

Development and Optimization of Atomic Layer Deposition Nanolaminate Protective Coatings

Plasma-Enhanced ALD Oxide Coatings for Metallic Mirror Protection:
From Single Layers to Nanolaminates

Master's thesis in Micro- and Nanotechnology

LORENZO VOLTA

DEPARTMENT OF MICRO- AND NANOTECHNOLOGY

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2026

www.chalmers.se

MASTER'S THESIS 2026

**Development and Optimization of
Atomic Layer Deposition
Nanolaminate Protective Coatings**

Plasma-Enhanced ALD Oxide Coatings for Metallic Mirror Protection:
From Single Layers to Nanolaminates

LORENZO VOLTA



CHALMERS
UNIVERSITY OF TECHNOLOGY

Department of Micro- and Nanotechnology
Division of Microtechnology and Nanoscience
Chalmers University of Technology
Gothenburg, Sweden 2026

Development and Optimization of Atomic Layer Deposition Nanolaminate Protective Coatings

Plasma-Enhanced ALD Oxide Coatings for Metallic Mirror Protection: From Single Layers to Nanolaminates

Lorenzo Volta

© Lorenzo Volta, 2026.

Supervisor: Dr. Theodor Weiss, RhySearch

Supervisor: Heidi Thomé, Head of Department, RhySearch

Academic supervisor and examiner: Prof. Avgust Yurgens, Department of Micro- and Nanotechnology, Chalmers University of Technology

Master's Thesis 2026

Department of Micro- and Nanotechnology

Division of Microtechnology and Nanoscience

Chalmers University of Technology

SE-412 96 Gothenburg

Telephone +46 31 772 1000

Typeset in L^AT_EX

Printed by Chalmers Reproservice

Gothenburg, Sweden 2026

Abstract

Protective coatings for metallic mirrors must resist environmental and chemical degradation while preserving the reflectance of the underlying surface. Atomic layer deposition (ALD) provides the precise thickness control and conformality required for ultra-thin protective barriers. However, plasma-enhanced ALD (PEALD) exposes oxidation-sensitive metallic substrates to reactive plasma species, while single-layer coatings may remain limited by material-specific properties and growth defects.

This work develops and optimizes PEALD oxide nanolaminate coatings deposited at 150 °C for the protection of silicon, silver, aluminium, and gold mirror substrates. An Ar/H₂ plasma pretreatment (50 W, 2% H₂, 60 s) was selected as providing suitable surface preparation while causing minimal optical and morphological modification. Silver was identified as the most oxygen-sensitive substrate, with its reflectance at 532 nm decreasing by more than 25% after only 30 s exposure to a 50 W O₂ plasma. A thermally deposited Al₂O₃ interlayer was therefore introduced to protect the substrate during subsequent PEALD processing. A thickness of 4 nm suppressed the plasma-induced reflectance loss comparably to 8 nm while limiting optical interference. Nanoscratch testing further showed consistently higher first critical loads for Al₂O₃ than for a PEALD AlN interlayer across all investigated substrates.

Five 50 nm single-layer oxides, Al₂O₃, SiO₂, TiO₂, HfO₂, and Ta₂O₅, were screened under HCl and KOH exposure using reflectance measurements and visual inspection. Based on this screening, SiO₂, TiO₂, and HfO₂ were selected for nanolaminate development. TiO₂/SiO₂ and HfO₂/SiO₂ architectures with individual layer ratios of 1:1, 5:5, 4:1, and 1:4 nm were subsequently evaluated in 10 wt% HCl for exposure times of up to 90 min. TiO₂/SiO₂ nanolaminates showed superior overall performance compared with HfO₂/SiO₂, while SiO₂-rich architectures provided the highest chemical stability. In particular, the 1 nm TiO₂:4 nm SiO₂ architecture provided the best balance between reflectance preservation, resistance to delamination, and chemical protection. Comparison of total coating thicknesses of 25, 50, and 100 nm identified 50 nm as the most suitable compromise between protective performance and preservation of optical properties. Potentiodynamic polarization measurements in 0.1 M HCl and electrochemical impedance spectroscopy in 0.1 M citric acid at pH 5.2 further supported the favourable barrier performance of the selected architecture, which exhibited low current densities and impedance magnitudes on the order of 10⁷ Ω–10⁸ Ω.

Overall, the results demonstrate that combining complementary oxides within a controlled nanolaminate architecture can improve the chemical protection of metallic mirrors while maintaining their optical functionality.

Keywords: atomic layer deposition, plasma-enhanced atomic layer deposition, nanolaminate, protective coating, metallic mirror, silver, corrosion protection, reflectance, TiO₂, SiO₂.

Acknowledgements

I would first like to express my sincere gratitude to RhySearch, and in particular to the Optical Coating and Characterization Laboratory, for the support, expertise, and assistance I received throughout this project. I am especially grateful to Heidi Thomé, Head of the department, for giving me the opportunity to carry out my Master's thesis in such a stimulating environment. My special thanks go to my project leader and supervisor, Theodor Weiss, who guided me throughout the project and with whom I shaped the scientific story behind this thesis. His constant encouragement to question results, explore further, and aim higher helped me grow both professionally and personally.

I would also like to thank Ostschweizer Fachhochschule for access to its facilities and for the collaboration in sample preparation and additional characterization. In particular, I thank Noemié Ott for carrying out the electrochemical impedance spectroscopy measurements.

My gratitude also goes to Chalmers University of Technology and especially to Avgust Yurgens, who throughout my Master's studies gave me the opportunity to deepen my interest in micro- and nanofabrication and from whom I learned a great deal through several projects under his supervision.

Beyond the scientific and professional side of this journey, there are people without whom reaching this point would not have been possible.

First and foremost, I want to thank my parents, Fausto and Barbara. They have given me the support, freedom, and opportunities that allowed me to arrive where I am today. Their encouragement has accompanied me through every step of my education, and this achievement is therefore not mine alone. I hope they can consider themselves a part of this title, because without them it would never have been possible.

A very special thank you goes to Caterina, my number one supporter, whether she was sitting right next to me or on the other side of the world. She has always encouraged me to keep going, to believe in myself, and to become the best version of myself. Switzerland, and St. Gallen in particular, became a special chapter for us. It was a period filled with long working days and many challenges, but also one in which we managed to create our own balance and make memories that I will always carry with me.

Finally, I want to thank myself. For continuing when things were difficult, for never settling too quickly, and for always searching for the next challenge and the next opportunity to grow. For remaining curious, ambitious, and willing to leave familiar paths behind in order to discover something new.

Never stop exploring.

Declaration of Use of AI Tools

I hereby declare that this thesis was carried out independently and that all external sources and contributions have been appropriately acknowledged and cited. Generative AI tools were used as supporting tools for code development, language refinement, text formulation, and the organization of written content.

Responsibility for the scientific content, analysis, interpretation, and conclusions presented in this thesis remains entirely with the author.

Contents

Abstract	i
Acknowledgements	iii
List of Figures	xv
List of Tables	xviii
List of Acronyms	xxi
1 Introduction	1
2 Theoretical Background	3
2.1 Reflective Properties and Surface Stability of Metallic Mirrors	3
2.1.1 Chemical Degradation Mechanisms	3
2.2 Thin Film Protective Coatings via ALD	4
2.2.1 Principles of Atomic Layer Deposition	4
2.2.2 Growth Mechanism and Process Parameters	5
2.2.3 Plasma-Enhanced ALD and Substrate Sensitivity	6
2.2.4 Nanolaminate Architectures and Barrier Mechanisms	7
2.3 Characterisation of Coated Optical Substrates	8
2.3.1 Light Polarisation and Reflectance Measurements	8
2.3.2 Spectroscopic Ellipsometry	9
2.3.3 Atomic Force Microscopy	9
2.3.4 Scratch Testing	10
2.4 Electrochemical Characterization	10
2.4.1 Potentiodynamic Polarization Measurements	11
2.4.2 Electrochemical Impedance Spectroscopy	11
3 Experimental Methods	13
3.1 Substrate	13
3.1.1 Substrate Materials and Architecture	13
3.1.2 Laser Dicing and Sample Preparation	14
3.2 Characterization Procedures	15
3.2.1 Ellipsometry Modeling	15

3.2.2	Reflectance Measurements	16
3.2.3	Atomic Force Microscopy	19
3.3	Pre-Cleaning and Plasma Surface Preparation	19
3.3.1	Process Parameters	20
3.3.2	Characterization	20
3.4	Mitigation of Oxygen Plasma Effects	20
3.4.1	O ₂ Plasma Sensitivity Study	21
3.4.2	Engineering of Protective Interlayers	21
3.5	Single-Layer ALD Coatings	23
3.5.1	Single-Layer Deposition Parameters	23
3.5.2	Chemical Resistance Testing	24
3.6	Nanolaminate ALD Coatings	24
3.6.1	Material Pairing Strategy	25
3.6.2	Layer Thickness Ratios and Deposition Parameters	26
3.7	Electrochemical Characterization	26
3.7.1	Electrochemical Impedance Spectroscopy	27
3.7.2	Potentiodynamic Polarization Measurements	28
4	Results	29
4.1	Baseline Characterization of Metallic Substrates	29
4.2	Influence of Ar/H ₂ Plasma Pretreatment	29
4.3	Oxygen Plasma-Induced Damage on Metallic Substrates	32
4.3.1	Development of a Protective Al ₂ O ₃ Interlayer	34
4.3.2	Comparison of Interlayer Materials	37
4.4	Single-Layer Protective Coatings	40
4.5	Nanolaminate Protective Coatings	42
4.6	Electrochemical Characterization	49
4.6.1	Influence of the Nanolaminate Layer Ratio	49
4.6.2	Influence of the Total Nanolaminate Thickness	52
5	Discussion	57
5.1	Development of an Optimized Protective Coating Process	57
5.2	From Single-Layer Coatings to Nanolaminate Architectures	58
5.3	Optimization of the Nanolaminate Architecture	59
5.4	Limitations	61
6	Conclusions	63
6.1	Key Findings	63
6.2	Possible Future Work	63
	Appendix	III
	Bibliography	XXIII

List of Figures

2.1	A schematic representation of an atomic layer deposition (ALD) cycle in which a surface is alternately exposed to a precursor (step A) and a coreactant (step B). These two reaction steps are separated by purge steps. Adapted from [1] - Figure 1	6
3.1	Schematic representation of the investigated substrate systems. The silicon reference substrate (S0) together with the three metallic mirror architectures (S1–S3) fabricated at OST served as the starting substrates for the subsequent ALD coating investigations.	14
3.2	Reflectance measurements of uncoated silicon substrates for all polarization states at (a) 730–770 nm and (b) 970–1010 nm.	17
3.3	Comparison between unpolarized and averaged polarized reflectance measurements for uncoated silicon substrates based on four repeated measurements to ensure reproducibility at (a) 730–770 nm and (b) 970–1010 nm. .	18
3.4	Schematic representation of the investigated single-layer and nanolaminate coating architectures. From left to right, the structures represent the Oxide A single layer, the Oxide A-rich 4:1 nanolaminate, the 1 nm A:1 nm B nanolaminate, the 5 nm A:5 nm B nanolaminate, the Oxide B-rich 1:4 nanolaminate, and the Oxide B single layer. The schematic illustrates both the variation in relative material contribution and, for the symmetric 1:1 compositions, the influence of the individual layer thickness. Within each supercycle, Oxide A is deposited first and Oxide B second. The drawings are not to scale.	25
3.5	Electrochemical configurations employed at OST. For both techniques, the coated sample served as the working electrode (WE) and a platinum sheet as the counter electrode (CE). The reference-electrode (RE) configuration and electrolyte were adapted to the respective measurement.	27
4.1	Influence of the Ar/H ₂ plasma pretreatment on the silicon substrate. The reflectance at 532 nm is shown as a function of plasma power together with the corresponding measurement uncertainty. Representative AFM topography images and the associated S_q values are shown for each plasma condition.	30

4.2	Influence of the Ar/H ₂ plasma pretreatment on the silver substrate. The reflectance at 532 nm is shown as a function of plasma power together with representative AFM topography images illustrating the corresponding morphological evolution.	31
4.3	Influence of the Ar/H ₂ plasma pretreatment on the aluminium substrate. The reflectance at 532 nm is shown together with representative AFM topography images for the investigated plasma powers.	31
4.4	Influence of the Ar/H ₂ plasma pretreatment on the gold substrate. The reflectance at 532 nm is shown together with representative AFM topography images for the investigated plasma powers.	32
4.5	Reflectance spectra of the investigated substrates before and after O ₂ plasma exposure at different plasma powers.	33
4.6	Reflectance at 532 nm as a function of oxygen plasma power for the silver substrate together with representative AFM topography images after plasma exposure. The pronounced reduction in reflectance is accompanied by substantial modifications of the surface morphology.	34
4.7	Reflectance spectra of silicon and silver after introducing a 2 nm thermally grown Al ₂ O ₃ interlayer prior to oxygen plasma exposure. Silicon serves as a reference substrate to evaluate the optical influence of the interlayer itself, whereas silver illustrates its ability to mitigate oxygen-induced reflectance losses.	35
4.8	Comparison of thermally deposited Al ₂ O ₃ interlayer thicknesses on silicon (left column) and silver (right column). Each subplot compares 2 nm, 4 nm and 8 nm Al ₂ O ₃ interlayers with the corresponding uncoated substrate under identical plasma conditions: without O ₂ plasma exposure (a, b), after 50 W O ₂ plasma exposure (c, d), and after 150 W O ₂ plasma exposure (e, f). The figure illustrates the influence of interlayer thickness on the optical response and allows identification of the optimum compromise between minimizing interlayer-induced optical losses and maximizing protection against oxygen-plasma-induced reflectance degradation.	36
4.9	AFM topography comparison of the investigated interlayer systems. The untreated substrates are compared with substrates coated with a 4 nm Al ₂ O ₃ interlayer, a 4 nm AlN interlayer, and the complete coating stacks consisting of 100 nm Al ₂ O ₃ deposited on top of each interlayer. The comparison allows evaluation of the influence of the interlayer material on the surface morphology before mechanical adhesion testing.	38
4.10	Representative nanoscratch measurement for the coating stack employing a 4 nm Al ₂ O ₃ interlayer. The applied load increases continuously from 3 mN to 350 mN over a scratch length of 1 mm. The identified critical loads are highlighted and correspond to distinct failure events occurring during scratching.	39

