 h at this temperature (cycle #6, Figure 5.18). The Raman data therefore indicate that crystallization does not occur during the steep trend observed in the first 2 h of the plateau (Figure 5.12, central panel). Instead, the onset of crystallization becomes detectable only after this initial stage and becomes more pronounced when the 600 °C plateau is extended from 10 to 20 h. These findings demonstrate that the characteristic inversion and the marked variations in refractive index and thickness observed at the beginning of the plateau cannot be attributed to crystallization. Rather, only a portion of the slow and steady evolution occurring later during the plateau is associated with the crystallization process.
- *Overall optical-gap variations.* In addition to the thickness and refractive-index variations, the behavior of the optical gap E_g provides an independent probe of the underlying structural dynamics. As shown in Fig. 5.17, E_g undergoes a pronounced reduction during the heating ramp and exhibits markedly different kinetic trends across the three thermal cycles. The most substantial variation occurs in the 600 °C cycle, where the gap

collapses rapidly at the end of the heating ramp and continues to decrease during the first ~ 2 h of the isothermal plateau. The steep and persistent decrease observed at 600°C , followed by an incomplete recovery upon cooling, indicates that the material experiences a genuine configurational reorganisation rather than a purely reversible thermo-optic response.

- *Mechanical-loss measurements.* Mechanical-loss measurements were carried out using the Gentle Nodal Suspension [147] system for ring-down measurements, which enables a precise determination of the coating loss by analyzing the decay times of selected vibrational modes of 3-inch, 1-mm-thick silica disks double-coated with $\text{TiO}_2\text{--GeO}_2$. The measurements were conducted as part of this work, in collaboration with Maastricht University during the research period abroad. Each sample was characterised across multiple eigenfrequencies, both in the as-deposited state and after the annealing cycle carried out in a muffle furnace (10 h at 550°C , with a heating rate of 60°C/h). Across all measured vibrational modes, the coating loss exhibits a clear and systematic reduction after annealing, with individual variations ranging from approximately 39% to 61%. The average decrease amounts to about 52%, with a dispersion of only a few percent across the different eigenfrequencies. Although the detailed results are not presented in this work, these measurements provide independent evidence that the thermal treatment substantially modifies the dissipative response of the $\text{TiO}_2\text{--GeO}_2$ coatings.

Chapter 6

Conclusions

In this thesis, a comprehensive investigation of the optical and structural evolution of amorphous oxide coatings through real-time spectroscopic ellipsometry has been presented. The motivation for this work arises from the stringent requirements of gravitational-wave interferometers, whose sensitivity is fundamentally limited by coating thermal noise. The introductory chapters established the scientific and technological context in which this challenge emerges: in Chapter 1, the operating principles of gravitational-wave detectors were introduced, from the theoretical foundations of gravitational waves (Section 1.1) to the first direct detection event (Section 1.2). The architecture of large-scale interferometers such as LIGO and Virgo (Section 1.3) and the main noise sources limiting their sensitivity were also discussed. Building on this foundation, Chapter 2 examined the optical performance and structural design of the input (ITM) and end (ETM) mirrors (Section 2.1) employed in these detectors. After addressing the mirrors at the component level, the chapter narrowed its focus to the multilayer Bragg reflectors (Section 2.2) and to the current state of high-index coating materials (Section 2.3). This progression highlighted the intrinsic limitations of existing oxides and motivated the objectives of the thesis, outlined in Section 2.4. These objectives center on developing a robust methodology capable of probing how the optical and structural properties of coating materials evolve during annealing. The methodological core of the thesis was introduced in Chapter 3, where the theoretical framework of spectroscopic ellipsometry (3.1) and the optical models used to describe amorphous materials (3.2) were presented. A substantial methodological contribution was then developed in Chapter 4, which detailed the design of the experimental apparatus 4.1 and the procedures required to en-

sure accurate, reproducible, and thermally stable measurements. In particular, Section 4.2 presented a systematic evaluation of the main sources of instrumental uncertainty, articulated into three dedicated studies: (i) the analysis of window-induced artifacts introduced by the Linkam heating stage (4.2.1); (ii) the characterization of temperature-induced misalignment of the reflected beam on the detector (4.2.2); and (iii) the assessment of scan-timing accuracy and the effective thermal response of the heating stage (4.2.3). These analyses established the limits of validity of the measurements and ensured that the observed trends could be attributed to the coating rather than to instrumental effects. The same approach was also applied to the choice of fitting protocol (4.3) for both the Cauchy and the Cody–Lorentz dispersion models, assessing the modeling error introduced by each parametrization and identifying the most reliable strategy for each case. This analysis shows that, for the Cauchy model, the choice of protocol has only a minor impact on the extracted parameters due to the limited number of degrees of freedom; in contrast, the Cody–Lorentz model is significantly more sensitive to the fitting strategy, and the appropriate protocol was identified and adopted to ensure physically meaningful results. Section 4.4 described the shift from conventional in-situ characterization to a fully real-time approach, enabled by the development of an automated script for data acquisition, pre-processing, fitting, and visualization of the results. In Chapter 5, the methodology was first applied to crystalline silicon (Section 5.1), the reference substrate used for all samples. This allowed us to construct accurate temperature-dependent optical models between 30 and 600 °C, which serve as the standard framework for analyzing both low- and high-index materials deposited on top of silicon. Silica (Section 5.2) coatings were also investigated with a dual objective: to characterize the native silica layer that naturally forms on crystalline silicon and lies beneath all deposited coatings, and to study the behavior of the IBS-deposited silica itself (i.e., the low-index material). The optical behavior of silica was measured as a function of annealing temperature through both real-time and ex-post ellipsometric analyses. These measurements enabled the validation of a tabulated optical model for silica, and the ex-post data in particular supported a study that has recently been published [110]. The analysis was then extended to three representative high-index coating materials: titania–tantala (Subsection 5.3.1), hafnia–tantala (Subsection 5.3.2), and titania–germania (Subsection 5.3.3).

Titania–tantala. The real-time measurements confirmed the well-established relaxation dynamics known from ex-situ studies and provided the first continuous in-situ observation of these processes, as originally documented in our work [74]. The most significant changes in refractive index and thickness occurred during the heating ramp, particularly between 200 °C and 350 °C, while the 500 °C plateau induced smaller but still measurable evolution. The coating exhibited a smooth, monotonic increase in physical thickness and a corresponding decrease in refractive index, primarily driven by stress relaxation and medium-range structural ordering, with only minor secondary contributions associated with argon release and with the reduction of oxygen deficiency during annealing. The decrease in Urbach energy observed during the plateau further supported the enhancement of structural order. Overall, $\text{TiO}_2\text{--Ta}_2\text{O}_5$ followed a continuous and predictable relaxation pathway, with no evidence of metastable states or abrupt transitions.

Hafnia–tantala. The $\text{HfO}_2\text{--Ta}_2\text{O}_5$ coating exhibited a thermal response closely resembling that of titania–tantala, despite being annealed at a higher temperature (600 °C instead of 500 °C). This behavior is consistent with the chemical proximity of hafnium and tantalum, which leads to comparable bonding environments and similar thermomechanical responses under thermal treatment. Similarly to titania–tantala, the onset of structural evolution appeared again around 200 °C, followed by the most pronounced variations between 350 °C and the maximum temperature. The coating continued to evolve throughout the 10-hour plateau at 600 °C, but at a markedly reduced rate compared to the ramp, fully consistent with the behavior observed in titania–tantala.

Titania–germania. In stark contrast to all other materials investigated in this work, $\text{TiO}_2\text{--GeO}_2$ exhibited a thermal response that has never been observed in any coating developed for GWD mirrors. This constitutes the most distinctive and impactful result of the thesis, and the main findings have been published in Ref. [111]. A systematic study was carried out by varying the annealing temperature (500, 550, and 600 °C), the heating rate (50 and 100 °C/h), and the duration of the isothermal plateau (0, 1.5, 10, and 20 h, where the 20 h condition corresponds to two consecutive 10 h cycles). During the heating ramp, the coating initially behaved similarly to the other transition-metal oxides, but its evolution during the temperature plateaus diverged markedly. At 500 °C the response was minimal and closely matched that of titania–tantala and hafnia–tantala, while the 550 °C plateau represented an intermediate regime

with respect to the behavior observed at 600 °C. Indeed, a dramatic change occurred at 600 °C, where the coating exhibited a clear inversion of the trend observed during the ramp: the thickness, which had increased during the heating phase, began to decrease as soon as the plateau was reached, whereas the refractive index showed the opposite behavior. This inversion is associated with a substantial release of argon, together with pronounced variations in both thickness and refractive index. A consistent signature also appeared in the optical gap, which underwent a steep reduction within a comparable time window. Remarkably, at the end of the cooling phase the film thickness returned to its pre-annealing value, a behavior that would have been difficult to identify without real-time monitoring. In contrast, the refractive index and the optical gap did not recover their initial values. The overall evidence therefore points to an irreversible structural reorganization rather than merely reversible thermally induced effects. Among the possible mechanisms considered to explain the inversion, we also evaluated the partial crystallization of the titania component, detected with Raman spectroscopy. This explanation was discarded by comparing annealing cycles with different dwell times at 600 °C, since crystallization signatures appear only after prolonged exposure, whereas the inversion in thickness and optical constants takes place within the first two hours of the plateau. We therefore suggest that the interplay between enhanced atomic mobility near the glass transition and the release of incorporated argon is the most plausible mechanism underlying the rapid inversion regime observed at 600 °C. Future studies on pure GeO_2 films will be essential to isolate the role of the germania network and clarify the mechanisms underlying this unusual behavior.

In summary, this dissertation provides a unified framework for the real-time optical characterization of amorphous thin films during thermal processing. By integrating theoretical modeling, the development of advanced experimental methods, and automated analysis, it offers a powerful tool for understanding and optimizing the materials that define the performance of next-generation gravitational-wave detectors. Beyond its direct relevance to GWD mirror coatings, the versatility of the methodology developed here enables its application to a much broader class of materials. This framework has, for instance, been successfully employed to investigate the insulator–metal transition in vanadium oxide, a prototypical Mott insulator, allowing the optical response to be tracked continuously across the transition. Similarly, it has been used to study

amorphous semiconductors for photovoltaic applications, such as zinc–tin oxide, where the dependence of the optical properties on dopant concentration was characterized. The same approach has also proven effective for probing active multilayer devices under applied bias, enabling real-time monitoring of voltage-dependent optical behavior. This latter study has resulted in a dedicated publication [148].

Chapter A

Interferometric Gravitational-Wave Detectors: Operating Principles, Sensitivity, and Noise Sources

In this chapter of the appendix, two of the main noise sources limiting the sensitivity of gravitational-wave detectors are discussed, namely:

- Seismic noise at low frequencies (Section [A.1](#));
- Quantum noise at intermediate and high frequencies (Section [A.2](#)).

While the discussion of quantum noise applies to both Virgo and LIGO, the treatment of seismic noise differs substantially between the two instruments. Since this thesis focuses primarily on the Virgo detector, only the Virgo Super Attenuator (SA) is described in the following section. For completeness, it is worth noting that LIGO mitigates seismic disturbances through its Seismic Isolation System (SIS), whose design and performance are detailed in [\[149\]](#).

A.1 Seismic Noise

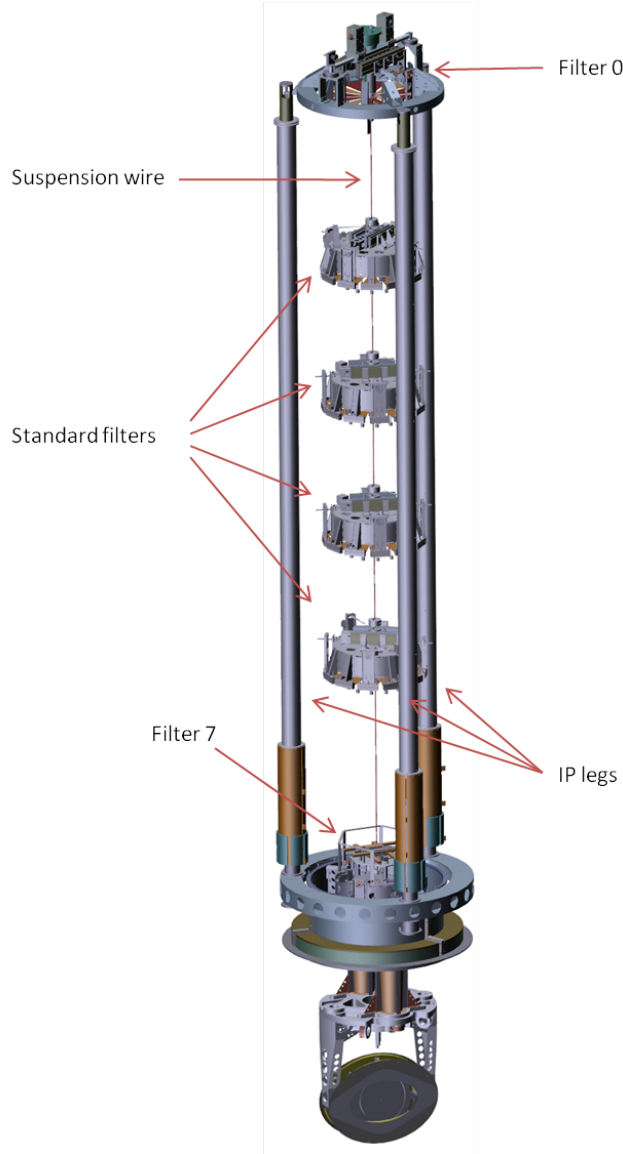


Figure A.1: Schematic representation of the Advanced Virgo Super Attenuator (SA), showing the three inverted-pendulum (IP) legs, the top seismic stage (Filter 0), the suspension wires connecting the cascade of standard seismic filters, the payload assembly, and the interferometric mirror at the bottom. Image reproduced from [10].

The sensitivity of the Virgo interferometer at low frequencies is strongly limited by seismic disturbances originating from both natural and anthropogenic sources. The dominant contributions include the oceanic microseism, typically below 1 Hz, generated by the interaction of ocean waves; local human activity and traffic, producing vibrations mainly below 10 Hz [150]. To

drastically suppress seismic noise, the suspension system known as the *Super Attenuator (SA)* was developed for Advanced Virgo. The SA is a hybrid passive-active attenuation system capable of reducing seismic noise by more than ten orders of magnitude in all six Degrees of Freedom (DoF) above a few Hertz in Virgo [151]. The mechanical structure of the SA consists of three main elements [10]:

- *Inverted Pendulum (IP)*: composed of three monolithic aluminum legs, each 6 meters long, connected to the ground through flexible joints. The legs support an upper ring that serves as the mechanical base for the so-called *Filter 0*, an additional seismic filter. This ring is equipped with sensors and actuators¹ arranged in a circular configuration, used to actively damp the resonance modes of the IP. The sensors include three Linear Variable Differential Transformers (LVDTs)², sensitive above 100 mHz, and five accelerometers (three horizontal and two vertical) with sensitivity below a few Hertz.
- *Seismic filter chain*: suspended from Filter 0, it is composed of five cylindrical passive filters, each 8 meters long. These filters are designed to provide progressive attenuation of vibrations beyond their resonance frequencies, reducing seismic noise by approximately 40 dB each. Their function is crucial for mechanically isolating the mirror from environmental vibrations.
- *Mirror Payload*: suspended from the last filter of the chain, known as Filter 7, this is the terminal stage hosting the mirror. Filter 7 is equipped with six LVDT sensors and six coil-magnet actuators, arranged in a circular configuration, enabling precise control of the payload in all DoF. The mirror is connected by four fused silica wires, 400 μm thick, fixed to the mirror using silicate bonding [152] to a metallic structure called the *marionette*, which is itself suspended from Filter 7 by a single central wire made of maraging steel³.

¹The longitudinal and angular actuators consist of coil-magnet devices that provide fine, low-noise control, complemented by spring-loaded motors used for larger-range alignment and positioning adjustments.