4.11	Potentiodynamic polarization curves of the investigated 50 nm single-layer and nanolaminate coatings measured in 0.1 M HCl. Lower current densities indicate reduced electrochemical activity and improved corrosion resistance. Measurements were performed at OST.	50
4.12	Bode plots of the investigated 50 nm single-layer and nanolaminate coatings measured in 0.1 M citric acid at pH 5.2. The impedance magnitude (lines) and phase angle (triangles) are shown as a function of frequency. Measurements were performed at OST.	52
4.13	Potentiodynamic polarization curves of the selected 1 nm TiO ₂ :4 nm SiO ₂ nanolaminate for total coating thicknesses of 25, 50, and 100 nm measured in 0.1 M HCl. Measurements were performed at OST.	53
4.14	Bode plots of the selected 1 nm TiO ₂ :4 nm SiO ₂ nanolaminate for total coating thicknesses of 25, 50, and 100 nm measured in 0.1 M citric acid at pH 5.2. Measurements were performed at OST.	54
A.1	Reflectance reproducibility of the silicon substrate. Subfigures (a)–(c) show short-term repeated measurements, while (d)–(f) show long-term measurements performed at one-week intervals on different samples from the same wafer. Error bars are based on the standard deviation.	IV
A.2	Reflectance reproducibility of the silver-coated substrate. Subfigures (a)–(c) show short-term repeated measurements, while (d)–(f) show long-term measurements performed at one-week intervals on different samples from the same wafer. Error bars represent one standard deviation.	V
A.3	Reflectance reproducibility of the aluminum-coated substrate. Subfigures (a)–(c) show short-term repeated measurements, while (d)–(f) show long-term measurements performed at one-week intervals on different samples from the same wafer. Error bars represent one standard deviation.	VI
A.4	Reflectance reproducibility of the gold-coated substrate. Subfigures (a)–(c) show short-term repeated measurements, while (d)–(f) show long-term measurements performed at one-week intervals on different samples from the same wafer. Error bars represent one standard deviation.	VII
A.5	Reflectance spectra of Si, Ag, Al, and Au substrates after Ar/H ₂ plasma treatment under varying process conditions, including power, hydrogen concentration, and exposure time.	VIII
A.6	Reflectance comparison of 4 nm Al ₂ O ₃ and 4 nm AlN interlayers on silicon and silver substrates under different oxygen plasma exposure conditions. The rows correspond to no O ₂ plasma exposure, 50 W, 150 W, and 400 W O ₂ plasma exposure, respectively.	X

A.7	Reflectance-based protection screening of the silver substrate protected by different 50 nm single-layer oxide coatings during HCl exposure. The uncoated Ag substrate provides the reference response to HCl, while the Al_2O_3 , SiO_2 , TiO_2 , HfO_2 , and Ta_2O_5 coatings illustrate the influence of the individual oxide materials on the preservation of the optical properties of the silver mirror.	XI
A.8	Reflectance-based protection screening of the aluminium substrate protected by different 50 nm single-layer oxide coatings during HCl exposure. The uncoated Al substrate provides the reference response to HCl, while the Al_2O_3 , SiO_2 , TiO_2 , HfO_2 , and Ta_2O_5 coatings illustrate the influence of the individual oxide materials on the preservation of the optical properties of the aluminium mirror.	XII
A.9	Reflectance-based protection screening of the silicon substrate protected by different 50 nm single-layer oxide coatings during KOH exposure. The uncoated Si substrate provides the reference response to KOH, while the Al_2O_3 , SiO_2 , TiO_2 , HfO_2 , and Ta_2O_5 coatings illustrate the influence of the individual oxide materials on the preservation of the optical properties of the silicon mirror.	XIII
A.10	Reflectance-based protection screening of the aluminium substrate protected by different 50 nm single-layer oxide coatings during KOH exposure. The uncoated Al substrate provides the reference response to KOH, while the Al_2O_3 , SiO_2 , TiO_2 , HfO_2 , and Ta_2O_5 coatings illustrate the influence of the individual oxide materials on the preservation of the optical properties of the aluminium mirror.	XIV
A.11	Reflectance-based HCl protection screening of 50 nm $\text{TiO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on silicon. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.	XV
A.12	Reflectance-based HCl protection screening of 50 nm $\text{TiO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on silver. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.	XVI
A.13	Reflectance-based HCl protection screening of 50 nm $\text{TiO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on aluminium. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.	XVII
A.14	Reflectance-based HCl protection screening of 50 nm $\text{TiO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on gold. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.	XVIII
A.15	Reflectance-based HCl protection screening of 50 nm $\text{HfO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on silicon. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.	XIX
A.16	Reflectance-based HCl protection screening of 50 nm $\text{HfO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on silver. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.	XX

A.17 Reflectance-based HCl protection screening of 50 nm HfO ₂ /SiO ₂ nanolaminate coatings with different individual layer thickness ratios on aluminium. All nanolaminates were deposited on a 4 nm Al ₂ O ₃ interlayer.	XXI
A.18 Reflectance-based HCl protection screening of 50 nm HfO ₂ /SiO ₂ nanolaminate coatings with different individual layer thickness ratios on gold. All nanolaminates were deposited on a 4 nm Al ₂ O ₃ interlayer.	XXII

List of Tables

3.1	Extracted reflectance deviations for both spectral sampling pitches at the investigated wavelengths for short- and long-term time intervals.	18
3.2	Experimental matrix for single-layer coatings, combining material system, total deposition thickness, and process temperature. The highlighted column (50 nm, 150°C) indicates the starting condition used for screening. .	24
3.3	Initial experimental matrix for nanolaminate coatings, combining the individual layer thickness ratio, total deposition thickness, and process temperature. The highlighted column (50 nm, 150°C) indicates the starting condition used for screening.	25
4.1	Critical loads obtained from nanoscratch measurements for coating stacks employing either a 4 nm Al ₂ O ₃ or a 4 nm AlN interlayer. The first critical load L_{c1} is used as the main comparison parameter for evaluating adhesion at the coating–substrate interface.	40
4.2	Reflectance-based grading of 50 nm single-layer coatings after chemical exposure. A score of 3 indicates no measurable degradation, while 0 indicates complete coating failure or substrate exposure.	41
4.3	Visual inspection of 50 nm single-layer coatings after chemical exposure. Green cells indicate coating systems that showed no visible degradation or delamination after etching.	42
4.4	Comparison between the coating thickness and refractive index obtained from ellipsometric fitting and the calculated ordinary (n_o) and extraordinary (n_e) refractive indices of the investigated nanolaminate architectures. The calculated values were obtained using $n_{\text{SiO}_2} = 1.46$, $n_{\text{TiO}_2} = 2.40$, and $n_{\text{HfO}_2} = 2.02$ at $\lambda = 632$ nm. The ellipsometric spectra were fitted using an Isotropic Cauchy model.	44
4.5	Reflectance-based grading of 50 nm TiO ₂ /SiO ₂ nanolaminates with different ratios of TiO ₂ :SiO ₂ layer thickness on different substrates after 30 min exposure to 10 wt% HCl, evaluated with a grading system from 0 for drastic changes to 3 for no/minimum changes.	45
4.6	Reflectance-based grading of 50 nm TiO ₂ /SiO ₂ nanolaminates with different ratios of TiO ₂ :SiO ₂ layer thickness on different substrates after 90 min exposure to 10 wt% HCl, evaluated with a grading system from 0 for drastic changes to 3 for no/minimum changes.	45

4.7	Reflectance-based grading of 50 nm HfO ₂ /SiO ₂ nanolaminates with different ratios of HfO ₂ :SiO ₂ layer thickness on different substrates after 30 min exposure to 10 wt% HCl, evaluated with a grading system from 0 for drastic changes to 3 for no/minimum changes.	46
4.8	Reflectance-based grading of 50 nm HfO ₂ /SiO ₂ nanolaminates with different ratios of HfO ₂ :SiO ₂ layer thickness on different substrates after 90 min exposure to 10 wt% HCl, evaluated with a grading system from 0 for drastic changes to 3 for no/minimum changes.	46
4.9	Visual grading of 50 nm TiO ₂ /SiO ₂ nanolaminates after 30 min exposure to 10 wt% HCl. The scores account for visible degradation such as delamination, localized failure and substrate bubbling.	47
4.10	Visual grading of 50 nm TiO ₂ /SiO ₂ nanolaminates after 90 min exposure to 10 wt% HCl.	47
4.11	Visual grading of 50 nm HfO ₂ /SiO ₂ nanolaminates after 30 min exposure to 10 wt% HCl.	48
4.12	Visual grading of 50 nm HfO ₂ /SiO ₂ nanolaminates after 90 min exposure to 10 wt% HCl.	48
A.1	Measurement parameters used for all reflectance measurements performed with the PHOTON RT Spectrophotometer Model 0252 (EssentOptics). .	III
A.2	Surface roughness S_q of Si, Ag, Al, and Au substrates as a function of Ar/H ₂ plasma power. The untreated values correspond to the reference surface roughness measurements, while all plasma-treated samples were exposed using 2% H ₂ for 60 s.	IX
A.3	Surface roughness S_q of Si, Ag, Al, and Au substrates as a function of O ₂ plasma power. Plasma-treated samples were exposed for 30 s at 150 °C. .	IX

List of Acronyms

AFM	Atomic Force Microscopy
ALD	Atomic Layer Deposition
ALE	Atomic Layer Epitaxy
CE	Counter Electrode
CVD	Chemical Vapor Deposition
EIS	Electrochemical Impedance Spectroscopy
GPC	Growth per Cycle
HCl	Hydrochloric Acid
IR	Infrared
KOH	Potassium Hydroxide
L_c	Critical Loads
MSE	Mean Square Error
OCP	Open-Circuit Potential
OST	Ostschweizer Fachhochschule
PEALD	Plasma-Enhanced Atomic Layer Deposition
RE	Reference Electrode
S_q	Root Mean Square Surface Roughness
TALD	Thermal Atomic Layer Deposition
TMA	Trimethylaluminium
UPM	Ultra-Precision Manufacturing Laboratory
UV	Ultraviolet
WE	Working Electrode

1 Introduction

Protective coatings play an essential role in both industrial applications and scientific research fields, ranging from optics and microelectronics to energy systems and corrosion protection. Their primary purpose is to protect functional surfaces against environmental influences such as atmospheric degradation, chemical corrosion, and mechanical damage [2, 3]. In many applications, however, the protective coating must simultaneously preserve the original functionality of the underlying substrate. This requirement is particularly critical for optical systems, where even nanometer-scale variations in film thickness or interface quality can measurably alter the reflectance or transmission properties of the coated component [4]. Consequently, there is a strong demand for ultra-thin, conformal, and defect-reduced protective coatings capable of providing environmental stability while minimising changes to the functional properties of the substrate.

Atomic Layer Deposition (ALD) has attracted increasing attention for such applications due to its self-limiting surface reactions, which enable highly controlled thin-film growth with thickness precision at the atomic scale and excellent conformality even on complex surface geometries [5, 6, 7]. Compared to conventional thin-film deposition techniques such as sputtering or evaporation, ALD provides superior uniformity and reduced pin-hole formation, making it particularly suitable for ultra-thin barrier and encapsulation coatings. Among the oxide materials investigated for ALD protective coatings, Al_2O_3 , TiO_2 , ZrO_2 , and Y_2O_3 have each demonstrated relevant barrier and corrosion resistance properties, though their comparative performance under combined optical and chemical stress conditions remains incompletely characterised [7, 8, 9]. Identifying which single-layer material offers the most favourable combination of optical transparency, chemical stability, and substrate compatibility therefore represents a necessary prerequisite before more complex coating architectures can be rationally designed.

A further unresolved challenge concerns the deposition of protective coatings on oxidation-sensitive reflective substrates, such as silver or copper, which are widely used in optical mirror applications due to their high reflectivity but remain highly susceptible to surface modification during film growth. Purely thermal ALD processes can reduce the risk of plasma-induced oxidation, but they typically require elevated substrate temperatures that are incompatible with temperature-sensitive components and may themselves alter the optical properties of the underlying metal [4]. Plasma-enhanced Atomic Layer Deposition (PEALD) offers the advantage of lower deposition temperatures and improved film densification [10, 11], but the reactive plasma species introduce a competing risk of substrate oxidation before a sufficiently protective film has formed. This trade-off between process compatibility and substrate integrity has received limited systematic attention in the literature, particularly in the context of ultra-thin coatings on metallic optical reflectors.

While single-layer coatings provide a useful performance baseline, their intrinsic limitations, including residual stress, susceptibility to pinhole formation, and defect propaga-

tion associated with crystallisation, have motivated increasing interest in nanolaminate architectures alternating two or more oxide materials [10, 9, 12]. Such nanolaminate structures introduce internal interfaces capable of interrupting diffusion pathways, redistributing mechanical stress, and suppressing crystallisation-driven degradation, collectively improving barrier performance beyond what equivalent single-layer thicknesses can be achieved [6, 10]. However, for architectures with very small individual layer thicknesses, the distinction between a structurally discrete nanolaminate and an effectively mixed or compositionally graded film becomes increasingly difficult to establish. In particular, nucleation effects and incomplete layer formation may influence the resulting structure when only a small number of ALD cycles is deposited per material. Direct verification of the internal layer structure therefore requires dedicated structural characterisation. In the present work, the investigated coatings are referred to as nanolaminates based on their sequential deposition architecture, while the formation and continuity of the individual layers are not independently verified. Structural validation by techniques such as X-ray reflectometry and cross-sectional transmission electron microscopy (TEM) is therefore left for follow-up work [10, 12].

Despite the extensive body of literature on individual ALD oxide materials and nanolaminate encapsulation layers, a systematic study linking single-layer material selection, PEALD process compatibility with oxidation-sensitive metallic substrates, and the structural integrity of the nanolaminate architecture within a single experimental framework is largely absent.

The aim of this work is to establish a coherent basis for the rational design of PEALD-compatible protective oxide coatings for optically sensitive metallic substrates. To this end, the study follows a stepwise optimization strategy that is reflected in the structure of the thesis. Following the theoretical background presented in Chapter 2 and the experimental procedures described in Chapter 3, Chapter 4 first examines how different plasma-based surface treatments affect the investigated mirror substrates, with the aim of identifying suitable conditions for surface preparation while limiting substrate modification. The sensitivity of the substrates to oxygen plasma exposure is then evaluated, together with the use of a protective interlayer to mitigate plasma-induced degradation of oxygen-sensitive substrates. The study subsequently addresses which single-layer oxides provide the most suitable basis for further coating development, before investigating which material combinations and individual layer-thickness ratios provide the most effective nanolaminate architectures. Finally, the influence of the total coating thickness on the balance between optical preservation and barrier performance is evaluated, with electrochemical measurements providing complementary validation of the selected architectures. These results are interpreted and brought together in Chapter 5, while Chapter 6 summarizes the main conclusions and recommendations for future work.

2 Theoretical Background

2.1 Reflective Properties and Surface Stability of Metallic Mirrors

Metallic mirrors derive their high reflectance from the interaction between the incident electromagnetic wave and the free electrons within the metal. In contrast to dielectric materials, which are largely transparent over broad wavelength ranges, metals contain a high density of delocalized conduction electrons that collectively oscillate in response to the electric field of the incident light. This response strongly reduces the propagation of electromagnetic waves into the material and results in efficient reflection over a broad spectral range [13, 14]. Among metallic materials, aluminium, silver, and gold are of particular technological importance because of their characteristic spectral reflectance. Aluminium exhibits high reflectance from the ultraviolet (UV) into the infrared (IR), silver provides the highest reflectance throughout most of the visible and near-IR region, while gold combines excellent IR reflectance with high chemical stability [14, 15].

The optical response of an ideal metallic surface is determined by the intrinsic optical properties of the material. Therefore, even nanometer-scale modifications of the surface may produce changes in optical performance. Surface roughness increases scattering, contaminants introduce additional absorption, while chemical modifications alter the electronic structure and optical constants of the surface layer. As a result, degradation processes affecting only a few nanometres of the surface can already reduce reflectance significantly.

For optical mirror applications, preserving the chemical and morphological integrity of the surface is therefore as important as preserving the bulk material itself. This requirement motivates the use of protective thin-film coatings capable of isolating the reflective metal from aggressive environments while maintaining their optical performance.

2.1.1 Chemical Degradation Mechanisms

The chemical durability of a protective coating is determined not only by its intrinsic resistance to the surrounding environment but also by its ability to prevent aggressive species from reaching the underlying substrate. In practice, deposited thin films are never completely defect-free. Structural imperfections such as pinholes, pores, micro-cracks, or grain boundaries provide preferential pathways through which corrosive media can penetrate the coating [16, 5].

Once the chemical medium reaches the coating-substrate interface, degradation can initiate locally, resulting in corrosion of the underlying material, coating delamination, and ultimately coating failure. Consequently, the protective performance of a coating is governed by both its chemical stability and its ability to minimize defect density while

increasing the diffusion path of aggressive species through the coating. Dense amorphous coatings and multilayer architectures therefore provide improved barrier properties by reducing the number of continuous transport pathways available for corrosive species [16, 7].

The degradation mechanism further depends on both the substrate material and the surrounding chemical environment. Acidic solutions generally promote metal dissolution, whereas alkaline solutions predominantly attack materials through hydroxide-induced dissolution mechanisms [17].

Metallic mirrors exhibit fundamentally different degradation mechanisms. Aluminum is protected by a naturally formed oxide layer that passivates the surface under many environmental conditions. However, this passive layer readily dissolves in both acidic and alkaline media, exposing fresh metal to further corrosion [18]. Silver is considerably more susceptible to atmospheric corrosion and chemical attack, where the formation of oxides, sulfides, or chlorides increases surface roughness and reduces optical reflectance [19]. Gold, in contrast, is chemically noble and remains largely unaffected by non-oxidizing acids such as hydrochloric acid, making it a useful chemically stable reference material in corrosion studies [17].

2.2 Thin Film Protective Coatings via ALD

To allow protection against external factors, and more specifically against chemical degradation, thin layers of materials can be implemented aiming to keep performance high and resist to changes caused by defects.

2.2.1 Principles of Atomic Layer Deposition

The concept of Atomic Layer Deposition (ALD) originates from the work of Suntola, who introduced Atomic Layer Epitaxy (ALE), a method where alternating precursor pulses enable atomic-scale thin film growth with high uniformity [20]. In conventional Chemical Vapor Deposition (CVD), precursors react simultaneously in the gas phase, which can lead to less controlled growth dominated by gas-phase kinetics rather than surface reactions. ALD separates the precursor reactions in time, allowing film thickness to be precisely controlled at the atomic scale through a sequential and cyclic deposition process, based on well-defined chemical reaction mechanisms [21].

A significant advantage of ALD over CVD is its conformality. The diffusion of gaseous precursors and the self-limiting nature of the surface reactions allow ALD to coat complex three-dimensional structures uniformly, including high aspect ratio features, pores, and curved surfaces [22]. For protective coatings, this is particularly important, as it ensures complete surface coverage and minimizes defects such as pinholes or uncoated regions. These aspects are directly relevant to the chemical stability and corrosion testing carried out in this work.

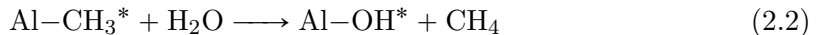
The depositions in this work were performed using a FlexAL[®] II ALD system, which consists of a vacuum chamber, loadlock, precursor delivery system, and plasma source. The system supports operation in both thermal and plasma-enhanced modes, with precise control over temperature, pressure, and precursor exposure conditions [23].

2.2.2 Growth Mechanism and Process Parameters

A complete ALD cycle consists of four sequential steps. In the first step, the first precursor is introduced into the reaction chamber, where it chemisorbs onto the substrate surface and reacts with available surface functional groups, typically hydroxyl groups ($-\text{OH}$). This reaction is self-limiting: sites are occupied until maximum surface saturation is reached, allowing no further adsorption, regardless of excess precursor present in the chamber. Using Al_2O_3 deposition with trimethylaluminum (TMA) as a representative example, this step proceeds as:



Methane (CH_4) is released as a gaseous by-product and the surface becomes terminated with $-\text{CH}_3$ groups. In the second step, an inert gas, typically N_2 or Ar , is introduced to remove excess precursor molecules from the chamber. This prevents gas-phase reactions in the subsequent step and ensures that all further chemistry occurs exclusively at the surface. In the third step, the second precursor is introduced and reacts with the surface species formed in the first step, completing the surface reaction and regenerating the functional groups required for the subsequent ALD cycle. For Al_2O_3 with water as the second precursor, this reaction proceeds as:



This step restores the hydroxyl-terminated surface and prepares it for the next cycle. In the fourth step, a second purge removes any remaining precursor and reaction by-products before the sequence can be repeated to create further layers. A schematic overview of the four-step ALD cycle is shown in Figure 2.1. Each ALD cycle generally deposits only a fraction of a complete monolayer, since precursor ligands and the finite density of reactive surface sites limit the amount of material incorporated per cycle. Film growth is therefore described by the growth per cycle (GPC), which for Al_2O_3 is typically around $1.1 \text{ \AA}/\text{cycle}$. The total film thickness can nevertheless be controlled accurately through the number of repeated ALD cycles once steady-state growth is established [21]. The Al_2O_3 example used here serves as an illustration of the general mechanism. Other oxide materials used in this work, such as TiO_2 , HfO_2 , and Ta_2O_5 , follow the same cyclic process but involve different precursor chemistry and reaction kinetics.

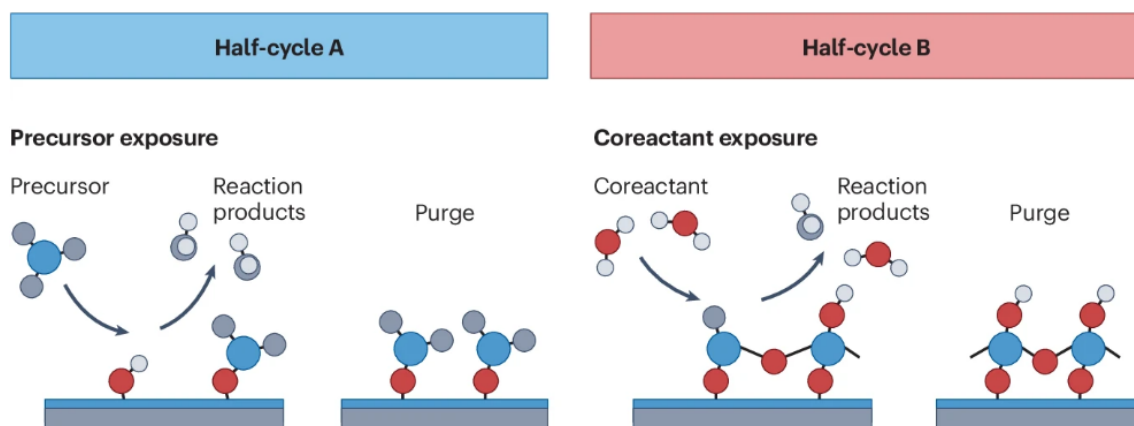


Figure 2.1: A schematic representation of an atomic layer deposition (ALD) cycle in which a surface is alternately exposed to a precursor (step A) and a coreactant (step B). These two reaction steps are separated by purge steps. Adapted from [1] - Figure 1

Stable and reproducible precursor delivery is essential for maintaining process quality. Precursors with sufficiently high vapour pressure can be introduced directly into the chamber, while those with lower volatility require a bubbler system, through which an inert carrier gas is passed through the liquid precursor bottle and transports its vapour into the chamber in a controlled manner [23]. Fluctuations in precursor flux directly affect surface saturation and therefore the uniformity and reproducibility of the deposited film [24].

Temperature is a critical parameter in ALD processes. Surface reactions are only effective within a defined temperature range, commonly known as the ALD window [22]. Below this window, surface reactions may be incomplete due to insufficient precursor condensation or reactant activation. Above it, thermal decomposition of the precursor or desorption of adsorbed species disrupts the self-limiting character of the process. When the correct combination of precursor, co-reactant, and substrate temperature is maintained within this window, a stable and constant growth per cycle (GPC) is achieved, as the surface chemistry remains well controlled.

2.2.3 Plasma-Enhanced ALD and Substrate Sensitivity

Both thermal ALD (TALD) and plasma-enhanced ALD (PEALD) follow the same cyclic process and rely on self-limiting surface reactions. They differ in the mechanism by which these reactions are activated. In TALD, surface reactions are driven purely by thermal energy. The substrate is heated to a temperature at which precursor molecules can react with surface functional groups through ligand exchange mechanisms, as illustrated in the Al_2O_3 example above [21]. The process is characterized by well-defined reaction pathways, high film uniformity, and a strong dependence on substrate temperature. For less reactive precursor systems, however, higher temperatures may be required to ensure

complete surface reactions, which can be a limitation when working with thermally sensitive substrates or underlying layers. In PEALD, one of the reaction steps is replaced by exposure to a plasma. This plasma produces reactive species including radicals, ions, and excited molecules [23]. For Al₂O₃ PEALD using an oxygen plasma, reactive oxygen radicals (O*) take the role of water in the thermal process:



Plasma-generated radicals significantly increase surface reactivity, enabling enhanced reaction kinetics, lower required substrate temperatures, and increased film density compared to the thermal process [24]. However, the presence of energetic species can introduce film stress and affect interface properties, which must be carefully controlled when selecting process conditions [24].

2.2.4 Nanolaminate Architectures and Barrier Mechanisms

For the formation of a nanolaminate, alternating layers of at least two materials with different properties are arranged in a periodically repeated structure. In the context of this work, a nanolaminate is defined as consisting of at least ten individual layers (e.g. five repeated pairs), with an individual layer thickness between 1 and 100 nm, resulting in a total coating thickness between 10 and 1000 nm. While the total coating thickness may remain constant, the material combination, the relative thickness of the individual layers, and consequently the number of repeated interfaces can be varied in order to tailor the overall coating properties.

Single-layer coatings can provide excellent barrier properties owing to their high density, conformality, and chemical stability. Nevertheless, their protective performance ultimately remains limited by structural imperfections introduced during film growth or service. Even highly conformal ALD coatings may contain isolated defects or local discontinuities which, once extending through a significant portion of the coating thickness, can provide preferential pathways for the transport of aggressive species towards the coating-substrate interface [16, 25]. As a result, the protective performance of a single-layer coating depends not only on the intrinsic properties of the deposited material, but also on the probability that such defects remain continuous throughout the coating thickness.