²Linear Variable Differential Transformer (LVTD): Is a high-precision sensor for measuring small linear displacements.

³Maraging steels are a class of ultra-high-strength steels distinguished by their very

A.2 Quantum Noise

Quantum noise constitutes the fundamental limit to the sensitivity of gravitational-wave interferometers and arises from the quantum nature of electromagnetic radiation. It is composed of two principal contributions: *shot noise*, which dominates at high frequencies, and *radiation pressure noise*, which prevails at low frequencies. The combination of these two effects defines the total quantum noise [154]:

$$h_{\text{QN}}(f) = \sqrt{h_{\text{shot}}^2(f) + h_{\text{rad}}^2(f)}, \quad (\text{A.1})$$

where:

- $h_{\text{QN}}(f)$: strain-equivalent quantum noise spectrum
- $h_{\text{shot}}(f)$: contribution from shot noise
- $h_{\text{rad}}(f)$: contribution from radiation pressure noise

A.2.1 Shot Noise

Shot noise arises from statistical fluctuations in the number of photons reaching the detector. These fluctuations, described by a Poisson distribution [154], introduce uncertainty in the measurement. The amplitude spectral density (ASD) of the phase noise is given by [2]:

$$S_{\Delta\phi, \text{shot}}^{1/2} = \sqrt{\frac{\hbar\omega_0}{2P}}, \quad (\text{A.2})$$

where $\hbar$ is the reduced Planck constant, ω_0 the carrier optical frequency, and P the average incident power. The square root appears because the uncertainty is expressed in terms of the ASD. In this form, the units are consistent with phase fluctuation amplitude. To obtain the equivalent strain noise and compare it directly with the effective amplitude of gravitational-wave signals,

low carbon content and by the use of substitutional alloying elements that promote age-hardening in iron–nickel martensites. The name “maraging” derives from the combination of martensite and age-hardening [153]. These alloys are widely used in precision mechanical systems, including components of gravitational-wave detectors. This design allows corrective forces to be applied both to the marionette and directly to the mirror, ensuring optical stability and alignment

Eq. (A.2) must be divided by the transfer function that relates phase variations to strain variations (Eq. (1.13)). This yields the ASD of the equivalent strain noise for the shot noise:

$$S_{h,\text{shot}}^{1/2}(f) = \frac{K}{F L} \sqrt{\frac{\lambda_{\text{laser}}}{P}} \sqrt{1 + \left(\frac{f_{\text{gw}}}{f_p}\right)^2}, \quad (\text{A.3})$$

where K is a dimensionless constant collecting all numerical factors. This expression makes explicit the conversion from phase uncertainty to the ASD of the equivalent strain noise, showing that increasing the incident laser power P reduces the shot-noise contribution, while the frequency dependence $\propto f_{\text{gw}}^2$ causes it to dominate the high-frequency region of the detector sensitivity. where K is a dimensionless constant collecting all numerical factors. This expression makes explicit the conversion from phase uncertainty to the equivalent strain noise, showing that increasing the incident laser power P reduces the shot-noise contribution, while the frequency dependence $\propto f_{\text{gw}}^2$ causes it to dominate the high-frequency region of the detector sensitivity.

A.2.2 Radiation Pressure Noise

Radiation pressure noise is associated with fluctuations in the force exerted by photons on the suspended mirrors. Since the mirrors are free to move, radiation pressure induces random displacements that become significant particularly at low frequencies. The ASD of the equivalent strain noise due to this effect is [2]:

$$S_{h,\text{rad}}^{1/2}(f) = \frac{4}{LM(2\pi f_{\text{gw}})^2} \sqrt{\frac{2 \hbar \omega_{\text{laser}} P}{c^2}}. \quad (\text{A.4})$$

This expression shows that larger mirror masses M and arm length L reduce the noise, while higher laser power P increases it. The dependence on $1/f_{\text{gw}}^2$ makes radiation pressure noise most significant at low frequencies.

A.2.3 Standard Quantum Limit

Since shot noise decreases with increasing optical power, while radiation pressure noise grows, there exists an optimal trade-off that defines the so-called *Standard Quantum Limit* (SQL). This limit reflects the Heisenberg uncertainty principle applied to the measurement of the position of the test masses in an

interferometer. The minimum achievable sensitivity is characterized by the ASD of the strain noise [155]:

$$S_{\text{h,SQL}}(f)^{1/2} = \sqrt{\frac{8\hbar}{M(2\pi f)^2 L^2}} = \frac{1}{\pi f L} \sqrt{\frac{2\hbar}{M}}. \quad (\text{A.5})$$

where:

- f_{gw} : signal frequency (Hz)
- L : interferometer arm length (m)
- M : mass of the test mirrors (kg)
- $\hbar$: reduced Planck constant

This expression shows that the standard quantum limit is determined solely by fundamental parameters of the system and not by the readout system.

A.3 Complementary Thermal Noise Mechanisms

This section of the appendix offers a concise overview of the theoretical tools and secondary thermal-noise mechanisms that support the main discussion of this thesis. Subsection A.3.1 introduces the fluctuation–dissipation theorem, providing the framework used to derive the main thermal noise sources. Subsection A.3.2 discusses thermorefractive noise, while Subsection A.3.3 focuses on elastic thermal noise. Finally, Subsection A.3.4 summarizes the literature relevant to additional noise sources, namely photothermal noise, thermoradiation noise, and suspension thermal noise.

A.3.1 Fluctuation-Dissipation Theorem

The Fluctuation–Dissipation Theorem states that, in thermal equilibrium, the power spectral density of the fluctuations of a generic observable A is related to the dissipative part of the linear response function $\chi(\omega)$ as [156, 3]:

$$S_A(\omega) = 2k_B T \Im[\chi(\omega)]. \quad (\text{A.6})$$

where $S_A(\omega)$ is the spectral density of the fluctuations, $\Im[\chi(\omega)]$ denotes the dissipative component of the susceptibility, k_B is Boltzmann’s constant, and T is the absolute temperature. This classical form is valid in the regime $k_B T \gg$

$\hbar\omega$, which is well satisfied in the frequency band relevant to gravitational-wave detectors. For interferometric applications, it is convenient to rewrite the theorem in terms of the mechanical admittance $Y(f)$, which directly relates the applied force to the velocity response of the system. Expressed in terms of the linear frequency f , the relation becomes [3]:

$$S(f) = \frac{k_B T}{\pi^2 f^2} |\Re[Y(f)]| . \quad (\text{A.7})$$

Thermal noise in test masses can be analyzed by introducing the average displacement of the mirror surface as the observable, weighted by the normalized laser beam profile. The external force is modeled as a distributed pressure with the same spatial profile. Assuming a harmonic probing force, the system's response is described by the admittance, and the average dissipated power in the test mass is given by [3]:

$$W_{\text{diss}}(f) = \frac{F_0^2}{2f} \Re[Y(f)] . \quad (\text{A.8})$$

where F_0 is the amplitude of the probing force. Substituting this expression into the FD theorem (A.7) yields the operational form proposed by Levin [157, 158]:

$$S_x(f) = \frac{2k_B T}{\pi^2 f} \frac{W_{\text{diss}}(f)}{F_0^2} . \quad (\text{A.9})$$

This universal formulation provides a direct link between macroscopic dissipation and thermal noise. Brownian noise and thermoelastic noise arise from mechanical and thermal internal dissipation, respectively, and are direct applications of (A.9). Temperature fluctuations also induce variations in the coating refractive index (thermorefractive noise). Since thermoelastic and thermorefractive mechanisms originate from the same underlying temperature field, they must be treated coherently to obtain the total thermo-optic noise, following the framework introduced by Evans *et al.* [159].

In the gravitational-wave community, detector sensitivity and noise budgets are customarily evaluated in terms of Amplitude Spectral Density (ASD). Since the Fluctuation-Dissipation theorem natively provides the Power Spectral Density (PSD), the corresponding ASD is simply obtained by taking its square root,

$$S_{MT}^{1/2}(f) = \sqrt{\frac{2k_B T}{\pi^2 f} \frac{W_{\text{diss}}(f)}{F_0^2}} . \quad (\text{A.10})$$

For consistency with this standard representation, all the noise contributions discussed in the following sections will be expressed directly in terms of their ASD.

A.3.2 Thermorefractive Noise

Thermorefractive noise refers to optical phase noise arising from local coating temperature fluctuations that induce variations in the refractive index

$$\beta_{l,h} = \frac{dn_{l,h}}{dT}, \quad (\text{A.11})$$

where $\beta_{l,h}$ denotes the thermorefractive coefficient of the low- (l) and high-index (h) layer materials. These variations alter the effective optical thickness⁴ of dielectric layers, producing random phase shifts in the reflected waves [160]. The amplitude spectral density (ASD) of the equivalent surface displacement due to thermorefractive noise is given by [29]:

$$\sqrt{S_{\text{coat}}^{\text{TR}}} = \sqrt{\frac{2k_B T^2 \beta_{\text{eff}}^2 \lambda^2}{\pi^{3/2} \sqrt{\kappa_s \rho_s C_s} w^2 f^{1/2}}} \quad (\text{A.12})$$

where:

- k_B : Boltzmann constant
- T : temperature
- β_{eff} : effective thermorefractive coefficient of the coating,

$$\beta_{\text{eff}} = \frac{1}{4} \frac{\beta_h n_l^2 + \beta_l n_h^2}{n_h^2 - n_l^2}$$

valid when the upper layer has $n_l < n_h$ and optical thickness $d = \lambda/(4n_l)$.

- λ : wavelength of the incident radiation
- κ_s : thermal conductivity of the substrate
- ρ_s : density of the substrate
- C_s : specific heat capacity of the substrate
- w : Gaussian beam radius defined at the $1/e^2$ intensity level
- f : frequency

⁴The optical thickness d_{opt} is defined as $d_{\text{opt}} = n L$, where n is the refractive index of the material and L its geometrical thickness.

A.3.3 Thermoelastic Noise

Thermoelastic noise originates from the irreversible dissipation of mechanical energy, caused by heat flow induced by temperature gradients (∇T). In homogeneous solids, such thermal gradients are generated by local fluctuations of mechanical strain ($\nabla \epsilon$). In the case of inhomogeneous bodies, such as the mirrors employed in interferometers, *thermoelastic noise* can also arise in the presence of a uniform strain field, due to differences in thermoelastic properties between the substrate and the coating deposited on its surface [161]. The amplitude spectral density (ASD) of the equivalent surface displacement due to thermoelastic noise in the substrate is described in [29]:

$$\sqrt{S_{\text{sub}}^{\text{TE}}} = \sqrt{\frac{4k_B T^2 \alpha_s^2 (1 + \sigma_s)^2 \kappa_s}{\pi^{5/2} (C_s \rho_s)^2 w^3 f^2}} \quad (\text{A.13})$$

where:

- k_B : Boltzmann constant
- T : temperature
- α_s : thermal expansion coefficient of the substrate
- σ_s : Poisson's ratio of the substrate
- κ_s : thermal conductivity of the substrate
- C_s : specific heat capacity of the substrate
- ρ_s : density of the substrate
- w : Gaussian beam radius defined at the $1/e^2$ intensity level
- f : frequency

For the coating [29]:

$$\sqrt{S_{\text{coat}}^{\text{TE}}} = \sqrt{\frac{8k_B T^2 (1 + \sigma_s)^2 \alpha_c^2 d_N^2}{\pi^{3/2} \sqrt{\kappa_s C_s \rho_s} w^2 f^{1/2}}} G_{\text{coat}}^{\text{TE}}(\omega) \quad (\text{A.14})$$

with:

$$\alpha_c = \frac{1}{2} \left\langle \frac{\alpha}{1 - \sigma} \left(\frac{1 + \sigma}{1 + \sigma_s} + (1 - 2\sigma_s) \frac{Y}{Y_s} \right) \right\rangle - \alpha_s \frac{\langle C \rho \rangle}{C_s \rho_s} \quad (\text{A.15})$$

where:

- $\langle \dots \rangle$: denotes the volume average over the multilayer coating materials
- σ, σ_s : Poisson's ratios of the coating materials and the substrate
- $\alpha_c, \alpha, \alpha_s$: thermal expansion coefficients (effective coating, coating materials, and substrate, respectively)
- Y, Y_s : Young's moduli of the coating materials and the substrate
- C, C_s : specific heat capacities of the coating materials and the substrate
- ρ, ρ_s : densities of the coating materials and the substrate
- d_N : total coating thickness (depending on the number of layers N)
- $G_{\text{coat}}^{\text{TE}}(\omega)$: frequency-dependent correction function

A.3.4 Additional Thermal Noise Contributions

Photothermal noise and *thermoradiation noise* are encompassed within the framework of the Fluctuation–Dissipation Theorem. As secondary contributions compared to the three principal mechanisms, they are not treated in detail in this thesis; for a more comprehensive analysis, the reader is referred to [29]. On the contrary, the Brownian contribution from the suspensions, commonly referred to as *suspension thermal noise*, represents a dominant source at low frequencies (5-50 Hz [162]). Nevertheless, it is not addressed here, as it lies beyond the scope of this work. A thorough discussion of suspension systems and the associated thermal noise can be found in [163, 162].

Chapter B

Advanced Mirror Technologies for Ground-Based Gravitational Wave Interferometers

This chapter of the appendix provides a concise overview of the structural properties of the materials investigated in this work. Specifically, it summarizes:

- *Crystalline silicon* (Appendix B.1), used as the substrate;
- *Silica* (Appendix B.2), investigated both as the low-refractive-index material in the DBR and as the native silica layer that naturally grows on crystalline silicon;
- *High-index coating candidates* (Appendix B.3), investigated as potential alternatives for advanced optical coatings.

B.1 Substrate Used in Representative Samples: Crystalline Silicon

Crystalline silicon (c-Si) is a benchmark substrate in ellipsometric studies [74, 111, 164, 72, 70, 165] due to its high purity, exceptional surface quality, and the availability of precision-tabulated optical constants [166]. In this work, P-doped (100) silicon wafers (Siltronix, $\pm 0.5^\circ$ miscut) were employed [167], featuring a resistivity $\rho < 1 \Omega \cdot \text{cm}$ and a nominal thickness of 0.5 mm. A native

oxide layer of approximately 2 nm was present on all substrates. To prevent systematic errors arising from incoherent backside reflections, single-side polished wafers were selected, ensuring that the detected signal originates solely from the top surface and the deposited films [100].

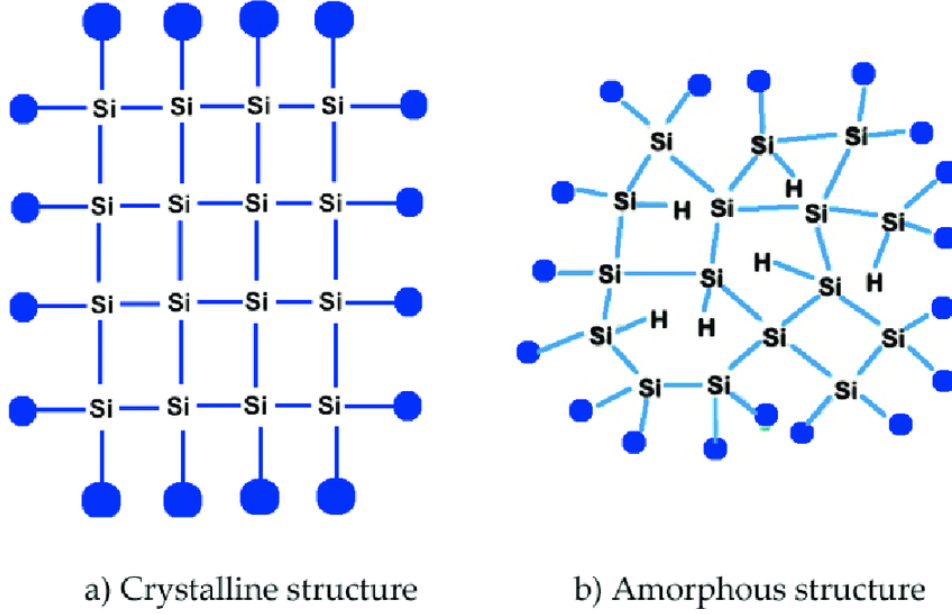


Figure B.1: Comparison between crystalline and amorphous silicon structures. (a) Crystalline silicon exhibits a long-range periodic lattice where each Si atom is tetrahedrally bonded to four neighbors, resulting in a highly symmetric diamond cubic network. (b) Amorphous silicon lacks this long-range order, displaying a disordered arrangement with deviations in bond angles and lengths. Adapted from [168].