The motivation for nanolaminate architectures originates from overcoming this limitation through the introduction of repeated interfaces. Instead of relying on one continuous barrier, the coating is divided into multiple individual layers, each acting as an additional obstacle for chemical transport. Structural defects present within one layer are unlikely to remain aligned throughout the complete coating stack and may therefore be interrupted by the subsequent layer, preventing the formation of continuous transport pathways. Consequently, aggressive species no longer encounter a direct diffusion path but instead follow a longer and more tortuous route before reaching the

substrate, thereby delaying the initiation of corrosion [25, 26]. In addition, the repeated interfaces can influence the microstructural evolution of the coating by restricting continuous grain growth, redistributing residual stresses, and altering crack propagation. These all further improve the structural integrity of the barrier [16, 27]. The protective performance of a nanolaminate therefore arises not only from the intrinsic properties of the constituent materials, but also from the architecture created through their periodic repetition [26, 27].

2.3 Characterisation of Coated Optical Substrates

To evaluate the deposited protective coatings on the substrates, a set of fixed methods is always used and can then be complemented by some further measurements. The following sections present the theoretical foundations needed to understand the working principles of the characterization techniques.

2.3.1 Light Polarisation and Reflectance Measurements

Light is an electromagnetic wave in which the electric and magnetic field vectors oscillate perpendicular to each other and propagate over a distance in a given direction in space [28]. Depending on the orientation and behaviour of the electric field, light is defined by different polarisation states. The two extremes are fully polarised light, in which the electric field traces a well-defined ellipse over time, and unpolarised light, in which the electric field orientation is completely disordered. Everything between these two states is quantified by the degree of polarisation ρ . Once light encounters a surface, the plane of incidence, defined by the incident ray and the surface normal, determines how the polarisation state interacts with that surface. Relative to this plane, p-polarised light (p for parallel) has its electric field oscillating parallel to the plane of incidence, while s-polarised light (from the German *senkrecht*, meaning perpendicular) has its electric field oscillating perpendicular to it. The reflectance of each polarisation component is governed by the Fresnel reflection coefficients, which for s- and p-polarised light are given respectively by [28]:

$$r_s = \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \quad (2.4)$$

$$r_p = \frac{n_2 \cos \theta_i - n_1 \cos \theta_t}{n_2 \cos \theta_i + n_1 \cos \theta_t} \quad (2.5)$$

where n_1 and n_2 are the refractive indices of the incident and transmitting media, θ_i is the angle of incidence, and θ_t is the angle of refraction as given by Snell's law. Since r_s and r_p differ in both magnitude and phase, s- and p-polarised light experience different reflectance values, $R_s = |r_s|^2$ and $R_p = |r_p|^2$, as well as different phase shifts upon reflection. Taking the average of the two polarisation states therefore yields a reflectance between R_s and R_p . Unpolarised light, containing equal contributions of all

field orientations, can equivalently be treated as an equal mixture of s and p components, such that its reflectance corresponds to the same average [13]. This distinction is central to the two optical characterisation techniques employed in this work. In spectrophotometry, the ability to select between s, p, or unpolarised illumination allows the polarisation-dependent reflectance of the mirror surface to be probed selectively, providing sensitivity to surface condition and thin film coatings that would otherwise be obscured in a polarisation-averaged measurement.

2.3.2 Spectroscopic Ellipsometry

Ellipsometry uses polarized light to characterize thin-film and bulk materials. It measures the changes in polarization of the incident light due to its interaction with the sample structure. In ellipsometry, the distinction between s and p is used more directly: the technique measures how a surface modifies the polarisation state of reflected light. This difference is in the reflection of the s and p components that carries information about the optical properties and thickness of thin film layers on the surface. The measurement is typically expressed as two values Ψ and Δ . The measured data is then analyzed to determine material properties of interest, based on the changes induced in the optical constants.

Since ellipsometry does not directly measure film thickness or refractive index, the measured Ψ and Δ spectra are fitted using an optical model representing the substrate and deposited layers. The optical response of each layer is described through the complex refractive index $\tilde{n} = n + ik$, while the layer thickness d is included as an additional fitting parameter. Transparent dielectric films can be described using a Cauchy dispersion model, whereas absorbing materials may require oscillator-based models such as the Tauc-Lorentz model. The agreement between the measured and modelled spectra is evaluated using the Mean Square Error (MSE), with lower MSE values indicating better agreement between model and experiment. In this work, ellipsometry is primarily used to determine the thickness d and refractive index n of the deposited ALD coatings on silicon reference substrates.

2.3.3 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a scanning probe microscopy technique capable of characterizing surface morphology with nanometre resolution. Unlike optical microscopy, AFM does not rely on the interaction of light with the sample, but on the interaction forces acting between a sharp probe tip and the sample surface. These forces arise from the balance between long-range attractive van der Waals interactions and short-range repulsive forces caused by the overlap of the electron clouds of the tip and sample [29]. By monitoring these interactions while scanning across the surface, a three-dimensional topographical map of the sample can be reconstructed.

In dynamic force operation, the cantilever oscillates continuously at its characteristic resonance frequency. As the oscillating tip approaches the sample surface, the interaction forces modify its oscillation behaviour. A laser beam reflected from the backside of the cantilever onto a position-sensitive photodetector continuously monitors these changes, while a feedback loop adjusts the vertical position of the scanner to maintain constant imaging conditions. The recorded height adjustments are subsequently converted into a topographical representation of the investigated surface.

Besides providing qualitative information on the surface morphology, AFM enables the extraction of quantitative roughness parameters, such as the root-mean-square roughness (S_q). Consequently, AFM is widely employed for the characterization of thin films and coatings, where changes in surface morphology, grain structure, cracks, pinholes, and other defects can be correlated with deposition processes and material performance.

2.3.4 Scratch Testing

Scratch testing is a mechanical characterization technique used to evaluate the adhesion and failure behaviour of thin films and coatings. During the test, a progressively increasing normal load is applied while an indenter moves across the coated surface. As the applied load increases, stresses develop within the coating and at the coating-substrate interface, which can eventually lead to cracking, delamination, or complete coating failure.

The onset of these failure events is described by characteristic critical loads, generally denoted as L_{c1} , L_{c2} , and L_{c3} . The first critical load, L_{c1} , is associated with the onset of coating failure and is commonly used as an indicator of adhesion. Subsequent critical loads correspond to progressively more severe damage and may increasingly involve cohesive failure within the coating or deformation of the underlying substrate.

The measured critical loads depend not only on the coating-substrate adhesion, but also on parameters such as coating thickness, the mechanical properties of the coating and substrate, indenter geometry, and loading conditions. Scratch testing therefore provides a comparative measure of coating adhesion and mechanical stability rather than a direct measurement of the interfacial adhesion energy.

2.4 Electrochemical Characterization

Previously discussed characterization techniques such as reflectance measurements and AFM provide information on the optical performance and surface morphology of protective coatings. However, they do not directly evaluate the electrochemical stability of the coating in a corrosive environment. Electrochemical characterization therefore complements these methods by assessing the barrier performance of the coating against electrolyte penetration. In this work, two complementary electrochemical techniques

were employed: potentiodynamic polarization (E-j) measurements and EIS. Together, these techniques provide information on the corrosion behaviour and protective performance of the investigated coating systems. [30, 31, 32]

2.4.1 Potentiodynamic Polarization Measurements

Potentiodynamic polarization is one of the most commonly used electrochemical techniques for evaluating the corrosion behaviour of metallic materials and protective coatings. During the measurement, the potential of the working electrode (WE) is swept at a constant scan rate with respect to a reference electrode (RE) while the resulting current density is continuously recorded. The obtained current density-potential (E-j) curve provides information on the electrochemical behaviour of the investigated system. [30]

From the polarization curve, characteristic parameters such as the corrosion potential (E_{corr}) and corrosion current density (j_{corr}) can be determined. In addition, many protective oxide coatings exhibit a passive region, characterised by a low and nearly constant current density over a range of applied potentials. Lower current densities and a broader passive region generally indicate improved corrosion resistance and enhanced barrier performance. [31]

2.4.2 Electrochemical Impedance Spectroscopy

EIS is a non-destructive electrochemical technique used to evaluate the barrier properties of protective coatings over a wide range of frequencies. A small sinusoidal voltage perturbation is applied to the electrochemical system and the resulting current response is measured. The ratio between the applied voltage and measured current defines the impedance of the system, which varies with frequency. The electrochemical behaviour can further be interpreted using equivalent electrical circuits composed of electrical elements such as resistors and capacitors, representing the physical processes occurring within the coating and at the coating-substrate interface. [32, 31]

EIS data are commonly represented either as Nyquist or Bode plots. Since only Bode diagrams are discussed in this work, the interpretation focuses on the impedance magnitude ($|Z|$) and the phase angle as a function of frequency. These plots provide information on the dielectric behaviour of the coating, the resistance to charge transfer, and consequently the effectiveness of the coating as a corrosion barrier. Higher impedance together with a phase angle closer to 90° generally indicate improved barrier properties and enhanced protection against electrolyte penetration.

3 Experimental Methods

This chapter describes the fabrication and preparation procedures of the investigated substrate systems and thin-film coatings, as well as the implemented characterization and durability testing methods.

3.1 Substrate

The objective of this work is the development and evaluation of protective ALD coatings for metallic mirrors. Since the performance of such coatings depends strongly on the underlying substrate, a representative set of optical mirror materials was selected and prepared prior to the coating experiments. The substrates were designed to cover both a silicon reference surface and metallic mirrors commonly employed in industrial optical applications, allowing the performance of the protective coatings to be evaluated on substrates exhibiting different optical and chemical properties.

3.1.1 Substrate Materials and Architecture

All substrates were fabricated on 4-inch silicon wafers supplied by Si-Mat. Silicon was selected as the base material due to its excellent surface quality, dimensional stability, and widespread use in semiconductor and optical manufacturing. Furthermore, silicon substrates provide a well-defined and reproducible platform for thin-film deposition and subsequent characterization. To create the different mirror systems investigated in this study, metallic coatings were deposited onto the silicon wafers at the Ostschweizer Fachhochschule (OST) using evaporation processes. In addition to an uncoated silicon reference substrate (S0), three metallic mirror architectures were fabricated:

- S0: Si/SiO₂
- S1: Si/SiO₂/Ti (25 nm)/Ag (150 nm)
- S2: Si/SiO₂/Al (150 nm)
- S3: Si/SiO₂/Ti (25 nm)/Pt (200 nm)/Au (375 nm)

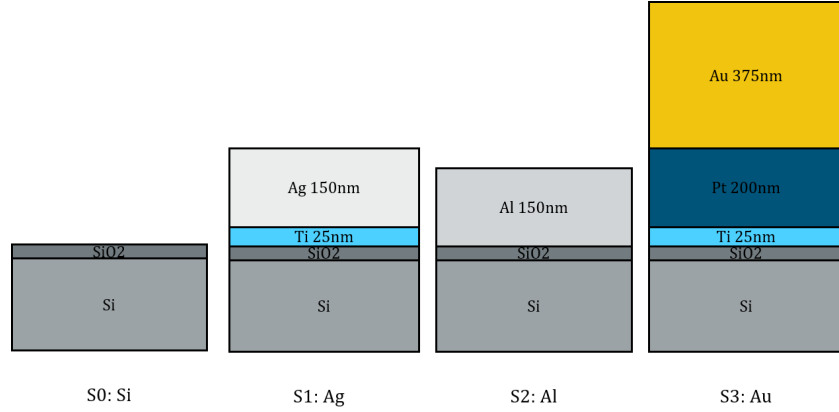


Figure 3.1: Schematic representation of the investigated substrate systems. The silicon reference substrate (S0) together with the three metallic mirror architectures (S1–S3) fabricated at OST served as the starting substrates for the subsequent ALD coating investigations.

For the silver and gold mirror architectures, a thin titanium adhesion layer was introduced between the oxide surface and the reflective metal. Such adhesion-promoting layers are commonly employed because noble metals generally exhibit poor adhesion to oxide surfaces. The titanium layer improves the mechanical stability of the coating stack and reduces the likelihood of delamination during handling, coating, and testing. For the gold substrate, an additional platinum layer was incorporated between titanium and gold according to the mirror fabrication route employed at Ostschweizer Fachhochschule (OST). Following mirror fabrication at OST, the wafers were additionally characterized using a KLA P-17 surface profiler to determine the residual stress introduced by the deposited mirror stacks through wafer curvature measurements. These measurements provide a baseline of the substrate stress state prior to the deposition of the protective coatings and may serve as a reference for future investigations of stress evolution following ALD deposition.

The selected mirror materials represent three of the most widely used metallic coatings for optical applications while exhibiting different optical and chemical characteristics. Their different susceptibilities to oxidation and chemical attack provide a representative platform for evaluating the effectiveness of protective oxide coatings under various degradation conditions.

3.1.2 Laser Dicing and Sample Preparation

After fabrication of the metallic mirror wafers, individual samples were produced by laser dicing at the Ultra-Precision Manufacturing Laboratory (UPM) of RhySearch. Laser cutting was selected because it enables accurate separation of samples while minimizing mechanical stresses that could otherwise damage the deposited metallic films. Several

sample dimensions were evaluated during the planning stage, including $10 \times 10 \text{ mm}^2$, $15 \times 15 \text{ mm}^2$, and $20 \times 20 \text{ mm}^2$. The final dimensions had to provide sufficient surface area for coating deposition and characterization while simultaneously maximizing the number of samples obtainable from a single wafer. A sample size of $15 \times 15 \text{ mm}^2$ was identified as the most suitable compromise. The wafers were diced from the non-polished backside by guiding the laser precisely along the predefined cutting lines at a moderate translation speed. Particles generated during cutting were largely removed by the vacuum extraction system inside the cutting chamber, while any remaining loose particles were removed after dicing by dry blowing with nitrogen. This geometry provided adequate space for optical, topographical, and chemical characterization while maintaining convenient handling during ALD processing and environmental testing. Furthermore, the selected dimensions enabled the extraction of a sufficiently large number of samples from each 4-inch wafer, supporting the extensive experimental matrix investigated in this work.