As illustrated in Fig. B.1, the stable optical response of c-Si stems from its long-range atomic order. It adopts a diamond cubic structure where each atom is covalently bonded to four nearest neighbors in a tetrahedral geometry [169]. At the target wavelength of 1064 nm, c-Si exhibits a high refractive index of approximately $n \approx 3.55$ [170]. This provides a strong dielectric contrast against the amorphous oxide layers typically investigated in this work, significantly enhancing the sensitivity of the ellipsometric parameters Ψ and Δ [142]. By maximizing the phase and amplitude differentiation between p - and s -polarized components, this contrast ensures a more accurate and robust extraction of thin-film parameters during the modeling phase.

B.2 Low Refractive Index Material: Silicon Dioxide

In this work, we examine two distinct forms of silicon dioxide (SiO_2), commonly known as silica, both of which are relevant but serve very different roles. *Native silica* refers to the ultrathin amorphous oxide layer that naturally forms on silicon substrates upon exposure to air [171]. This oxidation process, driven by silicon's high reactivity with oxygen, typically results in a layer approximately 1–3 nm thick under ambient conditions, with a complex composition that can include sub-stoichiometric SiO_x [171]. Although extremely thin, the native oxide significantly influences ellipsometric measurements and interfacial properties due to its distinct refractive index (approximately 1.45 at 1064 nm [172, 20]), which contrasts sharply with that of crystalline silicon (B.1). Accurate optical modeling must account for this native layer to avoid systematic errors in the extraction of film parameters. *Deposited silica*, on the other hand, is the primary focus of this work. It is intentionally deposited by techniques such as Ion Beam Sputtering (IBS) as a low-index material in multilayer dielectric coatings, where it acts as the low-index component in Bragg reflectors [39]. Its low mechanical losses and minimal absorption in the near-infrared make it particularly well-suited for such precision optics [173, 20].

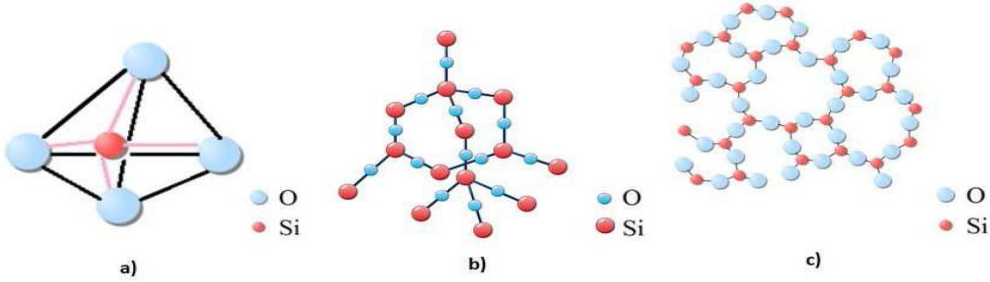


Figure B.2: Structural configurations of SiO_2 at different scales of order. (a) The fundamental SiO_4 tetrahedral unit, the building block of all silica polymorphs, featuring a central silicon atom covalently bonded to four oxygen atoms. (b) The crystalline lattice of quartz, characterized by a long-range periodic arrangement of corner-sharing SiO_4 tetrahedra. (c) The continuous random network of amorphous silica, where the short-range tetrahedral order is preserved, but long-range periodicity is lost. Image reproduced from [174].

To better understand the structural nature of the deposited silica, it is

worth noting that silicon dioxide primarily exists in two forms: crystalline and amorphous. As illustrated in Fig. B.2, Both phases share the same fundamental building block (a), the SiO_4 tetrahedron, in which a central silicon atom is covalently bonded to four oxygen atoms. While this short-range tetrahedral coordination is preserved across all structural forms of SiO_2 , their medium- and long-range arrangements differ markedly: crystalline silica (b), such as quartz, exhibits a periodic, ordered network of corner-sharing tetrahedra, while amorphous silica (c) forms a continuous, non-periodic network [175, 176]. In this work, both the native oxide and the deposited silica coatings adopt the amorphous configuration (c). Despite the absence of long-range periodicity, amorphous SiO_2 shows both short- and medium-range order. This is characterized by a statistical distribution of Si–O–Si bond angles (typically ranging between 120° and 180°) and by the formation of ring structures of various sizes, typically comprising 3- to 10-membered rings [175, 176, 57]. In particular, recent studies indicate that sputtered SiO_2 thin films exhibit a higher concentration of 3-membered rings compared to bulk silica, a feature empirically correlated with an increased room-temperature mechanical loss of the coating [57, 177].

B.3 High Refractive Index Materials

This section of the appendix provides a detailed characterization of the two primary high-refractive index materials investigated in this work:

- Titania-doped Tantalum ($\text{TiO}_2\text{--Ta}_2\text{O}_5$, see Appendix B.3.1);
- Titania-doped Germanium ($\text{TiO}_2\text{--GeO}_2$, see Appendix B.3.2).

B.3.1 Titania-Doped Tantalum ($\text{TiO}_2\text{--Ta}_2\text{O}_5$)

Amorphous tantalum pentoxide ($\alpha\text{-Ta}_2\text{O}_5$) serves as the primary structural matrix for titania-tantalum films. Both in its pure form and in mixed-oxide films, tantalum atoms predominantly adopt a six-fold coordination geometry (forming Ta-centered octahedra), alongside a smaller fraction of five-fold sites (trigonal bipyramids) [68]. Spectroscopic Extended X-ray Absorption Fine Structure (EXAFS) analyses indicate that this local environment is organized into four sequential atomic shells (O–Ta–O–Ta). Within the primary shell, two distinct Ta–O bond distances are observed at 1.85 Å and 2.00 Å, which

are attributable to oxygen sites bonded to two and three metal atoms, respectively [129]. When titanium is introduced as a dopant, it integrates into the existing amorphous scaffold. Molecular dynamics simulations demonstrate that Ti atoms predominantly occupy five-fold (45.0%) and six-fold (50.4%) coordination sites, with only a marginal 4.1% adopting a tetrahedral (four-fold) configuration. In this arrangement, the resulting TiO_n polyhedra effectively bridge the Ta-centered units, perturbing but preserving the continuous network structure of the glass [68]. This arrangement increases the structural constraints of the network, thereby limiting the atomic hops within so-called Two-Level Systems (TLS)¹ and subsequently reducing mechanical loss [130, 68].

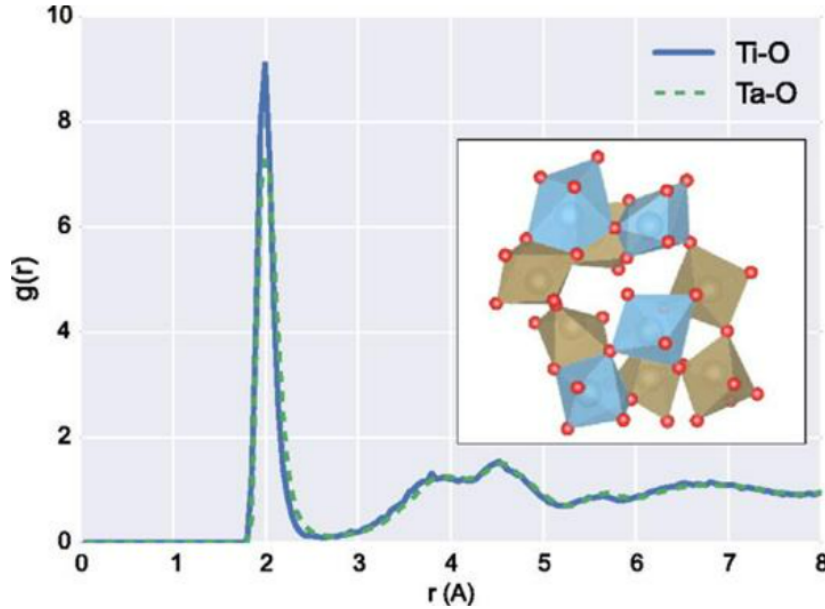


Figure B.3: Pair distribution functions for Ti–O and Ta–O in amorphous Ta_2O_5 – TiO_2 (20% Ti). The inset shows a representative section of the atomic structure, with oxygen atoms in red, Ta-centered polyhedra in brown, and Ti-centered polyhedra in blue. Image reproduced from [68].

As illustrated in Fig. B.3, pair distribution functions (PDF) allow for the differentiation of specific Ta–O and Ti–O bond contributions, highlighting how these diverse structural units coexist within the same atomic network. In particular, the significant overlap between the Ti–O (solid blue line) and

¹Theoretical models representing the transition of atoms between two nearly equivalent configurations. These transitions can involve either subtle atomic rearrangements (non-cage-breaking) or significant changes in the local oxygen environment (cage-breaking), each contributing to mechanical loss at different temperature scales [178].

Ta–O (dashed green line) profiles indicates that the dopant atoms occupy local environments structurally similar to those of the host matrix. This is further visualized in the inset, which provides a three-dimensional representation of the amorphous scaffold: Ta-centered (brown) and Ti-centered (blue) polyhedra are interconnected through shared oxygen atoms (red spheres), forming a disordered network [68]. Moving beyond short-range coordination, the overall stability of this network is also tied to its intermediate-range order (IRO). Recent studies on zirconia-tantala samples suggest that the performance enhancement observed after annealing is driven by a topological rearrangement. Specifically, this improvement is linked to an increase in the ratio of corner-sharing (CS) polyhedra relative to edge-sharing (ES) configurations [69]. In this context, corner-sharing involves polyhedra connected by a single shared oxygen atom, providing the network with more degrees of freedom to relax into a lower-energy state without crystallizing. Conversely, edge-sharing (sharing two oxygen atoms) and face-sharing (three or more) introduce higher structural rigidity and strain, which are often associated with higher mechanical loss at room temperature [69].

B.3.2 Titania–Germania (TiO_2 – GeO_2)

Amorphous germania (a- GeO_2) is a glass-former structurally analogous to amorphous silica (a- SiO_2 ; see Appendix B.2), characterized by a short-range order built from GeO_4 tetrahedra. These units are predominantly connected via corner-sharing (CS) oxygen atoms, forming a continuous random network comprising rings of various sizes, with only minor contributions from edge-sharing (ES) or face-sharing (FS) linkages [57, 75]. The lower glass transition temperature (T_g) of germania (~ 850 K) compared to silica (~ 1450 K) arises from differences in their medium-range order. Specifically, the GeO_2 network features a higher concentration of small (e.g., three-membered) rings compared to silica, which results in a more folded structure and a narrower average Ge–O–Ge inter-tetrahedral angle [176, 57]. This topological flexibility renders the GeO_2 network highly sensitive to pressure- and thermally-induced structural rearrangements, significantly reducing the thermal energy required to relax the glass [176]. When titanium is introduced into this matrix, it acts as both a network former and a network modifier [75]. Unlike in tantala matrices, where Ti distributes almost equally among five- and six-fold coordi-

nated sites [68], in the a-GeO₂ network Ti introduces a mixture of four-, five-, and six-fold coordinated polyhedra to integrate into the tetrahedral host [75]. This mixing produces a complex Ti–O–Ge network. Spectroscopic analyses show that for Ti cation concentrations up to 0.44, Ti atoms preferentially form Ti–O–Ge bonds rather than Ti–O–Ti clusters, indicating efficient atomic mixing [75]. At this concentration, the network reaches a structural balance between Ti–O–Ge (42%) and Ge–O–Ge (44%) linkages [75]. Beyond short-range coordination, the overall stability of the TiO₂:GeO₂ system is tied to its intermediate-range order (IRO). Post-deposition annealing facilitates a structural rearrangement that favors the formation of a more stable network [57]. Specifically, this improvement is empirically correlated with a reduction in the density of ES and FS polyhedral connections, structural motifs typically associated with higher mechanical loss [57]. Regarding structural thermal stability, while pure a-GeO₂ remains amorphous up to 500°C, proper Ti-doping can shift the crystallization onset to higher temperatures, keeping the films amorphous up to 600°C [57]. Conversely, trace Ti contaminations in poorly mixed films may act as local nucleation sites, triggering premature crystallization into the α -quartz-like GeO₂ phase (the typical high-temperature stable polymorph of germania [176]) [53].

Chapter C

Core Technique: Ellipsometry

This chapter of the appendix provides additional theoretical and modeling tools related to the main technique used in this work, ellipsometry. It is organized into three main parts:

- Section [C.1](#) presents the theoretical foundations of spectroscopic ellipsometry, providing background material that is not covered in the main body of the thesis.
- Section [C.2](#) introduces the optical models that support our data analysis, including both introductory formulations and the models employed in this work.
- Section [C.3](#) introduces the Jones formalism and describes the two ellipsometric configurations employed in this thesis: the rotating compensator ellipsometer (RCE) and the rotating analyzer ellipsometer (RAE).

C.1 Theoretical Foundations of Ellipsometry

This section of the appendix is organized into two subsections:

- Subsection [C.1.1](#) introduces the derivation of the Fresnel coefficients starting from Maxwell's equations and defines the p- and s-polarization states.
- Section [C.1.2](#) presents the calculation of the reflection coefficient for a single interface.

- Section C.1.3 extends the treatment to optical systems composed of two interfaces.

C.1.1 From Maxwell's Equations to Fresnel Coefficients

According to the electromagnetic theory of light, developed by James Clerk Maxwell (1831–1879) [179], light is an electromagnetic wave composed of two oscillating and mutually perpendicular vectors: the electric field $\vec{E}$ and the magnetic field $\vec{B}$, both orthogonal to the direction of propagation $\vec{z}$. The electric field of a monochromatic plane wave can be written as [104, 101]:

$$E(z, t) = E_0 e^{i(\omega t - qz)}, \quad (\text{C.1})$$

where:

- E_0 is the peak amplitude of the electric field;
- ω is the angular frequency ($\omega = 2\pi f$);
- t is time;
- q is the wave number, which in a medium is related to the complex refractive index $\tilde{n}$ and the vacuum wavelength λ by $q = 2\pi\tilde{n}/\lambda$.

If we now consider only the real part and include an initial phase term δ , the expression becomes:

$$E(z, t) = E_0 \cos(\omega t - qz + \delta). \quad (\text{C.2})$$

The electric field of a light wave can be decomposed into two components orthogonal to the direction of propagation [101]:

$$E_x = E_{0x} \cos(\omega t - qz + \delta_x), \quad (\text{C.3})$$

$$E_y = E_{0y} \cos(\omega t - qz + \delta_y), \quad (\text{C.4})$$

where:

- E_{0x} and E_{0y} are the field amplitudes along the x and y axes;
- δ_x and δ_y are the corresponding phase constants.

At a fixed point in space, the tip of the electric field vector traces a trajectory determined by the relative amplitudes and phases of these two components. This trajectory defines the polarization state of the light: it is linear when the field oscillates along a fixed direction, elliptical or circular when the direction rotates over time, and random for unpolarized light. A detailed discussion can be found in [180, p. 24–33].