3.2 Characterization Procedures

The primary objective of the protective coatings developed in this work is to improve the chemical durability of metallic mirrors while preserving the optical performance of the underlying substrates. Consequently, the characterization was not limited to evaluating the deposited coatings, but also included the determination of the initial optical and mechanical properties of the uncoated substrates. These baseline measurements served as references for all subsequent comparisons and were further used to establish and optimize the characterization procedures employed throughout this work. Particular emphasis was placed on assessing how the deposited coatings influence the optical performance of the mirrors, with the aim of identifying coating architectures that provide sufficient chemical protection while maintaining the reflectance as close as possible to that of the uncoated substrates. The following sections describe the implemented characterization methods and their role within this evaluation.

3.2.1 Ellipsometry Modeling

Ellipsometry was initially applied to the characterization of the starting substrates in order to establish a suitable optical model for the determination of ALD coating thickness and refractive index. The silicon reference substrate S_0 was first analysed, allowing the thickness of the native silicon oxide layer to be determined as $12.96 \text{ \AA}$, using the Cauchy model, with maximum variation of $0.1 \text{ \AA}$. The simple dielectric structure of the silicon substrate enables a reliable optical model with a low Mean Square Error (MSE), providing a suitable reference for subsequent ALD depositions.

An attempt was also made to determine the optical properties of the metallic starting substrates. However, the modelling of these samples becomes considerably more complex due to the multilayer mirror architecture and the additional modifications introduced during mirror fabrication at OST. The increased number of fitting parameters

results in a highly sensitive model, where small changes in individual parameters can lead to large variations in the fit and the resulting MSE. Consequently, the thickness and optical constants of the metallic mirror stacks cannot be determined with the same accuracy as for the silicon reference substrate. Therefore, the thickness measured on the simultaneously coated silicon reference substrate was taken as representative for the corresponding deposition on the metallic mirror substrates.

For this reason, the silicon substrate was used throughout this work to calibrate the deposition thickness and refractive index of the ALD coatings. Comparison between the measured and target values allowed a rapid verification of successful deposition. In cases where significant deviations were observed, samples could be excluded from further, more time-intensive characterization techniques before additional experimental effort was invested. For the nanolaminate coatings, the measured refractive index further provided an initial indication of whether the deposited layer composition corresponded to the intended material combination and layer ratio before subsequent characterization was performed.

3.2.2 Reflectance Measurements

Reflectance measurements were performed using a PHOTON RT Spectrophotometer Model 0252 (EssentOptics), capable of measuring the spectral reflectance and transmittance of planar optical components over a selected wavelength range from 210 nm to 1700 nm. Prior to each measurement series, an automatic instrument calibration was performed to establish the light source intensity and normalize the optical response of the system for the selected measurement geometry. This calibration was repeated approximately every two hours throughout the experimental campaign to ensure measurement stability. The sample was positioned flat against the sample holder, allowing perpendicular illumination through the measurement slit. The final measurement parameters adopted throughout this work are summarized in Appendix Table A.1.

To establish a reproducible measurement protocol, different measurement settings were evaluated using the uncoated silicon reference substrate. The influence of the polarization state was first investigated in order to determine the most suitable acquisition mode. Since none of the investigated materials exhibit polarization-dependent optical properties, the use of purely s- or p-polarized light was excluded for the subsequent evaluation. Nevertheless, both polarization states were measured, allowing comparison between averaged polarized (p+s) and unpolarized measurements. The calibration procedure is presented for the silicon reference substrate in Figure 3.2a and 3.2b, while the corresponding measurements performed on the Ag, Al, and Au mirror substrates are reported in the Appendix.

Comparison of the different polarization modes gives the expected characteristic reflectance spectrum of silicon for all measurement methods. Since no significant differences were initially visible, a zoomed analysis was performed. This revealed unexpected

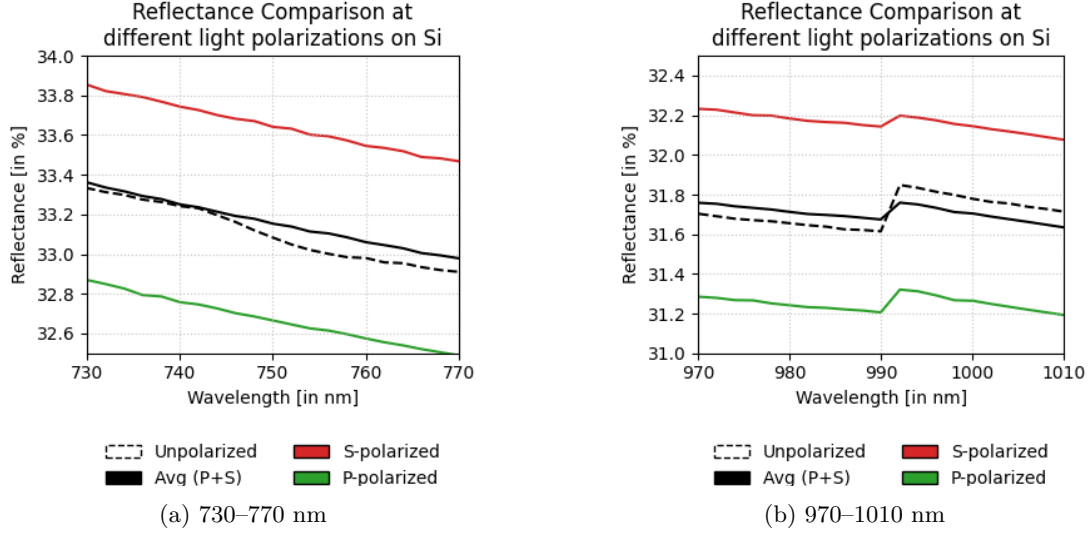


Figure 3.2: Reflectance measurements of uncoated silicon substrates for all polarization states at (a) 730–770 nm and (b) 970–1010 nm.

deviations for the unpolarized measurements within two wavelength ranges. To verify the reproducibility of these observations, the measurements were repeated, resulting in four data sets for each polarization mode. The repeated measurements confirmed the observed differences between averaged polarized (P+S) and unpolarized measurements. Consequently, averaged polarized (P+S) light was selected for all subsequent reflectance measurements.

The influence of the spectral sampling pitch on measurement precision and acquisition time was subsequently evaluated by comparing sampling pitches of 2 nm and 5 nm. Although no significant differences were observed over the complete wavelength range, a detailed analysis was performed at the three laser harmonics (355 nm, 532 nm and 1064 nm), enabling a direct comparison of the measurement repeatability at the most relevant wavelengths.

From the collected data, the extracted values were summarized in a table to facilitate comparison. The absolute difference between the two sampling pitches remained below 0.1 % at all three investigated wavelengths. The calculated errors indicate that the 5 nm sampling pitch exhibits slightly larger variability only in the UV range, while both sampling pitches provide comparable precision at 532 nm and 1064 nm. Since the UV range is of lower relevance for the present work and a 5 nm sampling pitch considerably reduces the measurement time, this setting was selected for all subsequent reflectance measurements.

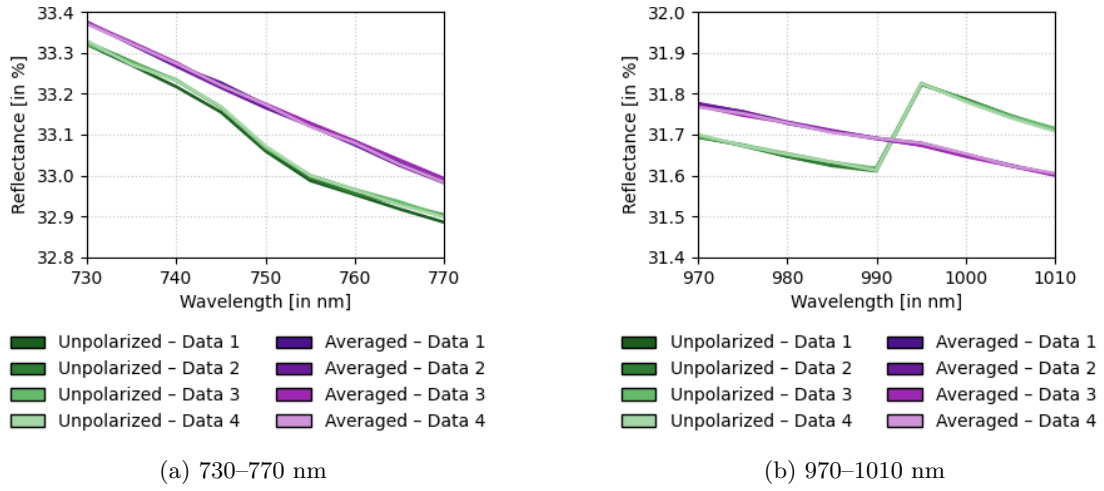


Figure 3.3: Comparison between unpolarized and averaged polarized reflectance measurements for uncoated silicon substrates based on four repeated measurements to ensure reproducibility at (a) 730–770 nm and (b) 970–1010 nm.

In addition to the short-term repeatability, the long-term stability of the selected measurement settings was evaluated by repeating the measurements on different samples originating from the same wafer at one-week intervals. The complete analysis is reported in the Appendix, while the extracted deviations are summarized in Table 3.1.

Table 3.1: Extracted reflectance deviations for both spectral sampling pitches at the investigated wavelengths for short- and long-term time intervals.

Wavelength λ (in nm)	355	532	1064
Error (in %) — 2 nm sampling pitch	0.006	0.005	0.007
Error (in %) — 5 nm sampling pitch	0.033	0.006	0.005
Error (in %) — 5 nm sampling pitch (long-term)	0.041	0.006	0.008
$\Delta\mu = \mu_{5\text{ nm}} - \mu_{2\text{ nm}}$	0.079	0.030	-0.091

The extracted error values were primarily used for the reflectance–power analysis, enabling the influence of the substrate pre-clean and oxygen plasma treatments to be evaluated while accounting for the measurement uncertainty. This provides greater confidence when comparing measurements performed on different substrates and over the extended time period of the experimental campaign.

3.2.3 Atomic Force Microscopy

Surface morphology and roughness measurements were performed using a CoreAFM system (Nanosurf) operated in dynamic force mode. AFM was employed throughout this work as a complementary characterization technique to the reflectance measurements, providing localized, high-resolution information on the surface morphology of the investigated substrates and coatings.

All measurements were acquired using identical imaging parameters of 256 points per line and an acquisition speed of 0.78 s per line. To determine an appropriate scan size for the different substrate systems, scans of $0.5 \times 0.5 \mu\text{m}^2$, $2.5 \times 2.5 \mu\text{m}^2$, and $5 \times 5 \mu\text{m}^2$ were initially performed on all substrates. Increasing the scan area resulted in higher measured roughness values, as larger surface areas capture a greater fraction of the underlying morphology. Based on this evaluation, scan sizes of $0.5 \times 0.5 \mu\text{m}^2$ for the silicon reference substrate and $5 \times 5 \mu\text{m}^2$ for the metallic mirror substrates were selected for the initial substrate characterization. Since different scan areas were used for the silicon and metallic substrates, the resulting S_q values cannot be compared directly between these substrate types, as the measured roughness depends on the investigated scan area.

The acquired topographic maps were evaluated both qualitatively and quantitatively. Surface morphology was assessed through visual inspection of the AFM images, while the root-mean-square roughness (S_q) was extracted as the principal quantitative parameter for comparison between the investigated surfaces.

During the subsequent coating investigations, AFM primarily served as an additional characterization method to complement the reflectance measurements. Whereas reflectance measurements provided the principal evaluation of coating performance over the complete substrate surface, AFM was employed to investigate localized morphological changes introduced by the deposited nanometre-thick ALD coatings. For these measurements, a scan size of $0.5 \times 0.5 \mu\text{m}^2$ was preferentially used, as it allowed fine structural modifications, changes in grain morphology, and the occurrence of local defects to be resolved with higher detail. This additional information was subsequently correlated with the optical characterization and the protective performance of the investigated coating systems.

3.3 Pre-Cleaning and Plasma Surface Preparation

To ensure reproducible surface conditions prior to ALD deposition, all substrates were subjected to an Ar/H₂ plasma pre-cleaning step. The objective of this treatment was to remove surface contaminants while promoting surface activation before film growth. The process was applied to all four substrate types and systematically varied to identify parameter regimes suitable for a universal pretreatment prior to coating deposition.

3.3.1 Process Parameters

The choice of an Ar/H₂ plasma was motivated by the inert nature of argon and the need to avoid further oxidation of sensitive metallic surfaces, particularly silver mirrors. In contrast to oxygen-based plasma cleaning processes, the selected gas mixture enables surface cleaning while minimizing the risk of additional oxide formation.

No conventional wet-solvent cleaning was performed prior to the plasma treatment. The metallic mirror substrates were freshly deposited by PVD at OST and subsequently stored under cleanroom conditions before processing. The silicon reference substrates were likewise handled and stored under cleanroom conditions.

The plasma process was performed at an electrode temperature of 150 °C and a chamber pressure of 20 mTorr, with a wall temperature of 110 °C. Before plasma exposure, the samples were preheated for 15 min and the plasma gas flow was stabilized for 30 s. A total Ar/H₂ flow of 100 sccm was used. The process was systematically varied in terms of plasma power, hydrogen concentration, and treatment duration. Plasma power ranged from 50 to 400 W, while the H₂ fraction was varied between 2%, 4%, and 20%. The standard plasma exposure time was 60 s, which was reduced to 30 s for the most aggressive condition of 400 W and 20% H₂. A post-plasma purge of 60 s was applied after each treatment.