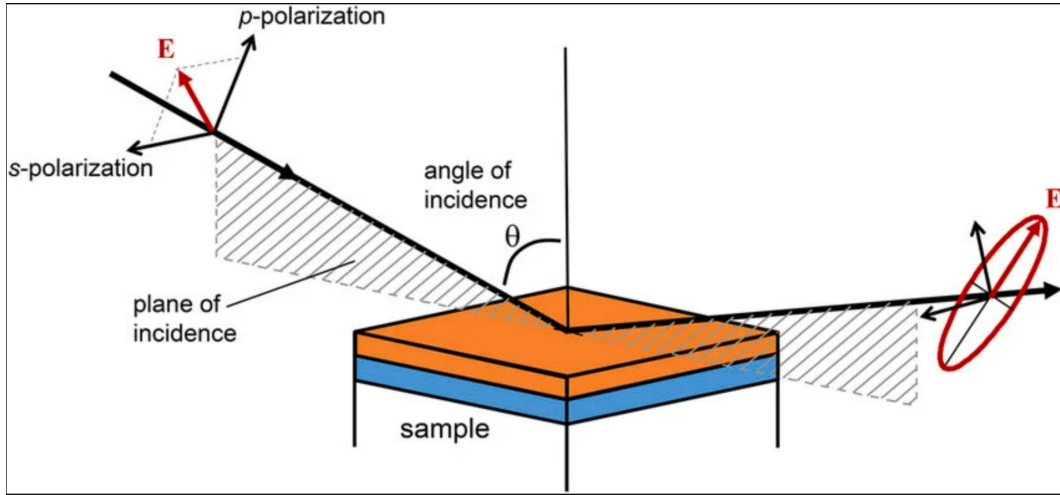
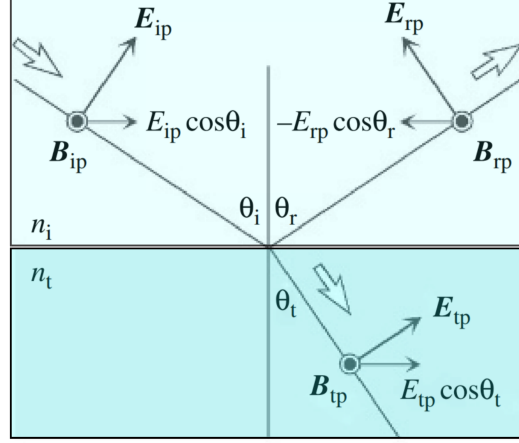


Figure C.1: Representation of the electric field components of polarized light: p-polarized (in-plane) and s-polarized (out-of-plane). Image reproduced from [181].

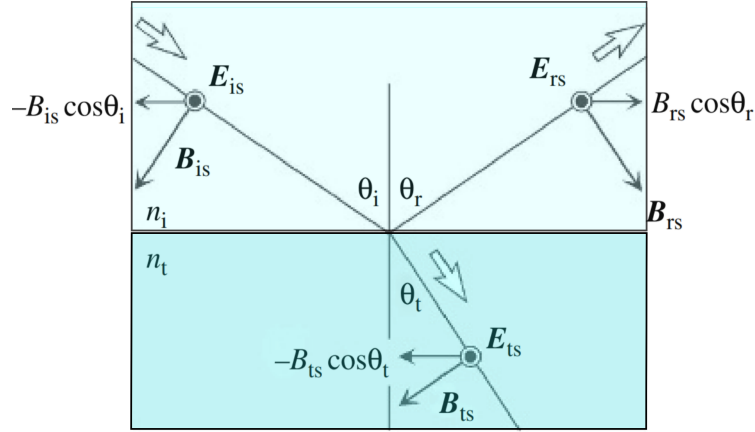
When polarized light impinges on an interface at an oblique angle, it is convenient to express the electric field in a basis aligned with the plane of incidence. Any polarization state can be decomposed into two orthogonal components: a p-polarized (*parallel*) component, with the electric field lying in the plane of incidence, and an s-polarized (*senkrecht*, i.e., perpendicular) component, with the electric field orthogonal to that plane [104]. These components, illustrated in Fig. C.1, can be treated independently when analyzing reflection and transmission at an interface.

C.1.2 Determining Reflection and Transmission Coefficients in a Single-Interface Optical System

Once the electromagnetic wave description based on Maxwell's equations and the concept of polarization have been introduced, we can, following the treatment in [101, p. 32–38], analyze the behavior of polarized light at a *single-interface system* (see Figure C.2) in terms of reflection and transmission.



(a) p-polarization



(b) s-polarization

Figure C.2: Bilayer system with a single interface: incident medium (layer "i") and transmitted medium (layer "t"). Back-reflection is suppressed because the substrate (layer "t") is polished on only one side, while the bottom surface remains rough. The interaction is illustrated for (a) p-polarized light and (b) s-polarized light. Image adapted from [101].

The resulting expressions, known as the Fresnel relations, describe how the amplitude of light is modified at each interface. Using the boundary conditions derived from Maxwell's equations, which require the continuity of the tangential components of the electric field ($\vec{E}$) and magnetic induction ($\vec{B}$) at the interface between two media with refractive indices n_i and n_t , we obtain, for p-polarized light:

$$E_{i,p} \cos \theta_i - E_{r,p} \cos \theta_r = E_{t,p} \cos \theta_t \quad (\text{C.5})$$

$$B_{i,p} + B_{r,p} = B_{t,p} \quad (\text{C.6})$$

Using the relationship between the electric field E and the magnetic induction B in a medium with refractive index n :

$$E = \frac{c}{n}B, \quad (\text{C.7})$$

where c is the speed of light in vacuum. Substituting this relation into Equation (C.6), we obtain:

$$n_i E_{i,p} + n_i E_{r,p} = n_t E_{t,p} \quad (\text{C.8})$$

where:

- $E_{i,p}$: amplitude of the incident electric field (p-polarized);
- $E_{r,p}$: amplitude of the reflected electric field (p-polarized);
- $E_{t,p}$: amplitude of the transmitted electric field (p-polarized);
- n_i : refractive index of the incident medium;
- n_t : refractive index of the transmitted medium;
- θ_i : angle of incidence;
- θ_r : angle of reflection;
- θ_t : angle of transmission (or refraction), calculated using the relation below [104]:

$$\tilde{n}_i \sin \theta_i = \tilde{n}_t \sin \theta_t \quad (\text{C.9})$$

Equation (C.9), known as Snell's law, describes how light refracts when passing from one medium to another with different optical properties, relating the angles of incidence and refraction to the corresponding complex refractive indices. In what follows, all expressions and derivations are based on the treatment presented in [101]. Assuming $\theta_i = \theta_r$ (law of reflection), we can now derive the amplitude reflection coefficient for p-polarized light using Equations (C.5) and (C.8):

$$r_p \equiv \frac{E_{r,p}}{E_{i,p}} = \frac{\tilde{n}_t \cos \theta_i - \tilde{n}_i \cos \theta_t}{\tilde{n}_t \cos \theta_i + \tilde{n}_i \cos \theta_t} \quad (\text{C.10})$$

The corresponding transmission coefficient is:

$$t_p \equiv \frac{E_{t,p}}{E_{i,p}} = \frac{2\tilde{n}_i \cos \theta_i}{\tilde{n}_t \cos \theta_i + \tilde{n}_i \cos \theta_t} \quad (\text{C.11})$$

Similarly, for s-polarized light, the boundary conditions requiring the continuity of the tangential components of the electric and magnetic fields become:

$$E_{i,s} + E_{r,s} = E_{t,s} \quad (\text{C.12})$$

$$-B_{i,s} \cos \theta_i + B_{r,s} \cos \theta_r = -B_{t,s} \cos \theta_t \quad (\text{C.13})$$

From these equations, we derive the Fresnel coefficients for s-polarization (perpendicular to the plane of incidence):

$$r_s \equiv \frac{E_{r,s}}{E_{i,s}} = \frac{\tilde{n}_i \cos \theta_i - \tilde{n}_t \cos \theta_t}{\tilde{n}_i \cos \theta_i + \tilde{n}_t \cos \theta_t} \quad (\text{C.14})$$

$$t_s \equiv \frac{E_{t,s}}{E_{i,s}} = \frac{2\tilde{n}_i \cos \theta_i}{\tilde{n}_i \cos \theta_i + \tilde{n}_t \cos \theta_t} \quad (\text{C.15})$$

These expressions, known as the *Fresnel equations*, describe the behavior of polarized light at the interface between two media, and more specifically, how the amplitude and phase of light are modified at each interface after reflection and/or transmission. They remain valid even when the refractive indices are complex, as is the case for absorbing materials.

C.1.3 Determining Reflection and Transmission Coefficients in Two-Interface Optical Systems

We now extend the analysis to phase effects and to systems with two interfaces. The procedure is as follows:

1. We introduce the *two-interface system*, where multiple internal reflections generate optical interference. The key quantity is the film phase thickness β , which determines the total phase difference 2β between the primary and secondary reflected beams.
2. Using β , we derive the reflection and transmission coefficients for a two-interface system, representing the substrates covered by their native oxide.
3. The same formalism is later applied to a *three-interface system*, corresponding to our standard sample (see Subsection 3.1.1).

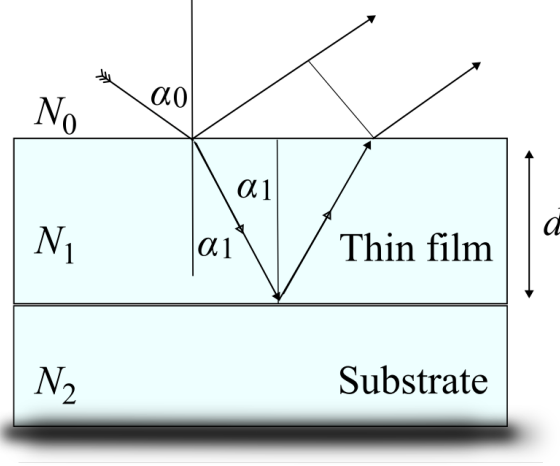


Figure C.3: Two-interface system: air (layer 0) / film (layer 1); film / substrate (layer 2). The primary reflection occurs at the layer-0/layer-1 interface, while the secondary reflection originates from the layer-1/layer-2 interface. Their superposition leads to constructive or destructive interference depending on the phase difference. Image adapted from [101].

In this configuration, part of the incident light is reflected at the air–film interface, while the remainder reaches the film–substrate interface and is reflected back. The interference between the two reflected waves depends on their relative phase:

- in-phase waves $\rightarrow$ constructive interference;
- out-of-phase waves $\rightarrow$ destructive interference.

Using Maxwell’s wave equation (C.2), Snell’s law, and basic geometry [101, p. 43–46], the phase thickness is:

$$\beta = \frac{2\pi d}{\lambda} \sqrt{\tilde{n}_1^2 - \tilde{n}_0^2 \sin^2 \theta_0} \quad (\text{C.16})$$

where:

- d is the film thickness;
- λ is the vacuum wavelength;
- $\tilde{n}_1$ is the complex refractive index of the film;
- $\tilde{n}_0$ is the complex refractive index of the incident medium;
- θ_0 is the angle of incidence.

At each interface, the amplitudes of reflected and transmitted waves are given by the Fresnel coefficients r_{ij} and t_{ij} (Eqs. (C.10)–(C.14)). Combining these with the phase factor β yields the total reflection and transmission coefficients as the sum of all internally reflected and transmitted contributions.

Reconsidering the *two-interface system*, this time also with the transmitted light at the film-substrate interface, as shown in Figure C.4:

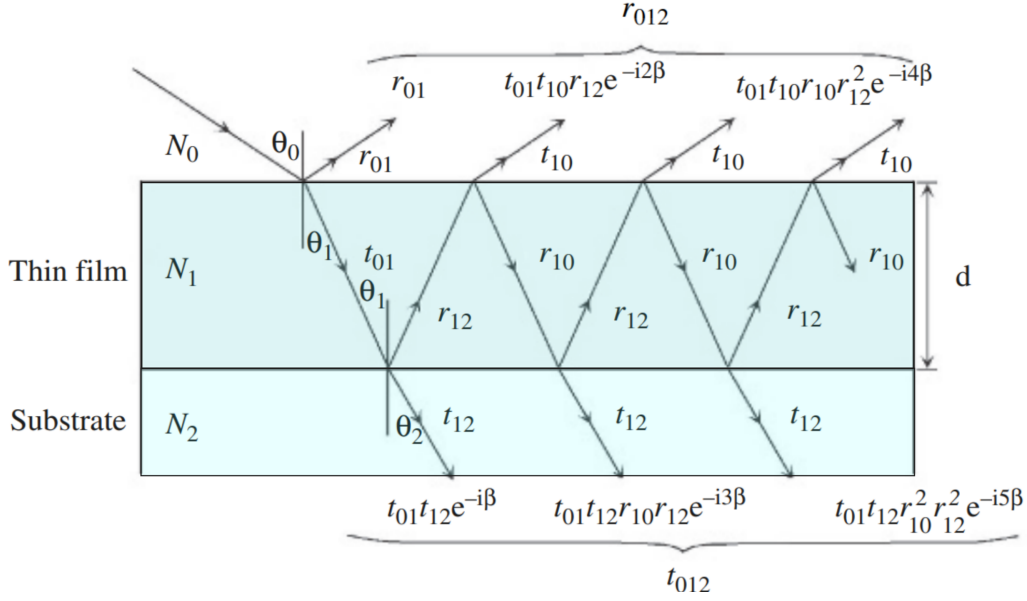


Figure C.4: Multilayer system with two interfaces: air (layer 0) / native oxide (layer 1); native oxide / single-side polished substrate (layer 2). Back-reflection is suppressed because the substrate is polished on only one side, while the bottom surface remains rough. This model provides a good approximation of our bare substrate, which includes its native silica overlayer. Image adapted from [101].

The formulas for calculating the total reflection and transmission coefficients for a two-interface system are [101]:

$$r_{012,p} = \frac{r_{01,p} + r_{12,p} \exp(-i2\beta)}{1 + r_{01,p} r_{12,p} \exp(-i2\beta)} \quad (\text{C.17})$$

$$r_{012,s} = \frac{r_{01,s} + r_{12,s} \exp(-i2\beta)}{1 + r_{01,s} r_{12,s} \exp(-i2\beta)} \quad (\text{C.18})$$

$$t_{012,p} = \frac{t_{01,p} t_{12,p} \exp(-i\beta)}{1 + r_{01,p} r_{12,p} \exp(-i2\beta)} \quad (\text{C.19})$$

$$t_{012,s} = \frac{t_{01,s} t_{12,s} \exp(-i\beta)}{1 + r_{01,s} r_{12,s} \exp(-i2\beta)} \quad (\text{C.20})$$

where:

- $r_{012,p}$, $r_{012,s}$: total reflection coefficients for p and s polarizations;
- $t_{012,p}$, $t_{012,s}$: total transmission coefficients for p and s polarizations;
- $r_{01,p}$, $r_{01,s}$: reflection coefficients at the air/film interface;
- $r_{12,p}$, $r_{12,s}$: reflection coefficients at the film/substrate interface;
- $t_{01,p}$, $t_{01,s}$: transmission coefficients at the air/film interface;
- $t_{12,p}$, $t_{12,s}$: transmission coefficients at the film/substrate interface;
- β : film phase thickness defined in Equation (C.16).

C.2 Optical Models

This section of the appendix is divided into two parts. Subsection C.2.1 outlines introductory optical models that establish the necessary background, whereas Subsection C.2.2 details the models used to describe the samples analyzed in this thesis.

C.2.1 Introductory Optical Models

1. *High-frequency dielectric constant* (ε_∞). It represents the dielectric response in the high-frequency limit and accounts for the contribution of electronic transitions lying outside the measured spectral range.
2. *Lorentz Oscillator Model*. This classical model describes the frequency-dependent dielectric response of bound electrons. Solving the damped harmonic oscillator equation yields [101]:

$$\varepsilon_{n,\text{Lorentz}}(E) = \frac{A_n E_n}{E_n^2 - E^2 - i B_{rn} E}, \quad (\text{C.21})$$

where A_n is the oscillator strength, E_n the resonance energy, B_{rn} the broadening, and E the photon energy. This model is widely used in ellipsometry to describe absorption features near electronic transitions.

3. *Pole Oscillator Model*. A special case of the Lorentz oscillator with zero broadening ($B_{rn} \rightarrow 0$), affecting only the real part of the dielectric

function. It accounts for absorption processes outside the measurement range [3]:

$$\varepsilon_{n,\text{pole}} = \frac{A_n}{E_n^2 - E^2}. \quad (\text{C.22})$$

C.2.2 Key Models

1. *Cauchy Model.* An empirical model for transparent materials in the visible/NIR range [101]:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}. \quad (\text{C.23})$$

All samples were first fitted in their transparency range (1000–1550 nm) using this model to extract thickness and refractive index, then refined over the full ellipsometer range (245–1685 nm) using more advanced models.