3.3.2 Characterization

The effects of the plasma treatments were evaluated using optical reflectance measurements and AFM. Reflectance spectra were acquired over the full spectral range from the UV to the IR, and additionally evaluated at a fixed wavelength of 532 nm as a reference point for direct comparison between process conditions. For this evaluation, the measurement uncertainties determined during the spectrophotometer calibration were propagated throughout the analysis and are considered in the results section.

AFM measurements complemented the optical characterization by assessing plasma-induced changes in surface morphology and roughness. Quantitative comparison was based on the root-mean-square roughness (S_q), together with qualitative inspection of the surface topography. Since plasma treatments directly modify the substrate surface, scan sizes were selected according to the characteristic morphology of each material, using $0.5 \times 0.5 \mu\text{m}^2$ for silicon substrates and $5 \times 5 \mu\text{m}^2$ for the metallic mirror substrates.

3.4 Mitigation of Oxygen Plasma Effects

As previously mentioned, ALD can be executed in two deposition modes: TALD and PEALD. In this work, PEALD is of particular interest for two reasons. First, certain materials, such as SiO₂, require plasma to achieve the desired film properties. Second, PEALD enables deposition at lower temperatures, which is advantageous when working

with temperature-sensitive substrates that may not withstand the higher temperatures typically associated with thermal ALD processes.

However, the use of PEALD also introduces a fundamental challenge, as oxide deposition processes rely on oxygen plasma. The reactive oxygen species generated during the plasma step can interact with the substrate surface, particularly in the case of oxidation-sensitive metallic mirrors such as silver. This interaction can lead to undesired surface modifications and degradation of optical performance. Consequently, a mitigation strategy must be developed to ensure compatibility between oxygen-plasma-based PEALD processes and sensitive optical substrates.

3.4.1 O₂ Plasma Sensitivity Study

In order to evaluate oxygen-induced substrate modifications, all substrates were subjected to an O₂ plasma process at 150 °C for 30 s while varying the plasma power (50 W, 150 W, and 400 W). This study was conducted to establish a baseline understanding of the substrate response to oxygen plasma exposure prior to film deposition.

Following plasma exposure, the substrates were evaluated using optical reflectance measurements over the full spectral range from the UV to the IR, as well as by AFM analysis to assess modifications in surface morphology and roughness.

3.4.2 Engineering of Protective Interlayers

Following the oxygen plasma sensitivity study, a mitigation strategy based on protective interlayers was investigated. The objective was to introduce a thin barrier layer between the substrate and subsequent PEALD coatings, thereby limiting direct interaction between reactive oxygen species and the substrate surface while maintaining the optical performance of the metallic mirrors as close as possible to the untreated condition.

The development of the interlayer system was carried out in three stages. First, the thickness of a thermally deposited Al₂O₃ interlayer was optimized. Second, different interlayer materials were compared using the selected thickness. Finally, the resulting coating systems were evaluated through optical, morphological, and mechanical characterization.

3.4.2.1 Interlayer Thickness Optimization

The first step of the mitigation strategy consisted of introducing thin Al₂O₃ interlayers deposited by thermal ALD at 150 °C. This approach provides conformal film growth while avoiding additional plasma exposure during interlayer deposition. Furthermore, Al₂O₃ is known to exhibit reliable and uniform growth behavior even at very low film thicknesses, making it suitable for the investigated application.

To determine a suitable interlayer thickness, a balance between optical losses introduced by the interlayer itself and the degree of protection against oxygen plasma exposure had to be established. Interlayer thicknesses of 2 nm, 4 nm, and 8 nm were investigated. Each interlayer configuration was subsequently exposed to oxygen plasma under conditions identical to those used in the sensitivity study. Optical reflectance measurements and AFM characterization were then performed to evaluate the influence of interlayer thickness on optical and surface properties.

3.4.2.2 Interlayer Material Comparison

Following the thickness optimization study, a comparison of different interlayer materials was performed. While thermally deposited Al_2O_3 provides a plasma-free encapsulation route, alternative materials may offer different optical and mechanical characteristics. For this reason, AlN deposited by PEALD was selected as an alternative interlayer material. In contrast to oxide deposition processes, AlN growth relies on an NH_3 plasma environment and therefore does not expose the substrate to oxygen during interlayer formation. This makes AlN a promising alternative for comparison with Al_2O_3 . Both interlayer systems were deposited using the selected thickness and subsequently exposed to identical O_2 plasma conditions. Their performance was evaluated through optical reflectance measurements and AFM characterization.

3.4.2.3 Mechanical Evaluation of Interlayer Materials

To further evaluate the suitability of the investigated interlayer systems for complete coating stacks, additional measurements were performed after deposition of a representative 100 nm Al_2O_3 layer on top of each interlayer configuration (4 nm Al_2O_3 and 4 nm AlN) for all substrate types.

Adhesion was first assessed qualitatively using a tape test. This consisted of covering approximately half of the coated substrate with 3M Scotch Tape and applying uniform pressure to ensure proper contact with the surface. The tape was then removed with a rapid pull while the substrate was held in place, allowing a preliminary assessment of coating adhesion.

For a more detailed comparison, scratch testing was performed on all substrates using an Anton Paar NST3 equipped with a Diamond Wedge Blade indenter (tip radius $r = 20 \mu\text{m}$) mounted on the High Load Cantilever HL-359. Scratches were generated over a distance of 1 mm while increasing the applied normal load from 3 mN to 350 mN. Failure events were identified through changes in penetration depth and verified by optical inspection of the resulting scratch tracks. The resulting critical loads were used to compare the adhesion performance of the investigated interlayer systems.

3.5 Single-Layer ALD Coatings

The first stage of the coating development focused on the investigation of single-layer protective coatings deposited by PEALD. Prior to coating deposition, a preliminary chemical etching screen was performed on the uncoated substrates to identify the substrate-etchant combinations that produce measurable surface modifications, thereby reducing the number of subsequent coating depositions and characterizations. Two etchants were selected based on their use in the literature for similar protective coating studies and their known interaction with the investigated mirror materials. HCl and potassium hydroxide (KOH) solutions were prepared from 12 M HCl (37 wt%) and 11.7 M KOH (45 wt%) stock solutions, respectively. Two concentrations were prepared for each etchant:

- HCl: 1.40 M (5 wt%) and 2.87 M (10 wt%)
- KOH: 0.93 M (5 wt%) and 1.94 M (10 wt%)

This preliminary screen established that only Ag and Al substrates exhibited measurable corrosion from HCl exposure, while Si and Al substrates were susceptible to KOH. The gold substrate showed no measurable response to either etchant and was therefore excluded from the single-layer coating investigation. It was however re-introduced in the nanolaminate deposition study, where the focus shifts to a broader coating stack evaluation.

3.5.1 Single-Layer Deposition Parameters

Based on optical industry requirements, identified through a review of relevant literature and past project experience, only a limited number of oxide materials were considered as candidates for single-layer protective coatings. Five oxide materials (Al_2O_3 , TiO_2 , SiO_2 , HfO_2 , Ta_2O_5) exhibiting different optical and functional properties were selected based on characteristics such as refractive index, chemical stability, and mechanical integrity. These differences motivated their selection as suitable candidates for the comparative screening.

All coatings were deposited by PEALD using the Oxford Instruments FlexAL[®] II system at a deposition temperature of 150 °C. This temperature was selected based on a review of prior ALD depositions carried out at RhySearch, which identified the 150–200 °C window as compatible with the GPC and refractive index requirements of all five oxide materials under plasma-enhanced conditions. An additional motivation for plasma-enhanced mode at 150 °C was the planned installation of a second ALD system at RhySearch, which operates primarily within this process window, making 150 °C the natural choice for future process transferability.

Prior to coating the mirror substrates, a dedicated deposition run was performed on a silicon reference substrate to determine the GPC of each material under the selected

process conditions. The resulting thickness distribution across the substrate was evaluated to assess deposition uniformity, and the extracted GPC was subsequently applied to achieve a target thickness of 50 nm on all mirror substrates. This thickness was chosen as a standard starting point for the protection screening, providing sufficient barrier coverage while keeping optical interference effects manageable.

Table 3.2: Experimental matrix for single-layer coatings, combining material system, total deposition thickness, and process temperature. The highlighted column (50 nm, 150°C) indicates the starting condition used for screening.

Single layer materials	10 nm, 150°C	50 nm, 150°C	100 nm, 150°C
Al ₂ O ₃			
TiO ₂			
SiO ₂			
HfO ₂			
Ta ₂ O ₅			

3.5.2 Chemical Resistance Testing

To perform the chemical resistance etching experiments, coated substrates were immersed in 25 ml of the selected etchant solutions for durations of 10 minutes and 30 minutes for single-layers and 30 minutes and 90 minutes for nanolaminate coatings. Both HCl and KOH were tested at concentrations of 5 wt% and 10 wt%. Care was taken during sample handling to ensure reproducible immersion conditions: each substrate was handled exclusively at the same corner during insertion and removal and placed vertically within the solution, so that any delaminated material would fall to the bottom and not influence further etching of the sample surface.

Reflectance measurements were acquired before and after immersion for each substrate-etchant combination at set times, allowing a direct comparison of spectral changes as a function of exposure duration and etchant concentration. In addition to spectral reflectance, visual inspection of the substrate surface was performed at each time point to assess macroscopic surface modifications such as discolouration, delamination, or visible etching attack.

3.6 Nanolaminate ALD Coatings

Building on the nanolaminate concept introduced in Section 2.2.4, the investigated parameters were organized in an initial experimental matrix combining the material system, individual layer thickness ratio, and total nanolaminate thickness. Since the final material pairings were selected only after evaluation of the single-layer coatings, the two

constituent materials were initially denoted as Oxide A and Oxide B. Four layer thickness ratios were considered for each pair: 1 nm A : 1 nm B, 5 nm A : 5 nm B, 4 nm A : 1 nm B, and 1 nm A : 4 nm B. Figure 3.4 schematically illustrates the investigated coating architectures considered throughout the nanolaminate optimization. A total thickness of 50 nm was selected as the initial screening condition to remain consistent with the starting thickness used for the single-layer coatings, as summarized in Table 3.3. Following this screening, the most suitable nanolaminate architecture was further investigated at total thicknesses of 25, 50, and 100 nm in order to evaluate the influence of coating thickness.

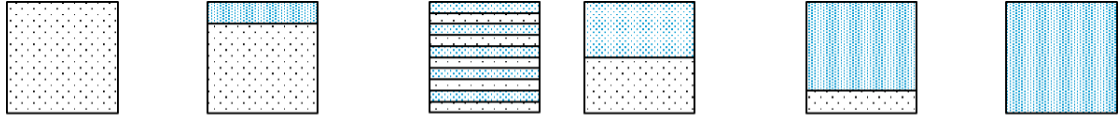


Figure 3.4: Schematic representation of the investigated single-layer and nanolaminate coating architectures. From left to right, the structures represent the Oxide A single layer, the Oxide A-rich 4:1 nanolaminate, the 1 nm A:1 nm B nanolaminate, the 5 nm A:5 nm B nanolaminate, the Oxide B-rich 1:4 nanolaminate, and the Oxide B single layer. The schematic illustrates both the variation in relative material contribution and, for the symmetric 1:1 compositions, the influence of the individual layer thickness. Within each supercycle, Oxide A is deposited first and Oxide B second. The drawings are not to scale.

Table 3.3: Initial experimental matrix for nanolaminate coatings, combining the individual layer thickness ratio, total deposition thickness, and process temperature. The highlighted column (50 nm, 150°C) indicates the starting condition used for screening.

Nanolaminate architecture	10 nm, 150°C	50 nm, 150°C	100 nm, 150°C	500 nm, 150°C
1 nm A / 1 nm B				
4 nm A / 1 nm B				
1 nm A / 4 nm B				
5 nm A / 5 nm B				

3.6.1 Material Pairing Strategy

The material combinations were selected based on the outcome of the single-layer protection screening described in the previous section. The individual oxides were compared according to their ability to retain reflectance after exposure to the corrosive media and according to the surface modifications observed during the etching experiments. The

materials showing the most promising performance according to the reflectance measurements and visual inspection were carried forward for combination into nanolaminate stacks. Based on this evaluation, two oxide pairing systems were selected for nanolaminate fabrication.

3.6.2 Layer Thickness Ratios and Deposition Parameters

For each selected material system, four individual layer thickness ratios were investigated: 1 nm A : 1 nm B, 5 nm A : 5 nm B, 4 nm A : 1 nm B, and 1 nm A : 4 nm B. Oxide A denotes the material deposited first within each supercycle, directly onto the underlying surface or preceding supercycle, while Oxide B denotes the material deposited subsequently. One complete sequence consisting of the selected thickness of Oxide A followed by the selected thickness of Oxide B was defined as one supercycle. The supercycle was repeated until the target total nanolaminate thickness was reached. The deposition parameters of the two constituent oxides were adopted from the corresponding single-layer processes. The growth per supercycle was determined from the growth per cycle of the two individual oxides and their respective layer thickness contributions. The specific deposition times applied for each material and nanolaminate architecture are reported in the Appendix.

Following deposition, the nanolaminate coatings were characterized by ellipsometry to determine coating thickness and refractive index, by AFM to evaluate surface morphology and roughness, and by spectrophotometry to assess reflectance. The coatings were subsequently subjected to chemical resistance testing using 10 wt% HCl. At this stage, the nanolaminates were deposited on all four substrate systems because the objective was to evaluate the protection provided by the complete coating architectures rather than to perform an additional substrate-etchant screening. This enabled direct comparison between the two material combinations, between the investigated layer thickness ratios within each combination, and across the different substrate systems.

3.7 Electrochemical Characterization

Electrochemical characterization was performed by the OST as a complementary evaluation of the coating systems previously compared through reflectance measurements and visual inspection. The measurements were not employed as the primary screening method, but as an additional means of assessing whether the selected single-layer and nanolaminate coatings also exhibited favourable electrochemical stability and barrier performance.