2. *Cody–Lorentz Model.* Used for amorphous semiconductors, this model combines an Urbach tail below the optical gap with a Cody-type onset and a Lorentz oscillator at higher energies [3, 182]:

$$\varepsilon_2(E) = \frac{E_1}{E} \exp\left(\frac{E - E_g - E_t}{E_u}\right) \quad \text{for } E \leq E_g + E_t \quad (\text{C.24})$$

$$\varepsilon_2(E) = \underbrace{\frac{(E - E_g)^2}{(E - E_g)^2 + E_p^2}}_{\text{Cody}} \underbrace{\frac{A_n E_n B r_n E}{(E^2 - E_n^2)^2 + B r_n^2 E^2}}_{\text{Lorentz}} \quad \text{for } E > E_g + E_t \quad (\text{C.25})$$

where E_g represents the optical bandgap, while E_u is the Urbach energy characterizing the exponential tail. The offset E_t shifts the onset of the Cody–Lorentz expression, so that $E_g + E_t$ marks the transition between Urbach-type sub-gap absorption and the Cody–Lorentz description of above-gap optical transitions. The constant E_1 is chosen to enforce continuity. From a physical standpoint, this model captures both the sub-gap absorption and the smooth onset of interband transitions typical of amorphous materials. Near the bandgap, the Cody factor produces an onset in ε_2 proportional to $(E - E_g)^2$, reflecting the gradual increase in optical absorption in disordered networks. In this region, the parameter E_p controls the energetic width over which the Cody-type behavior evolves

before saturating. At higher energies, the response becomes dominated by the Lorentz oscillator centred at E_n (see Eq. C.21), which represents the main interband transition associated with extended electronic states.

3. *GenOsc Model.* The dielectric function is constructed as a sum of oscillators [182]:

$$\varepsilon(E) = \varepsilon_\infty + \sum_j \varepsilon_j(E). \quad (\text{C.26})$$

For our samples, two configurations were used:

- Transparent range (1000–1550 nm): Cauchy + two pole oscillators,

$$\varepsilon(E) = \varepsilon_\infty + \frac{A_1}{E_1^2 - E^2} + \frac{A_2}{E_2^2 - E^2} + \text{Cauchy}(A, B, C). \quad (\text{C.27})$$

- Full spectral range: Cody–Lorentz + two pole oscillators,

$$\varepsilon(E) = \varepsilon_\infty + \frac{A_1}{E_1^2 - E^2} + \frac{A_2}{E_2^2 - E^2} + \text{Cody-Lorentz}(E_g, E_p, E_t, E_u, \dots). \quad (\text{C.28})$$

4. *Si-Parametrized Model.* A Parametric Semiconductor Model (PSEMI) developed by Herzinger and Johs (J.A. Woollam Co.) specifically designed to accurately reproduce the complex dielectric function of semiconductor materials [182]. Unlike standard Lorentz oscillators, the PSEMI model constructs the absorption profile using generalized oscillators made of connected polynomial spline functions that precisely capture the complicated Critical Point (CP) structures of crystalline silicon [3, 182]. This approach ensures strict Kramers-Kronig consistency and provides a smooth, analytical representation of the optical constants, avoiding the discrete noise typical of tabulated data. Because of its flexibility, the model reliably tracks the temperature-induced shifts and broadenings of the CPs, effectively simulating the silicon optical response over a wide temperature range, and was used here up to 600°C.

C.3 Ellipsometric Configurations Employed

In this section of the appendix, we begin by introducing the Jones formalism (Subsection C.3.1), which provides the mathematical framework for describing the optical behavior of polarized light in our ellipsometric system.

We then focus on the two experimental setups used in our measurements: the rotating compensator ellipsometer (RCE, M2000) and the rotating analyzer ellipsometer (RAE, VASE) (Subsection C.3.2).

C.3.1 Mathematical Tools: Jones Formalism

To describe the operation of the ellipsometer, we briefly introduce the Jones formalism, a mathematical framework used to represent the polarization state of light and its evolution through linear optical systems [101]. The polarization state of a wave propagating along the z axis is expressed by the Jones vector:

$$\mathbf{E} = \begin{bmatrix} E_x \\ E_y \end{bmatrix}, \quad (\text{C.29})$$

where E_x and E_y are the complex electric-field components along the transverse axes. Common normalized states include:

- Horizontal linear polarization:

$$\mathbf{E} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad (\text{C.30})$$

- Vertical linear polarization:

$$\mathbf{E} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (\text{C.31})$$

- Right-handed circular polarization:

$$\mathbf{E} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ i \end{bmatrix} \quad (\text{C.32})$$

- Left-handed circular polarization:

$$\mathbf{E} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix} \quad (\text{C.33})$$

Each linear optical component is represented by a 2×2 Jones matrix. Examples include:

- Horizontal polarizer:

$$P_x = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \quad (\text{C.34})$$

- Linear polarizer at angle θ :

$$P(\theta) = \begin{bmatrix} \cos^2 \theta & \cos \theta \sin \theta \\ \cos \theta \sin \theta & \sin^2 \theta \end{bmatrix} \quad (\text{C.35})$$

- Ideal retarder (compensator) with phase delay δ :

$$R(\delta) = \begin{bmatrix} 1 & 0 \\ 0 & e^{-i\delta} \end{bmatrix} \quad (\text{C.36})$$

The sample is described by a Jones matrix S , relating incident and reflected fields:

$$\mathbf{E}_{\text{out}} = S \mathbf{E}_{\text{in}}. \quad (\text{C.37})$$

For an isotropic sample (expressed in the (p, s) polarization basis):

$$S = \begin{bmatrix} r_p & 0 \\ 0 & r_s \end{bmatrix}, \quad (\text{C.38})$$

where r_p and r_s are the complex Fresnel reflection coefficients. An ellipsometric system composed of polarizer, sample, and analyzer is conceptually described by:

$$\mathbf{E}_{\text{out}} = A S P \mathbf{E}_{\text{in}}. \quad (\text{C.39})$$

More generally, a sequence of n optical elements is modeled as:

$$\mathbf{E}_{\text{out}} = M_n M_{n-1} \cdots M_1 \mathbf{E}_{\text{in}}, \quad (\text{C.40})$$

where each M_i is the Jones matrix of the corresponding component. This formalism enables accurate modeling of polarization transformations in complex optical systems and underpins the analysis of ellipsometric measurements.

C.3.2 Rotating Compensator Ellipsometry (RCE) and Rotating Analyzer Ellipsometry (RAE)

In this work, two spectroscopic ellipsometers from J.A. Woollam Co. were employed, selected for their complementary characteristics in terms of spectral range and optical configuration:

- *VASE (RAE)*: spectral range 190–2500 nm, vertical sample configuration. This is a rotating analyzer ellipsometer.
- *M-2000 (RCE)*: spectral range 245–1680 nm, horizontal sample configuration. This is a rotating compensator ellipsometer.

VASE – Rotating Analyzer Ellipsometer (RAE) According to [3, p. 58–60], the *VASE* is a broad-spectrum ellipsometer that uses a rotating analyzer to modulate the intensity of the reflected light. The optical system, used in this work for complementary *ex post* measurements, includes a linear polarizer at the input and a rotating analyzer at the output. A monochromator selects the wavelength of the incident light, enabling point-by-point spectral analysis.

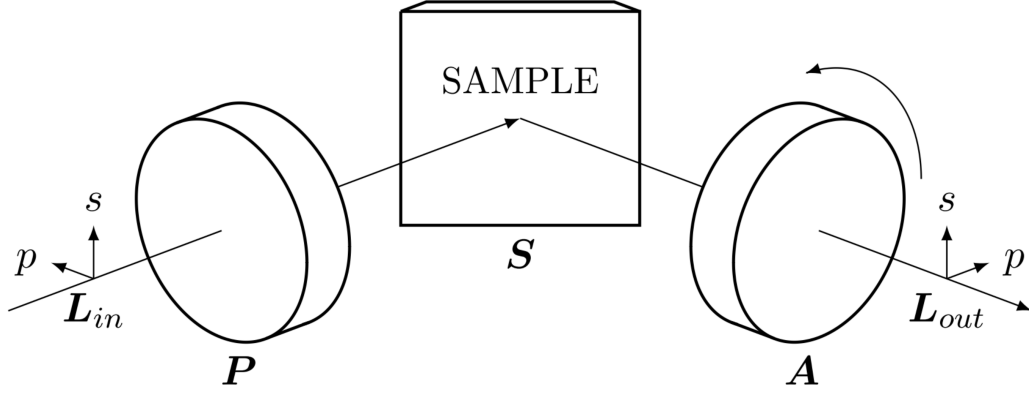


Figure C.5: Schematic diagram of a Rotating Analyzer Ellipsometer (RAE). The setup consists of a fixed polarizer (*P*), a sample (*S*), and a rotating analyzer (*A*). Linearly polarized light enters the system (L_{in}), reflects off the sample, and passes through the rotating analyzer before reaching the detector (L_{out}). The rotation of the analyzer modulates the detected intensity, allowing extraction of the ellipsometric parameters Ψ and Δ . The directions of the *s*- and *p*-polarized components are also indicated. Image reproduced from [3].

The light beam typically has a diameter on the order of a few millimeters, which restricts the probed area and helps minimize depolarization effects caused by local spatial inhomogeneities in the sample [101]. However, in the presence of high surface roughness, highly non-uniform films, or backside reflections, the reflected light may still become partially depolarized, introducing measurement errors. In the case of the Rotating Analyzer Ellipsometer (RAE), the intensity of the reflected light is modulated by the rotation of the analyzer. The optical system can be described using the Jones formalism as follows:

$$\mathbf{E}_{out} = A \cdot R(A(t)) \cdot S \cdot R(-\theta_p) \cdot P \cdot \mathbf{E}_{in} \quad (\text{C.41})$$

where:

- $\mathbf{E}_{in}$ and $\mathbf{E}_{out}$ are the Jones vectors of the incident and detected light, respectively;

- P is the Jones matrix of the ideal polarizer;
- $R(-\theta_p)$ is the coordinate rotation matrix, so that the product $R(-\theta_p)P$ represents the light transmitted through the polarizer oriented at an angle θ_p ;
- S is the sample matrix;
- $R(A(t))$ is the time-dependent rotation matrix of the analyzer;
- A is the analyzer matrix.

Expanding the terms [101]:

$$\underbrace{\begin{pmatrix} E_{\text{out}} \\ 0 \end{pmatrix}}_{\mathbf{E}_{\text{out}}} = \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}}_A \underbrace{\begin{pmatrix} \cos(\omega t) & \sin(\omega t) \\ -\sin(\omega t) & \cos(\omega t) \end{pmatrix}}_{R(A(t))} \underbrace{\begin{pmatrix} \sin \Psi e^{i\Delta} & 0 \\ 0 & \cos \Psi \end{pmatrix}}_S \underbrace{\begin{pmatrix} \cos \theta_p & -\sin \theta_p \\ \sin \theta_p & \cos \theta_p \end{pmatrix}}_{R(-\theta_p)} \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}}_P \underbrace{\begin{pmatrix} E_{\text{in}} \\ 0 \end{pmatrix}}_{\mathbf{E}_{\text{in}}} \quad (\text{C.42})$$

The intensity of the reflected light measured by the detector is [101]:

$$\begin{aligned} I_{\text{out}} = |E_{\text{out}}|^2 = \frac{I_{\text{in}}}{4} [& (1 - \cos 2\theta_p \cos 2\Psi) \\ & + (\cos 2\theta_p - \cos 2\Psi) \cos 2\omega t \\ & + (\sin 2\theta_p \sin 2\Psi \cos \Delta) \sin 2\omega t], \end{aligned} \quad (\text{C.43})$$

which can be rewritten as:

$$I_{\text{out}} = \frac{I_{\text{in}}}{4} [1 + \alpha \cos 2\omega t + \beta \sin 2\omega t], \quad (\text{C.44})$$

where:

$$\alpha = \frac{\tan^2 \Psi - \tan^2 \theta_p}{\tan^2 \Psi + \tan^2 \theta_p}, \quad \beta = \frac{2 \tan \Psi \cos \Delta \tan \theta_p}{\tan^2 \Psi + \tan^2 \theta_p}. \quad (\text{C.45})$$

By performing a Fourier analysis of the signal I_{out} , the normalized coefficients α and β can be determined, from which the ellipsometric parameters Ψ and Δ are directly extracted [101]:

$$\tan \Psi = \sqrt{\frac{1+\alpha}{1-\alpha}} |\tan \theta_p|, \quad \cos \Delta = \frac{\beta}{\sqrt{1-\alpha^2}}. \quad (\text{C.46})$$

M-2000 – Rotating Compensator Ellipsometer (RCE) According to [3, p. 60–61] and [183], the *M-2000*, the main measurement instrument used in this thesis, employs a rotating compensator to modulate the phase of polarized light. Unlike the VASE, it does not use a monochromator: all wavelengths are acquired simultaneously, significantly reducing measurement time and making it ideal for *in situ* or real-time applications. The M-2000 beam is broader than that of the VASE, but it can be narrowed using an iris (aperture) to minimize depolarization effects. However, reducing the beam size also decreases signal intensity, requiring a trade-off between spatial resolution and signal quality [3].

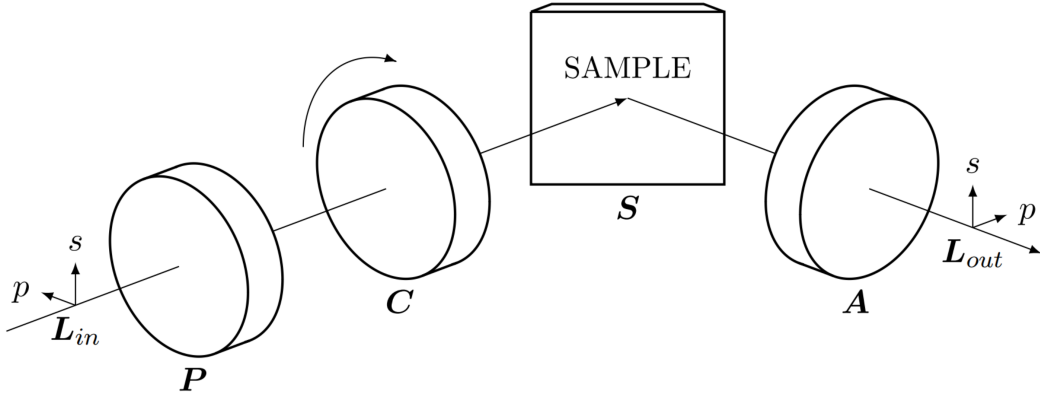


Figure C.6: Schematic diagram of a Rotating Compensator Ellipsometer (RCE). The setup consists of a fixed polarizer (P), a rotating compensator (C), and a fixed analyzer (A). Linearly polarized light enters the system ($\mathbf{L}_{in}$), passes through the compensator which modulates the polarization state, reflects off the sample (S), and then passes through the analyzer before being detected ($\mathbf{L}_{out}$). The compensator enables precise measurement of the ellipsometric parameters Ψ and Δ by introducing a known phase shift between its orthogonal components (fast and slow axes). Image reproduced from [3].

The optical system can be described using the Jones formalism as follows [3]:

$$\mathbf{E}_{out} = A \cdot R(\theta_a) \cdot S \cdot R(-C(t)) \cdot C \cdot R(C(t)) \cdot R(-\theta_p) \cdot P \cdot \mathbf{E}_{in} \quad (\text{C.47})$$

where:

- $\mathbf{E}_{in}$ and $\mathbf{E}_{out}$ are the Jones vectors of the incident and detected light, respectively;
- P is the Jones matrix of the ideal polarizer;

- $R(-\theta_p)$ is the coordinate rotation matrix for the polarizer at angle θ_p ;
- $R(C(t))$ is the time-dependent coordinate rotation matrix of the compensator;
- C is the compensator matrix, which introduces a phase shift ϕ between orthogonal components;
- $R(-C(t))$ is the inverse coordinate rotation matrix of the compensator;
- S is the sample matrix;
- $R(\theta_a)$ is the coordinate rotation matrix for the analyzer at angle θ_a ;
- A is the Jones matrix of the ideal analyzer.