The coated silver samples were stored under vacuum prior to measurement and mounted onto a copper plate. Since the deposited oxide coatings are electrically insulating, electrical contact between the metallic substrate and the copper plate was established using silver paint. For both electrochemical techniques, the exposed sample area was 0.85 cm^2 ,

the coated sample served as the WE, and a platinum sheet was used as the counter electrode (CE). The remaining components of the electrochemical setup were adapted according to the respective measurement, as illustrated schematically in Figure 3.5a and 3.5b.

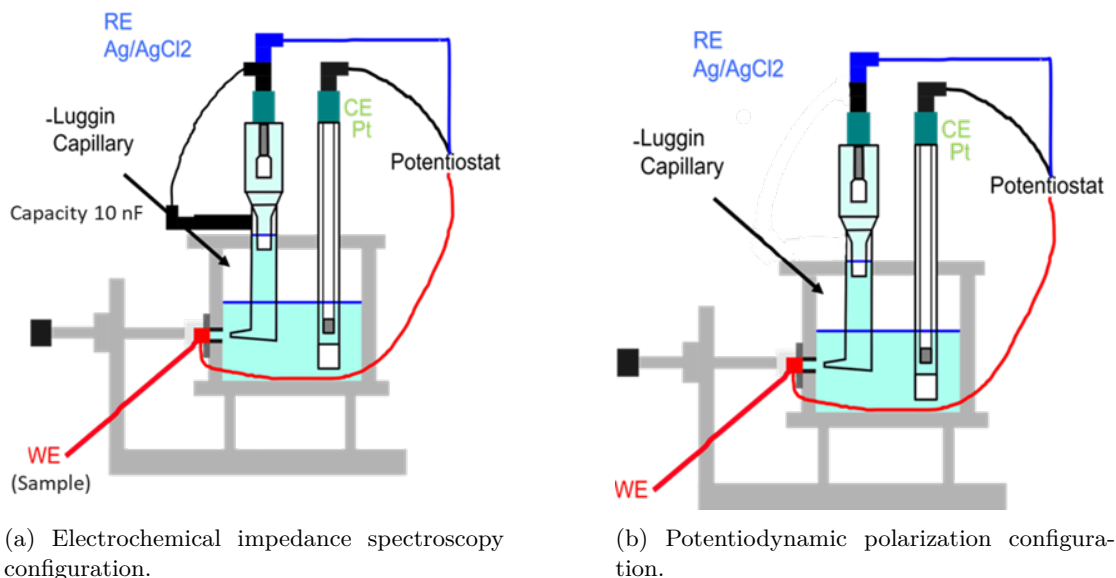


Figure 3.5: Electrochemical configurations employed at OST. For both techniques, the coated sample served as the working electrode (WE) and a platinum sheet as the counter electrode (CE). The reference-electrode (RE) configuration and electrolyte were adapted to the respective measurement.

3.7.1 Electrochemical Impedance Spectroscopy

EIS was performed in 250 mL of 0.1 M citric acid at pH 5.2. This comparatively mild electrolyte was selected to evaluate the intrinsic barrier response of the coatings without intentionally inducing rapid chemical degradation. The Ag/AgCl RE was coupled to a platinum wire connected in series with a 100 nF capacitor.

Before each impedance measurement, the open-circuit potential (OCP) was monitored for 20 min to allow stabilization of the electrochemical system. The impedance response was subsequently measured over a frequency range from 10^5 Hz to 2 mHz using a sinusoidal perturbation amplitude of 10 mV. The OCP was compared before and after the measurement to verify that no substantial change or degradation of the coating had occurred during EIS. The results were evaluated using the Bode representation of impedance magnitude and phase angle as a function of frequency.

3.7.2 Potentiodynamic Polarization Measurements

Potentiodynamic polarization measurements were performed in 250 mL of 0.1 M HCl to evaluate the coating response under a more aggressive chloride-containing environment. For this configuration, the Ag/AgCl RE was positioned in a Luggin capillary close to the exposed sample surface.

The OCP was monitored for 5 min before the potential sweep was initiated. For the comparison of the different single-layer materials and nanolaminate layer ratios, the polarization curves were recorded using a scan rate of 0.1 mV s^{-1} . For the separate comparison of the different total nanolaminate thicknesses, a scan rate of 1 mV s^{-1} was used. Since the scan rate influences the measured polarization response, results obtained using the two different scan rates were not directly compared quantitatively. Comparisons were therefore restricted to samples measured under identical scan-rate conditions. The resulting current density–potential curves were evaluated qualitatively, where lower current densities indicate reduced electrochemical activity and improved protective behaviour.

4 Results

4.1 Baseline Characterization of Metallic Substrates

Prior to the deposition of protective coatings, the untreated substrates were characterized by reflectance measurements and AFM to establish a baseline for the subsequent evaluation of the coating systems. Throughout this chapter, the reflectance spectra of the untreated substrates are represented by a dashed black line. To facilitate comparison between the different substrate materials, a consistent colour scheme is adopted: purple for silicon, blue for silver, green for aluminium, and orange for gold. Variations introduced by subsequent processing steps are indicated by lighter or darker shades of the respective substrate colour.

The preliminary chemical etching study further confirmed the different chemical stabilities of the investigated metallic mirrors. Gold remained inert under all investigated etching conditions, whereas silver and aluminium exhibited measurable degradation following exposure to HCl. In contrast, silicon and aluminium were susceptible to KOH. The observed degradation manifested through changes in visual appearance, delamination of the metallic coating from the silicon substrate, and modifications of the reflectance spectra. These findings established the substrate–etchant combinations employed for the subsequent evaluation of the protective coatings.

4.2 Influence of Ar/H₂ Plasma Pretreatment

As described in Section 3.3, an inert Ar/H₂ plasma pretreatment was introduced prior to all subsequent ALD processes in order to clean and activate the substrate surface while minimizing surface modifications. The influence of the pretreatment was first evaluated independently by combining optical reflectance measurements with AFM characterization. Since only minor changes are observed over the full reflectance spectra (reported in the Appendix), the discussion focuses on the reflectance at 532 nm as a representative comparison parameter. The untreated sample (0 W) serves as the reference, while the plasma power was varied between 50 W and 400 W under the conditions described in Section 3.3. The corresponding measurement uncertainties, determined during spectrophotometer calibration (Table 3.1), are included to assess the significance of the observed reflectance changes. Representative AFM topography images together with the corresponding root-mean-square roughness (S_q) complement the optical analysis by providing localized information on surface morphology. The S_q values are reported as a supplementary quantitative parameter, since isolated surface features can disproportionately influence the calculated average roughness.

Starting with the silicon substrate (Figure 4.1), only slight changes are observed over the investigated plasma power range. The highest reflectance is obtained at 50 W, although the values measured at 0 W, 50 W and 100 W overlap within their respective uncertain-

ties. A decrease becomes visible at 200 W and remains at a similar level for 300 W and 400 W when considering the measurement uncertainties. Overall, the reflectance variation remains below 0.1 %, consistent with the expected limited influence of the plasma treatment on the dielectric silicon surface, which was received directly from the manufacturer and handled exclusively under cleanroom conditions. Likewise, the AFM images reveal almost no modification of the surface morphology. The only noticeable difference is the slightly more granular appearance of the 50 W and 100 W samples, reflected by the increased S_q value of the 50 W measurement. Since this behaviour is not reproduced for higher plasma powers, it is most likely associated with local sample variability rather than a systematic plasma-induced effect. Overall, the plasma pretreatment does not induce measurable morphological restructuring of the silicon surface.

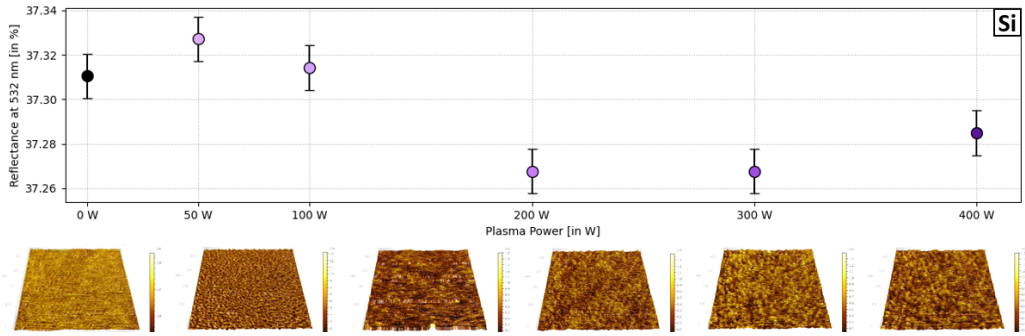


Figure 4.1: Influence of the Ar/H₂ plasma pretreatment on the silicon substrate. The reflectance at 532 nm is shown as a function of plasma power together with the corresponding measurement uncertainty. Representative AFM topography images and the associated S_q values are shown for each plasma condition.

For the silver substrate (Figure 4.2), a more pronounced dependence of the reflectance on plasma power is observed. Only the 50 W treatment results in an increase in reflectance compared to the untreated sample, whereas higher plasma powers lead to a decrease, although no monotonic trend is apparent. The AFM images are consistent with these optical observations. Compared to the untreated surface, the 50 W plasma treatment produces a noticeably smoother morphology, while increasing plasma power leads to the formation of larger surface islands and progressively modifies the surface structure. These morphological changes are accompanied by reflectance variations approaching an order of magnitude larger than those observed for the silicon substrate.

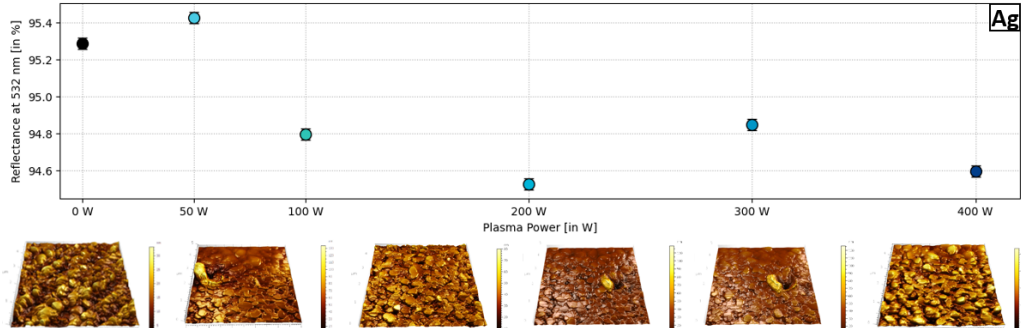


Figure 4.2: Influence of the Ar/H₂ plasma pretreatment on the silver substrate. The reflectance at 532 nm is shown as a function of plasma power together with representative AFM topography images illustrating the corresponding morphological evolution.

For the aluminium substrate (Figure 4.3), the largest scatter in reflectance is observed, with a maximum variation of almost 1.5 % between the untreated substrate and the 200 W plasma treatment, making it difficult to identify a clear correlation with plasma power. In contrast, the AFM images provide additional insight into the observed optical variations. The initially rough surface becomes noticeably smoother following the 50 W treatment, while the large crystalline structures visible on the untreated substrate become considerably less pronounced after exposure to 50 W and subsequently to 100 W. At higher plasma powers, new surface structures emerge. Although the S_q values vary considerably between the investigated conditions, the qualitative evolution of the surface morphology indicates that the extent of the structural modifications does not increase monotonically with plasma power.

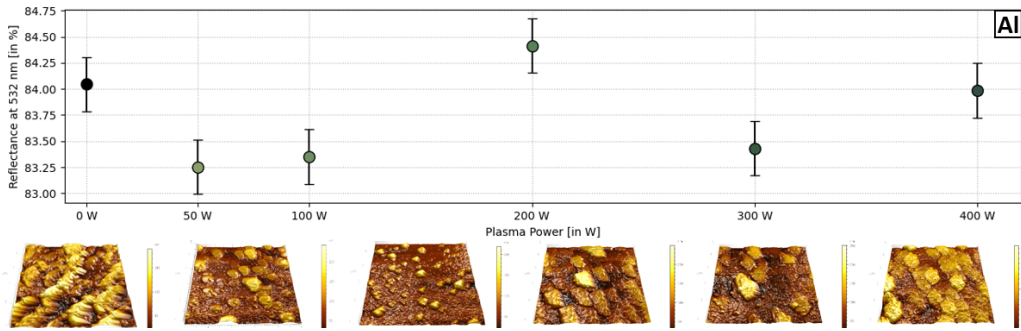


Figure 4.3: Influence of the Ar/H₂ plasma pretreatment on the aluminium substrate. The reflectance at 532 nm is shown together with representative AFM topography images for the investigated plasma powers.

Finally, the gold substrate (Figure 4.4) exhibits the smallest modifications among the investigated metallic mirrors, consistent with the high chemical stability of gold. The 50 W treatment results in the highest reflectance, whereas the remaining plasma powers produce values close to the untreated reference. Apart from the 50 W condition, the

corresponding error bars overlap substantially, indicating only minor differences between the investigated plasma powers. Similarly, the AFM images reveal only limited changes in surface morphology, as the fine surface features remain largely preserved after plasma exposure. Isolated structures appear for individual conditions (for example at 200 W), but these are more likely associated with local defects or isolated surface features than with systematic plasma-induced modifications. Overall, the surface morphology remains essentially unchanged over the investigated plasma power range.