Expanding the terms [101, 3]:

$$\underbrace{\begin{pmatrix} E_{\text{out}} \\ 0 \end{pmatrix}}_{\mathbf{E}_{\text{out}}} = \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}}_A \underbrace{\begin{pmatrix} \cos \theta_a & \sin \theta_a \\ -\sin \theta_a & \cos \theta_a \end{pmatrix}}_{R(\theta_a)} \underbrace{\begin{pmatrix} \sin \Psi e^{i\Delta} & 0 \\ 0 & \cos \Psi \end{pmatrix}}_S \underbrace{\begin{pmatrix} \cos(\omega t) & -\sin(\omega t) \\ \sin(\omega t) & \cos(\omega t) \end{pmatrix}}_{R(-C(t))} \\
 \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & e^{-i\phi} \end{pmatrix}}_C \underbrace{\begin{pmatrix} \cos(\omega t) & \sin(\omega t) \\ -\sin(\omega t) & \cos(\omega t) \end{pmatrix}}_{R(C(t))} \underbrace{\begin{pmatrix} \cos \theta_p & -\sin \theta_p \\ \sin \theta_p & \cos \theta_p \end{pmatrix}}_{R(-\theta_p)} \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}}_P \underbrace{\begin{pmatrix} E_{\text{in}} \\ 0 \end{pmatrix}}_{\mathbf{E}_{\text{in}}} \quad (\text{C.48})$$

The block $R(-C(t)) \cdot C \cdot R(C(t))$ represents the effect of the *rotating compensator* on the polarization state of light. This three-matrix approach is necessary to correctly model the action of the compensator as it rotates over time [101]:

- $R(C(t))$: rotates the electric-field vector into the instantaneous reference frame of the compensator, whose principal axes (ordinary and extraordinary) are physically rotated by an angle $C(t)$.
- C : Jones matrix of the compensator, introducing a phase delay ϕ between the ordinary and extraordinary components.
- $R(-C(t))$: transforms the electric field vector back into the laboratory coordinate system, where all subsequent optical elements (sample, analyzer, detector) are defined.

The intensity of the reflected light measured by the detector is [3]:

$$I_{\text{out}} = I_{\text{in}} (\alpha_0 + \alpha_2 \cos 2\omega t + \beta_2 \sin 2\omega t + \alpha_4 \cos 4\omega t + \beta_4 \sin 4\omega t), \quad (\text{C.49})$$

where the normalized Fourier coefficients are:

$$\begin{aligned} \alpha_0 = 1 + \frac{1}{2}(1 + \cos \phi) (\cos 2\theta_a \cos 2\theta_p - \cos 2\theta_p \cos 2\Psi + \sin 2\theta_a \sin 2\theta_p \sin 2\Psi \cos \Delta) \\ - \cos 2\theta_a \cos 2\Psi, \end{aligned} \quad (\text{C.50})$$

$$\alpha_2 = \sin 2\theta_a \sin 2\theta_p \sin \phi \sin 2\Psi \sin \Delta, \quad (\text{C.51})$$

$$\beta_2 = -\sin 2\theta_a \cos 2\theta_p \sin \phi \sin 2\Psi \sin \Delta, \quad (\text{C.52})$$

$$\begin{aligned} \alpha_4 = \frac{1}{2}(1 - \cos \phi) (\cos 2\theta_a \cos 2\theta_p - \cos 2\theta_p \cos 2\Psi - \sin 2\theta_a \sin 2\theta_p \sin 2\Psi \cos \Delta), \\ \end{aligned} \quad (\text{C.53})$$

$$\begin{aligned} \beta_4 = \frac{1}{2}(1 - \cos \phi) (\cos 2\theta_a \sin 2\theta_p - \sin 2\theta_p \cos 2\Psi + \sin 2\theta_a \cos 2\theta_p \sin 2\Psi \cos \Delta). \\ \end{aligned} \quad (\text{C.54})$$

where:

- θ_a is the analyzer angle (fixed),
- θ_p is the polarizer angle (fixed),
- ϕ is the phase delay introduced by the compensator (typically $\phi = \pi/2$),
- ωt is the angular phase of the rotating compensator.

These expressions enable the determination of the ellipsometric parameters Ψ and Δ from the harmonic components obtained via Fourier analysis of the reflected intensity.

Chapter D

Optimization of the Experimental Setup and Implementation of a Reproducible Optical Characterization Method

This chapter of the appendix provides additional technical material supporting the analyses presented in the main text. It includes the evaluation of instrumental and sample-related thermal effects, the detailed fitting strategies adopted for the optical modeling, and the tools developed to automate the data-processing workflow. The structure is as follows:

- Section [D.1](#) presents the evaluation of the thermal expansion of both the sample and the silver cylinder of the Linkam stage when heated up to 600 °C.
- Section [D.2](#) introduces the tables summarizing the fitting protocols tested, specifically those based on the Cody–Lorentz (Subsection [D.2.1](#)) and Cauchy (Subsection [D.2.2](#)) models.
- Section [D.3](#) describes the general functioning of the automation script.
- Section [D.3.4](#) provides the complete source code.

D.1 Thermal Expansion Effects in the Experimental Setup

To identify the origin of the observed X -misalignment, we evaluate the thermal expansion of all components involved in the experiment: the silicon substrate (0.5 mm thick), the native silica layer (2 nm thick), and the silver cylinder of the Linkam heating stage on which the sample is mounted. The temperature range spans from 25°C to 600°C:

$$\Delta T = 600^\circ\text{C} - 25^\circ\text{C} = 575 \text{ K}. \quad (\text{D.1})$$

The linear expansion is given by

$$\Delta L = \alpha L \Delta T, \quad (\text{D.2})$$

where α is the thermal expansion coefficient and L the initial thickness. It should be noted that the values of α used here correspond to room-temperature values and are treated as constant over the entire temperature interval. In reality, $\alpha(T)$ increases with temperature for all three materials. However, our goal is not to compute the exact thermal expansion but to compare the orders of magnitude of the different contributions.

Silicon substrate. For crystalline silicon, with a thickness of $L_{\text{Si}} = 0.5 \text{ mm} = 500 \text{ } \mu\text{m}$ and $\alpha_{\text{Si}} = 2.6 \times 10^{-6} \text{ K}^{-1}$ [184], the expansion over $\Delta T = 575 \text{ K}$ is

$$\Delta L_{\text{Si}} = (2.6 \times 10^{-6})(500)(575) = 0.7475 \text{ } \mu\text{m} \simeq 0.75 \text{ } \mu\text{m}. \quad (\text{D.3})$$

Native silica layer. For silica, with $L_{\text{SiO}_2} = 2 \text{ nm} = 2 \times 10^{-3} \text{ } \mu\text{m}$ and $\alpha_{\text{SiO}_2} = 0.5 \times 10^{-6} \text{ K}^{-1}$ [67], we obtain

$$\Delta L_{\text{SiO}_2} = (0.5 \times 10^{-6})(2 \times 10^{-3})(575) = 5.75 \times 10^{-7} \text{ } \mu\text{m}, \quad (\text{D.4})$$

a completely negligible value.

Silver cylinder (heater). For silver, with $\alpha_{\text{Ag}} = 18.9 \times 10^{-6} \text{ K}^{-1}$ [185], the expansion depends on its height L_{Ag} . For a representative value of $L_{\text{Ag}} = 1 \text{ cm} = 10\,000 \text{ } \mu\text{m}$:

$$\Delta L_{\text{Ag}} = (18.9 \times 10^{-6})(10\,000)(575) = 108.675 \text{ } \mu\text{m} \simeq 109 \text{ } \mu\text{m}. \quad (\text{D.5})$$

These results show that the thermal expansion of the silicon substrate and, even more significantly, of the silver cylinder occurs on the sub-micrometric to micrometric scale, and can therefore contribute to the observed X -misalignment. In contrast, the expansion of the native silica layer is orders of magnitude smaller than that of the silver cylinder and can therefore be safely excluded as a possible source of misalignment.

D.2 Choice of the Fitting Protocol

In this section of the appendix, we present the fitting protocols applied to both the Cauchy-based and the Cody–Lorentz-based models. While the choice of protocol has little impact on either the results or the fit quality for the Cauchy models, it becomes significant for the multiparametric Cody–Lorentz models.

D.2.1 Cody–Lorentz-Based Model

Table D.1: Steps of the fitting protocols for the Cody–Lorentz-based model. Parameter notation [107]: Thick.2 and Thick.3 = thicknesses of the coating and native silica layers; Amp1, Br1, En1, Eg1, Ep1, Et1, Eu1 = Cody–Lorentz oscillator parameters; PoleMag, PoleMag2 = magnitude of the poles (when included in the model); PolePos, PolePos2 = position of the poles (when included in the model).

Fitting Protocol A

Step	Parameters
1	Thick.2 + Thick.3
2	En1.2
3	Eg1.2 + Ep1.2
4	Eg1.2 + Ep1.2 + Et1.2
5	PolePos.2 + PoleMag.2
6	PolePos2.2 + PoleMag2.2
7	Eu1.2
8	Amp1.2 + Br1.2 + En1.2 + Eg1.2 + Ep1.2

9	Thick.2 + Thick.3
10	Eu1.2
11	PolePos.2 + PoleMag.2 + PolePos2.2 + PoleMag2.2

Fitting Protocol B

Step	Parameters
1	Thick.2 + Amp1.2 + Br1.2
2	Amp1.2 + Br1.2 + En1.2
3	Eg1.2 + Ep1.2 + Et1.2 + Eu1.2
4	Thick.2 + Thick.3
5	PolePos.2 + PoleMag.2
6	PolePos2.2 + PoleMag2.2
7	Eu1.2
8	Amp1.2 + Br1.2 + En1.2 + Eg1.2 + Ep1.2
9	Eu1.2
10	Thick.2
11	PolePos.2 + PoleMag.2 + PolePos2.2 + PoleMag2.2

Fitting Protocol C

Step	Parameters
1	Thick.2
2	Thick.2 + Amp1.2 + Br1.2
3	Amp1.2 + Br1.2 + En1.2
4	Eg1.2
5	Ep1.2 + Et1.2 + Eu1.2
6	Thick.2 + Amp1.2 + Br1.2
7	Eg1.2 + Ep1.2 + Et1.2 + Eu1.2
8	Thick.2 + Thick.3
9	PolePos.2 + PoleMag.2
10	PolePos2.2 + PoleMag2.2
11	Eu1.2
12	Amp1.2 + Br1.2 + En1.2 + Eg1.2 + Ep1.2

13	Eu1.2
14	Thick.2
15	PolePos.2 + PoleMag.2 + PolePos2.2 + PoleMag2.2

Fitting Protocol D

Step	Parameters
1	Thick.2
2	Amp1.2 + Br1.2 + Eg1.2
3	Thick.2 + Amp1.2 + Br1.2 + Eg1.2
4	Ep1.2 + Et1.2 + Eu1.2
5	Thick.2 + Thick.3
6	PolePos.2 + PoleMag.2
7	PolePos2.2 + PoleMag2.2
8	Eu1.2
9	Amp1.2 + Br1.2 + En1.2 + Eg1.2
10	Thick.2 + Thick.3
11	Ep1.2 + Et1.2 + Eu1.2
12	PolePos.2 + PoleMag.2 + PolePos2.2 + PoleMag2.2

Fitting Protocol E

Step	Parameters
1	Thick.2
2	Amp1.2 + Br1.2 + Eg1.2
3	Thick.2 + Amp1.2 + Br1.2 + Eg1.2
4	Ep1.2 + Et1.2 + Eu1.2
5	Thick.2 + Thick.3
6	PolePos.2 + PoleMag.2
7	PoleMag2.2
8	Eu1.2
9	Amp1.2 + Br1.2 + En1.2 + Eg1.2
10	Thick.2 + Thick.3
11	Ep1.2 + Et1.2 + Eu1.2

12	PolePos.2 + PoleMag.2 + PoleMag2.2
13	Amp1.2 + Br1.2 + En1.2 + Eg1.2 + Thick.2
14	Eg1.2
15	Eu1.2
16	Thick.2

Fitting Protocol F

Step	Parameters
1	Thick.2
2	Amp1.2 + Br1.2 + Eg1.2
3	Thick.2 + Amp1.2 + Br1.2 + Eg1.2 + En1.2 + Ep1.2
4	Ep1.2 + Et1.2 + Eu1.2
5	Thick.2 + Thick.3
6	PolePos.2 + PoleMag.2
7	PoleMag2.2
8	Eu1.2
9	Amp1.2 + Br1.2 + En1.2 + Eg1.2
10	Thick.2 + Thick.3
11	Ep1.2 + Et1.2 + Eu1.2
12	PolePos.2 + PoleMag.2
13	Eg1.2
14	Eu1.2
15	Thick.2
16	En1.2

D.2.2 Cauchy-Based Model

Table D.8: Steps of the fitting protocols for the Cauchy-based model. Parameter notation [107]: Thick1 = thickness of native silica; Thick2 = thickness of the coating layer; An and Bn = Cauchy dispersion parameters; PoleMag and PolePos = pole magnitude and position (when included in the model).

Fitting Protocol 1

Step	Parameters
1	Thick2 + A_n
2	$A_n + B_n$
3	Thick 1
4	PoleMag (if included in the model)
5	PolePos (if included in the model)
6	Thick1 + $A_n + B_n$

Fitting Protocol 2

Step	Parameters
1	Thick2 + A_n
2	$A_n + B_n$
3	Thick1
4	PoleMag + PolePos (if included in the model)
5	Thick1 + $A_n + B_n$

Fitting Protocol 3

Step	Parameters
1	Thick1 + A_n
2	$A_n + B_n$
3	Thick1

Fitting Protocol 4

Step	Parameters
1	A_n
2	Thick2
3	B_n
4	Thick2
5	PoleMag + PolePos (if included in the model)
6	Thick2 + $A_n + B_n$

Fitting Protocol 5

Step	Parameters
1	An
2	Thick2
3	Bn
4	Thick1

Fitting Protocol 6

Step	Parameters
1	Thick2 + An
2	Thick2 + Bn
3	PoleMag + PolePos (if included in the model)
4	An + Bn
5	Thick1

Fitting Protocol 7

Step	Parameters
1	An + Bn
2	Thick1 + Thick2
3	An
4	Bn
5	Thick2

D.3 Towards Fully Automated Real-Time Optical Characterization

The entire automation process (ellipsometric measurement and data analysis workflow) can be divided into three main components:

1. *Measurement* (Subsection [D.3.1](#));
2. *Model construction and fitting* (Subsection [D.3.2](#));
3. *Results processing and visualization* (Subsection [D.3.3](#)).

These three components are implemented through the script presented in Subsection [D.3.4](#), which enables the full automation of the workflow.

D.3.1 Stage 1 — Measurement Execution

The script interfaces directly with the ellipsometer. Users can input parameters such as sample name, annealing profile (heating/cooling rate, duration, temperature), and the number and interval - in time or temperature - between successive acquisitions. Once initiated, the program autonomously performs measurements throughout the entire annealing cycle. Beyond reducing time and user workload, the most significant advantage lies in the structured organization of the data. On average, a full measurement cycle generates approximately 2000 files. For each acquisition, three distinct files are produced:

- `.DAT`: raw data containing Ψ and Δ as a function of wavelength;
- `.env` and `.mod`: model definitions and fitting results;
- `.txt`: optical constants n and k as a function of wavelength.

Given the large volume of data, manual management would be impractical. The script automatically organizes files into structured folders, assigning clear and consistent names compatible with data analysis and visualization tools such as *IGOR*. Additionally, during the measurement phase, a `.log` file is generated, containing detailed information about each scan, including ellipsometric intensity, acquisition time/temperature and alignment. This ensures full traceability of the process and facilitates the identification of both random and systematic errors. During the data acquisition phase, the automation script enables real-time monitoring of potential beam misalignment on the detector, allowing the operator to intervene as needed and correct any deviations.

D.3.2 Stage 2 — Model Construction and Fitting

Once the measurement is completed and the raw data (Ψ and Δ) have been extracted, the script handles both the construction of the temperature-dependent model and its application to the measured data (fitting protocol; see Sec. 4.3). The script also logs all relevant information in the previously mentioned `.log` file. Specifically, it records details for each individual model, such as the differences between simulated (model) and experimental (measured) data, the fitting quality assessed through the Mean Squared Error (MSE), and

several physically relevant parameters, including the refractive index and coating thickness. Thanks to the log file, it is possible to quickly identify potential fitting or modeling errors.

D.3.3 Stage 3 — Results Processing and Visualization

The final stage of the automation process was carried out using IGOR Pro, a powerful scientific software environment developed by WaveMetrics, designed for data analysis, visualization, and programming. The results obtained in real time from the optical characterization are presented in a clear and structured format. Initially, the raw ellipsometric data (Ψ and Δ) are plotted as a function of temperature. Subsequently, the optical constants n and k are extracted and visualized. Finally, the refractive index at 1064 nm and 1550 nm-wavelengths of particular interest for Gravitational Wave Detectors (GWDs)-along with the coating thickness, are plotted as a function of temperature or annealing time.

D.3.4 Custom Script for Real-Time Ellipsometric Measurements

This subsection introduces the complete WVASE32 automation script, specifically developed to streamline ellipsometric data acquisition and analysis throughout thermal annealing cycles.

```

1      ;=====
2      ; AUTOMATED ELLIPSOMETRIC ANNEALING ANALYSIS SCRIPT
3      ;=====
4      ; Description: Complete workflow for ellipsometric data
5      ;               acquisition during
6      ;               thermal annealing cycles (Heating ->
7      ;               Plateau -> Cooling) with
8      ;               automatic data fitting and optical
9      ;               constants extraction.
10     ;=====
11
12     #DEBUGON
13     #TIMENOW
14
15     ;=====
16     ; SECTION 1: SAMPLE AND ANNEALING PARAMETERS

```

```

14      ; =====
15
16      SetVars(nome_campione='Program_1')
17      SetVars(nome_rtf='{nome_campione}_DATA-ANALYSIS_{
18      @NowStart}')
19
20      ; Spectral range for fitting
21      SetVars(wvlstart_fit=1000)
22      SetVars(wvlend_fit=1500)
23
24      ; Heating phase
25      SetVars(Tstart_H=30)
26      SetVars(Tend_H=50)
27      SetVars(intervallo_H=10)
28      SetVars(Heating_Rate=600)
29
30      ; Plateau phase
31      SetVars(T_plateau=500)
32      SetVars(tstart_P=0)
33      SetVars(tend_P=2)
34      SetVars(intervallo_P=1)
35
36      ; Cooling phase
37      SetVars(Tstart_C=590)
38      SetVars(Tend_C=560)
39      SetVars(intervallo_C=10)
40      SetVars(Cooling_Rate=600)
41
42      ; Timing corrections
43      SetVars(correction_time=19000)
44      SetVars(correction_time_P=16000)
45
46      ; =====
47      ; SECTION 2: FILE NAMING CONVENTIONS
48      ; =====
49
50      SetVars(nome_sub='substrato_lma_17-07-24_heating_')
51      SetVars(nome_Exp_H='Heating_')
52      SetVars(nome_Exp_P='Plateau_')
53      SetVars(nome_Exp_C='Cooling_')
54
55      ; =====

```

```

56      ; SECTION 3: OUTPUT PATHS (GENERIC VERSION)
57      ;=====
58
59      ; --- Define a single base directory for the entire
project ---
60      SetVars(base_path="C:/FIT_WVASE")
61
62      ; --- General save paths ---
63      SetVars(save_path="{base_path}")
64      SetVars(save_path_rtf="{base_path}")
65
66      ; --- Experimental data paths ---
67      SetVars(path_exp_H="{base_path}/DATI/HEATING")
68      SetVars(path_exp_P="{base_path}/DATI/PLATEAU")
69      SetVars(path_exp_C="{base_path}/DATI/COOLING")
70
71      ; --- Model paths ---
72      SetVars(save_pathS="{base_path}/MODELLI/
RT_starter_model")
73      SetVars(save_pathH="{base_path}/MODELLI/Heating")
74      SetVars(save_pathP="{base_path}/MODELLI/Plateau")
75      SetVars(save_pathC="{base_path}/MODELLI/Cooling")
76
77      ; --- Optical constants paths ---
78      SetVars(save_path_optH="{base_path}/COSTANTI_OTTICHE/
Heating")
79      SetVars(save_path_optP="{base_path}/COSTANTI_OTTICHE/
Plateau")
80      SetVars(save_path_optC="{base_path}/COSTANTI_OTTICHE/
Cooling")
81
82      ; --- Substrate library path ---
83      SetVars(AddSub_path="C:/WVASE32/MAT")
84
85      ;=====
86      ; SECTION 4: ELLIPSOMETER CONFIGURATION
87      ;=====
88
89      SetVars(revs=50)
90      SetVars(wvlstart=245.19)
91      SetVars(wvlend=1688.6)
92      SetVars(wvlby=0)
93      SetVars(angstart=70)

```

```

94     SetVars(angby=5)
95     SetVars(angend=70)
96
97     ;=====
98     ; SECTION 5: COMPUTED VARIABLES
99     ;=====
100
101     SetVars(scan_timeH={{intervallo_H}/{Heating_Rate/60}})
102     SetVars(scan_timeP={{intervallo_P}})
103     SetVars(scan_timeC={{intervallo_C}/{Cooling_Rate/60}})
104
105     SetVars(time_stopH={{scan_timeH*60000}-{correction_time
106 }})
107     SetVars(time_stopP={{scan_timeP*60000}-{
108 correction_time_P}})
109     SetVars(time_stopC={{scan_timeC*60000}-{correction_time
110 }})
111
112     ;=====
113     ; MAIN EXECUTION FLOW
114     ;=====
115
116     #GOSUB(crea_rtf_ALL)
117     rtfnl(56)
118     defaults(nm)
119     defaults(thick-nm)
120
121     #GOSUB(Heating_ALL)
122     rtfpage
123     rtfnl(63)
124
125     #GOSUB(Plateau_ALL)
126     rtfpage
127     rtfnl(63)
128
129     #GOSUB(Cooling_ALL)
130     rtfnl(3)
131
132     #TIMENOW
133     rtftext(Fine_Cooling: {@LastResponse})
134
135     #EXIT

```

```

134      ;=====
135      ; SUBROUTINE: HEATING_ALL
136      ;=====
137
138      #LABEL(Heating_ALL)
139
140      #timeelapsed
141      rtftext(Tempo_trascorso_da_primo_click: {@LastResponse
142      })
143      rtfnl(1)
144      #TIMENOW
145      rtftext(Inizio_ANNEALING: {@LastResponse})
146      rtfnl(2)
147      rtfsave({nome_rtf})
148
149      ; Save initial starter model
150      SaveEnv({save_pathS}/{nome_campione}_starter_model.env)
151
152      ; Initialize temperature loop
153      #setvars(Th={Tstart_H-intervallo_H})
154
155      #do(Th={Th+intervallo_H})
156
157      message("in loop, Th = {Th}")
158      RTFtext(Campione_{nome_campione}_Heating_{Th}C
159      *****)
160      rtfnl(1)
161
162      #TIMENOW
163      rtftext(pre_HEATING_{Th}C_orario: {@LastResponse})
164      rtfnl(1)
165
166      spectroscan(highaccuracy,samplotype=1,revs={revs},
167      wvlstart={wvlstart},wvlend={wvlend},wvlby={wvlby},
168      angstart={angstart},angend={angend},angby={angby})
169
170      #TIMENOW
171      rtftext(after_HEATING_{Th}C_orario: {@LastResponse})
172      rtfnl(1)
173
174      HardAlign(nodisplay)
175      rtftext(after_HEATING_{Th}C_ALLINEAMENTO: {
176      @LastResponse})

```

```

172     rtfnl(2)
173     rtfsave({nome_rtf})
174
175     expopen({path_exp_H}/{nome_Exp_H}{Th}C.dat)
176     expsave({path_exp_H}/Heating_{Th}C_{nome_campione}.dat)
177
178     #GOSUB(fit_routine)
179     #GOSUB(save_results_H)
180     #GOSUB(compila_rtf_fit)
181
182     doddle({time_stopH})
183
184     #loopwhile(Th<{Tend_H-intervallo_H})
185
186     message("out of loop, Th = {Th}")
187
188     ; Last Heating Point
189     #do(Th={Tend_H})
190     message("last point, Th = {Th}")
191     RTFtext(Campione_{nome_campione}_Heating_{Th}C
*****
192     rtfnl(1)
193     #TIMENOW
194     rtftext(pre_HEATING_{Th}C_orario: {@LastResponse})
195     rtfnl(1)
196     spectroscan(highaccuracy,samplotype=1,revs={revs},
wvlstart={wvlstart},wvlend={wvlend},wvlby={wvlby},
angstart={angstart},angend={angend},angby={angby})
197     #TIMENOW
198     rtftext(after_HEATING_{Th}C_orario: {@LastResponse})
199     rtfnl(1)
200     HardAlign(nodisplay)
201     rtftext(after_HEATING_{Th}C_ALLINEAMENTO: {
@LastResponse})
202     rtfnl(2)
203     rtfsave({nome_rtf})
204     expopen({path_exp_H}/{nome_Exp_H}{Th}C.dat)
205     expsave({path_exp_H}/Heating_{Th}C_{nome_campione}.dat)
206     #GOSUB(fit_routine)
207     #GOSUB(save_results_H)
208     #GOSUB(compila_rtf_fit)
209     #loopwhile(Th={Tend_H})
210

```

```

211     #RETURN
212
213     ; =====
214     ; SUBROUTINE: PLATEAU_ALL
215     ; =====
216
217     #LABEL(Plateau_ALL)
218
219     currentlayer(0)
220     Addlayer({AddSub_path}/{nome_sub}{T_plateau}C.mat)
221     currentlayer(0)
222     deletelayer
223     currentlayer(0)
224     editlayer(thick=1000000)
225
226     #setvars(tempo={tstart_P-intervallo_P})
227
228     #do(tempo={tempo+intervallo_P})
229
230     message("in loop, tempo = {tempo}")
231     RTFtext(Campione_{nome_campione}_Plateau_{tempo}min
232     *****)
233     rtfnl(1)
234     #TIMENOW
235     rtftext(pre_PLATEAU_{tempo}min_orario: {@LastResponse})
236     rtfnl(1)
237     spectroscan(highaccuracy,samplotype=1,revs={revs},
238     wvlstart={wvlstart},wvlend={wvlend},wvlby={wvlby},
239     angstart={angstart},angend={angend},angby={angby})
240     #TIMENOW
241     rtftext(after_PLATEAU_{tempo}min_orario: {@LastResponse
242     })
243     rtfnl(1)
244     HardAlign(nodisplay)
245     rtftext(after_PLATEAU_{tempo}min_ALLINEAMENTO: {
246     @LastResponse})
247     rtfnl(2)
248     rtfsave({nome_rtf})
249
250     expopen({path_exp_P}/{nome_Exp_P}{tempo}min.dat)
251     expsave({path_exp_P}/Plateau_{tempo}min_{nome_campione
252     }.dat)
253
254

```



```

248     ExpRange(WvlStart={wvlstart_fit},WvlEnd={wvlend_fit})
249     currentlayer(2)
250     FitParms(Thick.2,An1.2)
251     fitnormal()
252     FitParms(An1.2,Bn1.2)
253     fitnormal()
254     FitParms(Thick.2,An1.2,Bn1.2)
255     fitnormal()
256     FitParms(Thick.2)
257     fitnormal()
258
259     OptConstSave({save_path_optP}/Plateau_{tempo}min.txt,
Campione_{nome_campione}_Plateau_{@NowStart})
260     SaveEnv({save_pathP}/{nome_campione}_Plateau_{tempo}
min_{nome_campione}.env)
261     #GOSUB(compila_rtf_fit)
262
263     doddle({time_stopP})
264
265     #loopwhile(tempo<{tend_P-intervallo_P})
266
267     message("out of loop, tempo = {tempo}")
268
269     ; Last Plateau Point
270     #do(tempo={tend_P})
271     message("last point, tempo = {tempo}")
272     RTFtext(Campione_{nome_campione}_Plateau_{tempo}min
*****)
273     rtfnl(1)
274     #TIMENOW
275     rtftext(pre_PLATEAU_{tempo}min_orario: {@LastResponse})
276     rtfnl(1)
277     spectroscan(highaccuracy,samplotype=1,revs={revs},
wvlstart={wvlstart},wvlend={wvlend},wvlby={wvlby},
angstart={angstart},angend={angend},angby={angby})
278     #TIMENOW
279     rtftext(after_PLATEAU_{tempo}min_orario: {@LastResponse
})
280     rtfnl(1)
281     HardAlign(nodisplay)
282     rtftext(after_PLATEAU_{tempo}min_ALLINEAMENTO: {
@LastResponse})
283     rtfnl(2)

```

```

284     rtfsave({nome_rtf})
285     expopen({path_exp_P}/{nome_Exp_P}{tempo}min.dat)
286     expsave({path_exp_P}/Plateau_{tempo}min_{nome_campione}
}.dat)
287     ExpRange(WvlStart={wvlstart_fit},WvlEnd={wvlend_fit})
288     currentlayer(2)
289     FitParms(Thick.2,An1.2)
290     fitnormal()
291     FitParms(An1.2,Bn1.2)
292     fitnormal()
293     FitParms(Thick.2,An1.2,Bn1.2)
294     fitnormal()
295     FitParms(Thick.2)
296     fitnormal()
297     OptConstSave({save_path_optP}/Plateau_{tempo}min.txt,
Campione_{nome_campione}_Plateau_{@NowStart})
298     SaveEnv({save_pathP}/{nome_campione}_Plateau_{tempo}
min_{nome_campione}.env)
299     #GOSUB(compila_rtf_fit)
300     #loopwhile(tempo={tend_P})
301
302     #RETURN
303
304     ;=====
305     ; SUBROUTINE: COOLING_ALL
306     ;=====
307
308     #LABEL(Cooling_ALL)
309
310     #setvars(Tc={Tstart_C+intervallo_C})
311
312     #do(Tc={Tc-intervallo_C})
313
314     message("in loop, Tc = {Tc}")
315     RTFtext(Campione_{nome_campione}_Cooling_{Tc}C
*****)
316     rtfnl(1)
317     #TIMENOW
318     rtftext(pre_Cooling_{Tc}C_orario: {@LastResponse})
319     rtfnl(1)
320     spectroscan(highaccuracy,samplotype=1,revs={revs},
wvlstart={wvlstart},wvlend={wvlend},wvlby={wvlby},
angstart={angstart},angend={angend},angby={angby})

```

```

321     #TIMENOW
322     rtftext(after_Cooling_{Tc}C_orario: {@LastResponse})
323     rtfnl(1)
324     HardAlign(nodisplay)
325     rtftext(after_COOLING_{Tc}C_ALLINEAMENTO: {
    @LastResponse})
326     rtfnl(2)
327     rtfsave({nome_rtf})
328
329     expopen({path_exp_C}/{nome_Exp_C}{Tc}C.dat)
330     expsave({path_exp_C}/Cooling_{Tc}C_{nome_campione}.dat)
331
332     ExpRange(WvlStart={wvlstart_fit},WvlEnd={wvlend_fit})
333
334     currentlayer(0)
335     Addlayer({AddSub_path}/{nome_sub}{Tc}C.mat)
336     currentlayer(0)
337     deletelayer
338     currentlayer(0)
339     editlayer(thick=1000000)
340
341     currentlayer(2)
342     FitParms(Thick.2,An1.2)
343     fitnormal()
344     FitParms(An1.2,Bn1.2)
345     fitnormal()
346     FitParms(Thick.2,An1.2,Bn1.2)
347     fitnormal()
348     FitParms(Thick.2)
349     fitnormal()
350
351     OptConstSave({save_path_optC}/Cooling_{Tc}C.txt,
    Campione_{nome_campione}_Cooling_{@NowStart})
352     SaveEnv({save_pathC}/Cooling_{Tc}C_{nome_campione}.env)
353     #GOSUB(compila_rtf_fit)
354
355     doddle({time_stopC})
356
357     #loopwhile(Tc>{Tend_C})
358
359     message("out of loop, Tc = {Tc}")
360
361     #RETURN

```

```

362
363 ; =====
364 ; SUBROUTINE: fit_routine
365 ; =====
366
367 #LABEL(fit_routine)
368
369 ExpRange(WvlStart={wvlstart_fit},WvlEnd={wvlend_fit})
370
371 currentlayer(0)
372 Addlayer({AddSub_path}/{nome_sub}{Th}C.mat)
373 currentlayer(0)
374 deletelayer
375 currentlayer(0)
376 editlayer(thick=1000000)
377
378 currentlayer(2)
379 FitParms(Thick.2,An1.2)
380 fitnormal()
381 FitParms(An1.2,Bn1.2)
382 fitnormal()
383 FitParms(Thick.2,An1.2,Bn1.2)
384 fitnormal()
385 FitParms(Thick.2)
386 fitnormal()
387
388 #RETURN
389
390 ; =====
391 ; SUBROUTINE: save_results_H
392 ; =====
393
394 #LABEL(save_results_H)
395
396 OptConstSave({save_path_optH}/Heating_{Th}C.txt,
397 Campione_{nome_campione}_Heating_{@NowStart})
398 SaveEnv({save_pathH}/heating_{Th}C_{nome_campione}.env)
399
400 #RETURN
401
402 ; =====
403 ; SUBROUTINE: crea_rtf_ALL
404 ; =====

```

```
404
405     #LABEL(crea_rtf_ALL)
406
407     currentdir({save_path})
408     rtfcreate(filename={save_path}/{nome_rtf}.rtf, canclose
=1, logmode=0, fontsize=10, appendmode=1)
409     rtfmargins(left=1, right=0.1, top=1, bottom=1)
410
411     rtftext(2) VARIABILI "CAMPIONE + ANNEALING:")
412     rtfnl(2)
413
414     Message(Nome campione misurato= {nome_campione})
415     rtftext({@LastResponse})
416     rtfnl(2)
417     Message(wvlstart= {wvlstart} nm)
418     rtftext({@LastResponse})
419     rtfnl(1)
420     Message(wvlend= {wvlend} nm)
421     rtftext({@LastResponse})
422
423     rtfnl(2)
424     Message(Tstart_Heating= {Tstart_H}degC)
425     rtftext({@LastResponse})
426     rtfnl(1)
427     Message(Intervallo_Heating= {intervallo_H}degC)
428     rtftext({@LastResponse})
429     rtfnl(1)
430     Message(Tend_Heating= {Tend_H}degC)
431     rtftext({@LastResponse})
432
433     rtfnl(2)
434     Message(tstart_Plateau= {tstart_P}min)
435     rtftext({@LastResponse})
436     rtfnl(1)
437     Message(intervallo_Plateau= {intervallo_P}min)
438     rtftext({@LastResponse})
439     rtfnl(1)
440     Message(tend_Plateau= {tend_P}min)
441     rtftext({@LastResponse})
442
443     rtfnl(2)
444     Message(Tstart_Cooling= {Tstart_C}degC)
445     rtftext({@LastResponse})
```

```
446     rtfnl(1)
447     Message(intervallo_Cooling= {intervallo_C}degC)
448     rtftext({@LastResponse})
449     rtfnl(1)
450     Message(Tend_Cooling= {Tend_C}degC)
451     rtftext({@LastResponse})
452     rtfnl(3)
453
454     rtftext(3) VARIABILI "STANDARDIZZATE + PATH":)
455     rtfnl(2)
456
457     Message(Nome generico file.dat da esportare (Heating)=
{nome_Exp_H}xyC.dat)
458     rtftext({@LastResponse})
459     rtfnl(1)
460     Message(Path DA cui esporto file.dat (Heating)= {
path_exp_H})
461     rtftext({@LastResponse})
462     rtfnl(1)
463     Message(Path IN cui salvo file.env (Heating)= {
save_pathH})
464     rtftext({@LastResponse})
465     rtfnl(1)
466     Message(Path IN cui salvo costanti ottiche (Heating)= {
save_path_optH})
467     rtftext({@LastResponse})
468     rtfnl(2)
469
470     Message(Nome generico file.dat da fittare (Plateau)= {
nome_Exp_P}xymin.dat)
471     rtftext({@LastResponse})
472     rtfnl(1)
473     Message(Path DA cui esporto file.dat (Plateau)= {
path_exp_P})
474     rtftext({@LastResponse})
475     rtfnl(1)
476     Message(Path in cui salvo file.env (Plateau)= {
save_pathP})
477     rtftext({@LastResponse})
478     rtfnl(1)
479     Message(Path in cui salvo costanti ottiche (Plateau)= {
save_path_optP})
480     rtftext({@LastResponse})
```

```
481     rtfnl(2)
482
483     Message(Nome generico file.dat da fittare (Cooling)= {
nome_Exp_C}xyC.dat)
484     rtftext({@LastResponse})
485     rtfnl(1)
486     Message(Path DA cui esporto file.dat (Cooling)= {
path_exp_C})
487     rtftext({@LastResponse})
488     rtfnl(1)
489     Message(Path in cui salvo file.env (Cooling)= {
save_pathC})
490     rtftext({@LastResponse})
491     rtfnl(1)
492     Message(Path in cui salvo costanti ottiche (Cooling)= {
save_path_optC})
493     rtftext({@LastResponse})
494     rtfnl(2)
495
496     Message(Nome SUBSTRATO generico utilizzato = {nome_sub}
xyC.mat)
497     rtftext({@LastResponse})
498     rtfnl(1)
499     Message(Path da cui esporto SUBSTRATO generico = {
AddSub_path})
500     rtftext({@LastResponse})
501
502     rtfsave({nome_rtf})
503
504     #RETURN
505
506     ;=====
507     ; SUBROUTINE: compila_rtf_fit
508     ;=====
509
510     #LABEL(compila_rtf_fit)
511
512     rtfnl(2)
513
514     GraphStyle(dblyaxis=1)
515     graphdata(1)
516     rtfgraph(width=8)
517     graphdata(0)
```

```
518     rtfgraph(width=8)
519     rtfnl(2)
520
521     rtfmod(4)
522     rtfnl(2)
523
524     rtffit
525     rtfnl(2)
526
527     currentlayer(2)
528     Layeroptconst(1064)
529     rtftext(Costanti ottiche a 1064nm: {@LastResponse})
530     rtfnl(4)
531
532     rtfsave({nome_rtf})
533
534     #RETURN
535
```

Listing D.1: Script header and initialization

Conclusions This automation script enables high-throughput, unattended ellipsometric characterization during thermal annealing experiments. The combination of synchronized data acquisition, temperature-dependent substrate correction, and real-time optical modeling provides comprehensive datasets for studying thermally-induced film evolution. The multi-step fitting algorithm ensures robust parameter extraction across the full thermal cycle, while automated RTF report generation provides immediate visualization of results. This workflow has been successfully applied to nearly all the samples presented in this work.

Chapter E

Real-Time Optical Characterization of Materials for GWD Mirror Coatings During Annealing

This chapter of the appendix provides a general framework for interpreting the ellipsometric data obtained from a typical sample. These additional considerations allow for a deeper understanding of the results presented in the main body of the thesis.

E.1 Experimental Data Analysis: Spectral Regions and Interference Fringes

The aim of this section is to explore whether key optical and structural properties of thin films, such as refractive index, thickness, and optical gap, can be anticipated directly from raw ellipsometric data, without relying on explicit optical models. In ellipsometry, material parameters are typically extracted through model-based analysis, which describes the system's response in terms of physical and structural variables. However, the validity and uniqueness of such models are often debated. Here, we argue that optical (e.g., refractive index trends, optical gap shifts) and structural (e.g., film thickness) behavior can emerge clearly and consistently from a qualitative or semi-quantitative analysis of the raw Ψ and Δ data, independent of modeling assumptions [101].

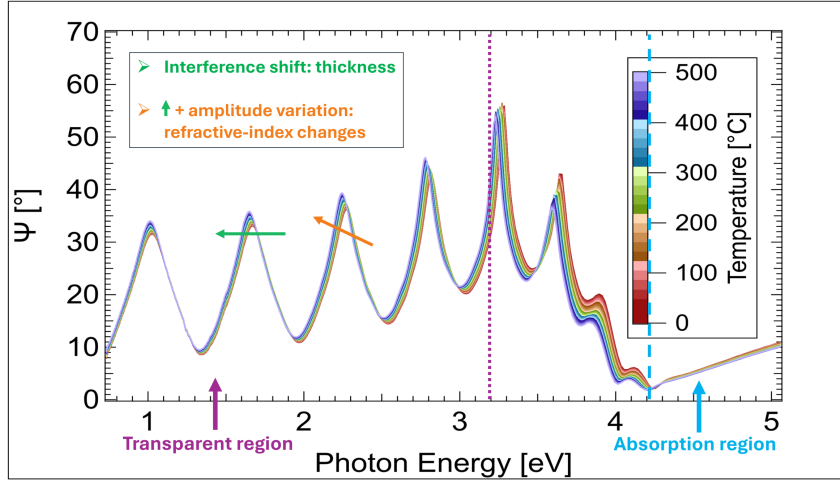


Figure E.1: Spectral behavior of the ellipsometric parameter Ψ as a function of photon energy for a titania-tantala sample during a heating ramp from 30°C to 500°C. The transition from the transparent to the absorption region is highlighted, with the disappearance of interference fringes marking the onset of absorption. The insets illustrate the effects of increasing film thickness (interference fringe shift) and refractive index (combined shift and amplitude modulation).

Figure E.1 shows a representative plot of the ellipsometric parameter Ψ as a function of photon energy, measured at various temperatures during the heating phase of the annealing process. The sample shown is a titania–tantala ($\text{Ti}:\text{Ta}_2\text{O}_5$) coating annealed from 30°C to 500°C at a heating rate of 100°C/h. Although this dataset refers to a specific sample, the behavior is representative of all high-index coatings measured in this study. Three main spectral regions can be clearly identified: the transparent region (up to approximately 3.2 eV), the absorption region (from about 4.2 to 5 eV), and the intermediate transition zone (between 3.2 and 4.2 eV) [101].

Within the *transparent region*, the Ψ parameter exhibits a regular sequence of maxima and minima, attributable to optical interference phenomena between the primary beam reflected at the film surface and the secondary beam reflected at the film-substrate interface.

The *absorption region* is experimentally identified by the complete disappearance of interference fringes in the Ψ data. At these photon energies, typically above 4 eV for the samples considered in this work, absorption is dominated by interband electronic transitions, which prevent the radiation from propagating through the film. Under such conditions (specifically, when the film thickness d exceeds the penetration depth of light by roughly a factor of five [101]), light

is absorbed before reaching the film-substrate interface. This eliminates the secondary beam, thereby preventing any interference with the primary beam reflected at the air-coating interface. Consequently, the detected signal originates solely from the top surface.

The *transition region*, located between the transparent and absorbing regimes, is of particular physical significance. In this region, absorption begins to emerge gradually, causing a progressive damping of the interference fringes amplitude. This damping marks the onset of transparency loss, often governed by Urbach tail absorption just below the fundamental optical gap [3]. Therefore, the optical gap E_g is closely related to the onset of this amplitude reduction, whereas the complete vanishing of the fringes simply indicates that the absorption has become fully dominant.

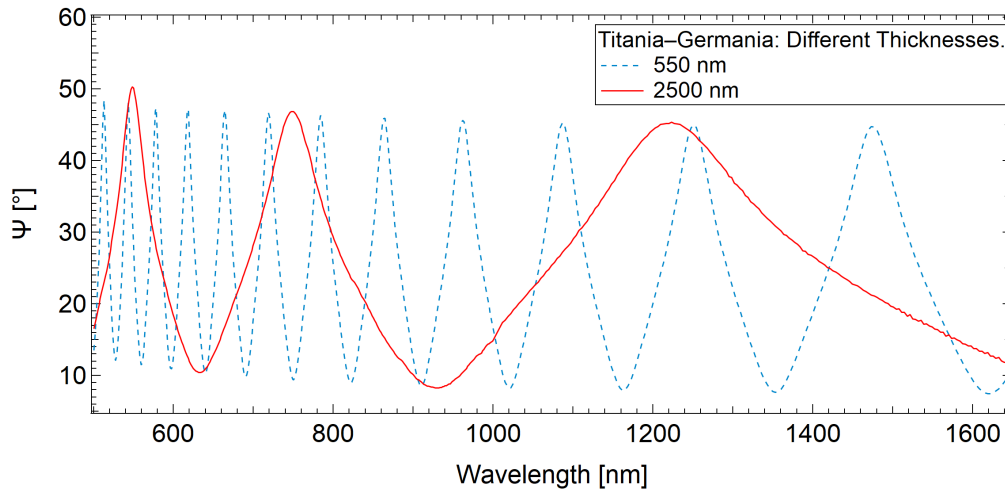


Figure E.2: Relationship between film thickness and number of interference fringes.

As emphasized by the analytical guidelines of J.A. Woollam Co. [182], it is possible to qualitatively observe variations in film thickness (via fringe density) and optical absorption (via fringe damping) directly in the raw experimental data, without the immediate need for mathematical model fitting. Figure E.1 illustrates how changes in thickness and refractive index affect the spectral behavior of the Ψ parameter in a transparent film.

The interference condition for a transparent thin film at oblique incidence is given by [101]:

$$2nd \cos \theta_t = m\lambda, \quad (\text{E.1})$$

where n is the refractive index, d the film thickness, θ_t the refracted angle inside the film, and m the interference order.

Solving the same expression for the interference order yields:

$$m = \frac{2nd \cos \theta_t}{\lambda}. \quad (\text{E.2})$$

This form makes it explicit that, for fixed wavelength and refractive index, the number of interference orders increases linearly with the film thickness. A thicker film therefore accommodates a larger number of maxima and minima within the same spectral range, resulting in a higher fringe density.

An increase in film thickness also produces a *redshift* of the fringe pattern. Solving the interference condition for the wavelength gives:

$$\lambda = \frac{2nd \cos \theta_t}{m}, \quad (\text{E.3})$$

which shows that, for fixed m , a larger thickness d leads to a larger wavelength λ . Thus, increasing the film thickness shifts all interference extrema toward lower photon energies (longer wavelengths).

A *variation in the refractive index* affects both the spectral position and the amplitude of the interference fringes. The spectral shift is governed by the interference phase condition (which incorporates Snell's law to determine the internal angle of propagation) [101], while the amplitude is determined by the refractive index contrast between the coating and the substrate. The amplitude increases as the optical contrast increases. For instance:

- Titania–tantala coating ($n \approx 2.3$) on a crystalline silicon substrate ($n \approx 3.5$): $\Rightarrow$ Moderate refractive index contrast $\Rightarrow \Psi$ exhibits visible but lower-amplitude oscillations, with less pronounced peaks compared to a high-contrast system.
- Hypothetical low-index coating (e.g., $n \approx 1.6$) on crystalline silicon ($n \approx 3.5$): $\Rightarrow$ High refractive index contrast $\Rightarrow \Psi$ displays well-defined, high-amplitude peaks due to the strong optical discontinuity at the interfaces.

Note: The absolute maximum value of Ψ is governed not only by the refractive-index contrast, but also by other parameters such as film thickness, angle of incidence, wavelength, material absorption, and composition.

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