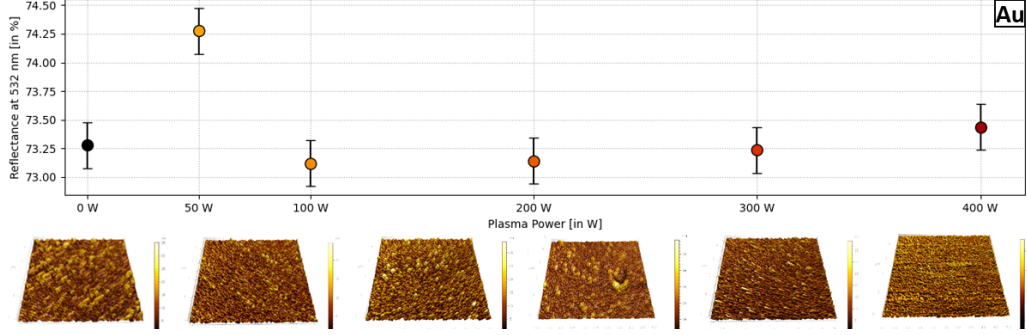


Figure 4.4: Influence of the Ar/H₂ plasma pretreatment on the gold substrate. The reflectance at 532 nm is shown together with representative AFM topography images for the investigated plasma powers.

Based on the combined optical and topographical evaluation, the pretreatment parameters for all subsequent ALD processes were selected. Since the objective of the Ar/H₂ plasma pretreatment is to activate and clean the substrate surface while minimizing substrate modification, both the preservation of optical performance and the retention of the original surface morphology were considered. Among the investigated conditions, 50 W, 2 % H₂, and 60 s consistently provided the highest reflectance for three of the four substrates while limiting the morphological changes observed by AFM. These parameters were therefore adopted as the standard pretreatment throughout the remainder of this work and are only modified for the dedicated O₂ plasma experiments discussed in the following section.

4.3 Oxygen Plasma-Induced Damage on Metallic Substrates

Unlike the inert Ar/H₂ plasma pretreatment discussed previously, oxygen plasma is directly involved in several plasma-enhanced ALD processes and therefore represents an unavoidable process step for oxide materials such as SiO₂. Consequently, the influence of oxygen plasma on the substrate itself was first investigated, with particular emphasis on the expected oxygen sensitivity of the silver substrate. This study establishes the reference condition against which all subsequent interlayer mitigation strategies are evaluated.

The substrates were exposed to an O_2 plasma for 30 s at $150^\circ C$ while varying the plasma power between 50 W, 100 W and 150 W. The resulting influence on the optical properties of the substrates is summarized by the reflectance spectra shown in Figure 4.5. Figure 4.5 highlights the markedly different response of the investigated substrates to

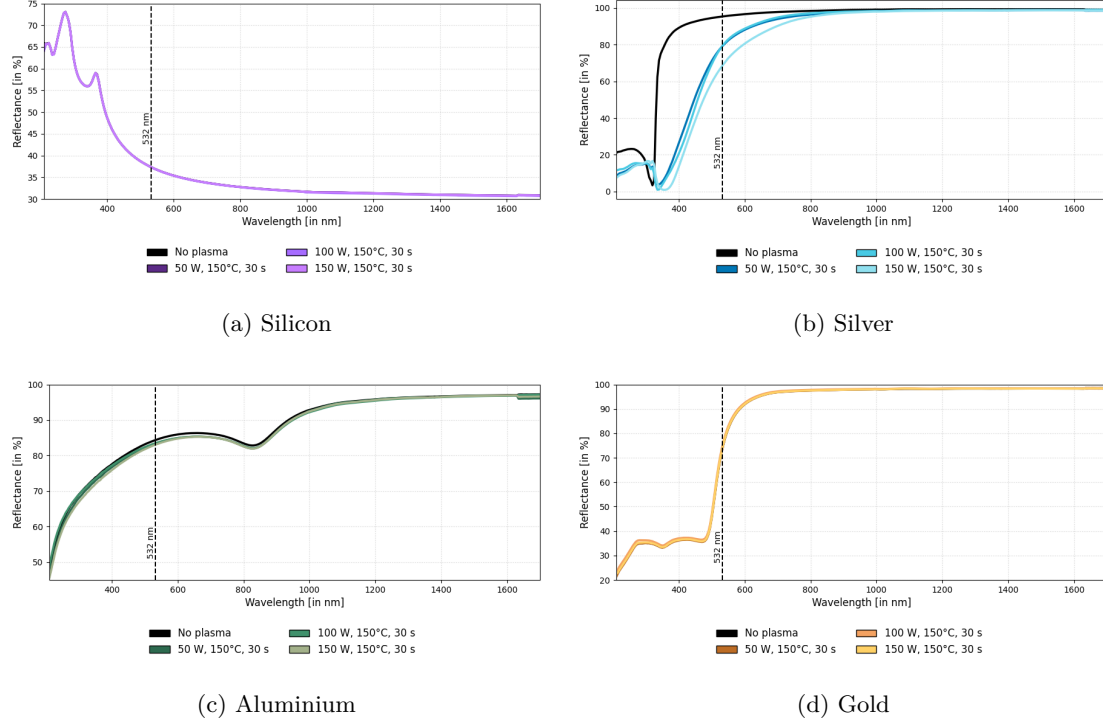


Figure 4.5: Reflectance spectra of the investigated substrates before and after O_2 plasma exposure at different plasma powers.

oxygen plasma. Silicon and gold remain largely unaffected over the investigated spectral range, whereas aluminium exhibits only moderate variations, primarily within the UV region. In contrast, silver undergoes a pronounced reduction in reflectance extending from the UV into the visible wavelength range, due to the silver oxidation. This behaviour is further supported by the visible browning of the silver surface after plasma exposure, indicating a substantially higher oxygen sensitivity than that observed for the remaining substrates.

Since the oxygen-induced degradation is most pronounced for silver, the subsequent analysis focuses primarily on this substrate. Silicon is retained as a reference substrate for film growth, whereas the effectiveness of the proposed mitigation strategy is assessed through the improvements achieved on silver. To correlate the optical degradation with changes in surface morphology, the reflectance at 532 nm is evaluated together with representative AFM topography images, analogous to the previous Ar/H_2 plasma study.

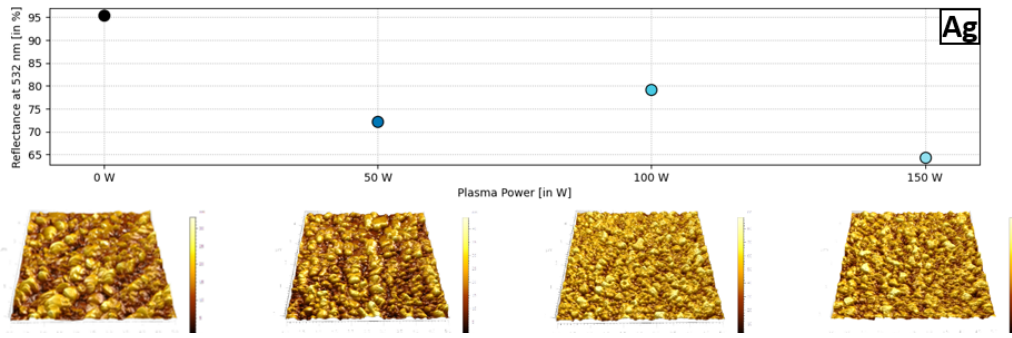


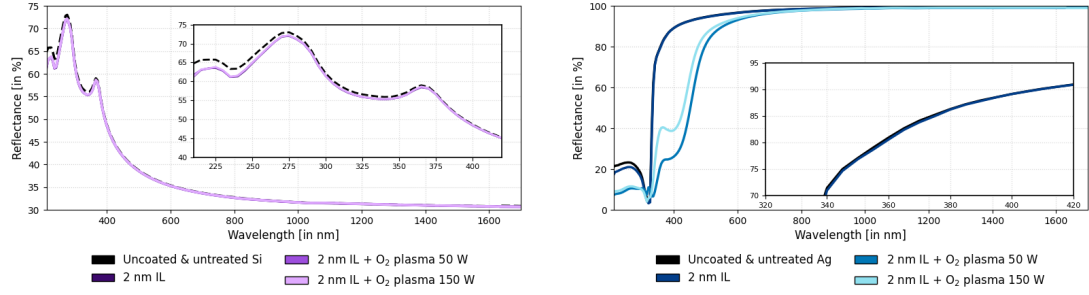
Figure 4.6: Reflectance at 532 nm as a function of oxygen plasma power for the silver substrate together with representative AFM topography images after plasma exposure. The pronounced reduction in reflectance is accompanied by substantial modifications of the surface morphology.

Already the lowest investigated plasma power of 50 W results in a pronounced decrease in reflectance, exceeding 25 % at 532 nm compared to the untreated substrate (Figure 4.6). Increasing the plasma power to 100 W and 150 W introduces only comparatively small additional changes, indicating that the majority of the oxygen-induced degradation occurs during the initial plasma exposure. The optical degradation is accompanied by substantial modifications of the surface morphology. Compared with the untreated sample, the AFM images reveal the formation of pronounced spike-like surface features following plasma exposure. Although these structures become slightly more pronounced with increasing plasma power, the differences between the three investigated plasma conditions remain small compared with the transition from the untreated substrate to the plasma-treated samples. This behaviour is likewise reflected by the S_q values, which increase markedly after plasma exposure before remaining at a similar level for higher plasma powers. Collectively, these observations indicate the high oxygen sensitivity of silver and show that even the mildest investigated oxygen plasma conditions lead to substantial optical and morphological degradation.

4.3.1 Development of a Protective Al_2O_3 Interlayer

Having established the oxygen sensitivity of the silver substrate, a mitigation strategy based on a thin protective interlayer was investigated. Thermal ALD was deliberately selected for the interlayer deposition in order to introduce the protective barrier without exposing the substrate to additional plasma during its growth. Since Al_2O_3 is one of the most established ALD materials and exhibits highly reproducible growth behaviour with only minor process variations, it was selected to evaluate the feasibility of the interlayer concept. At this stage, the objective was not to optimize either the interlayer thickness or the material itself, but rather to determine whether a thin dielectric barrier can reduce the oxygen-induced degradation observed on silver.

A 2 nm Al_2O_3 interlayer was therefore deposited on both silicon and silver prior to oxygen plasma exposure. Silicon was retained as the reference substrate to monitor the optical influence of the additional dielectric layer while allowing accurate determination of the deposited film thickness. Silver served as the primary substrate for evaluating the protective performance against oxygen plasma. Following deposition, the effectiveness of the interlayer concept was assessed by optical reflectance measurements.

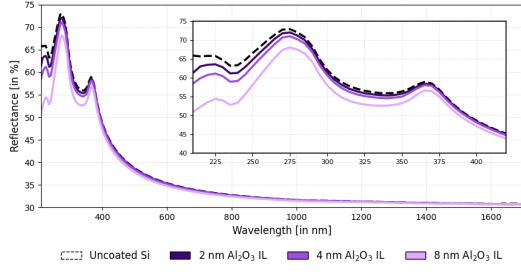


(a) Reflectance spectra of the silicon substrate before and after deposition of a 2 nm Al_2O_3 interlayer followed by O_2 plasma exposure.

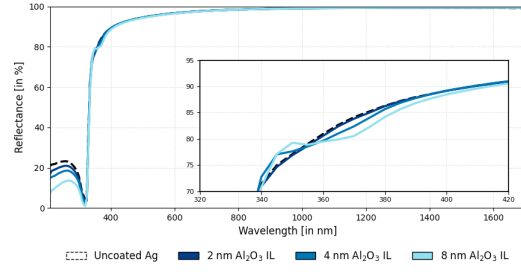
(b) Reflectance spectra of the silver substrate before and after deposition of a 2 nm Al_2O_3 interlayer followed by O_2 plasma exposure.

Figure 4.7: Reflectance spectra of silicon and silver after introducing a 2 nm thermally grown Al_2O_3 interlayer prior to oxygen plasma exposure. Silicon serves as a reference substrate to evaluate the optical influence of the interlayer itself, whereas silver illustrates its ability to mitigate oxygen-induced reflectance losses.

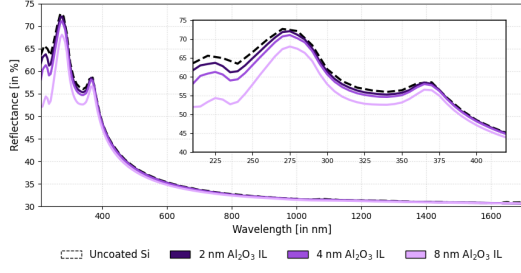
Figure 4.7 compares the reflectance spectra of silicon and silver after introducing the 2 nm Al_2O_3 interlayer. As expected, the additional dielectric layer introduces only a minor reduction in reflectance before plasma exposure. Following oxygen plasma treatment, the silicon substrate exhibits no significant differences between the investigated plasma powers, indicating that the interlayer has only a limited influence on the optical response of the dielectric substrate. In contrast, the silver substrate shows a clear improvement compared with the untreated reference presented in the previous section. The introduction of the Al_2O_3 interlayer noticeably reduces the oxygen-induced reflectance loss, particularly within the UV region where the degradation was previously most pronounced. Although the initial optical performance is not fully recovered, the spectra demonstrate that even a 2 nm interlayer provides measurable protection against direct oxygen plasma exposure. These results motivate a systematic investigation of different interlayer thicknesses to identify the optimum compromise between minimizing optical losses introduced by the interlayer and maximizing protection against oxygen-induced degradation.



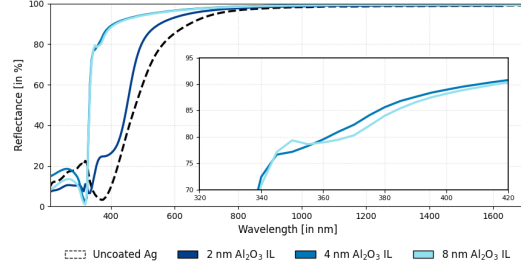
(a) 2 nm, 4 nm and 8 nm Al_2O_3 interlayers on silicon substrate without O_2 plasma exposure.



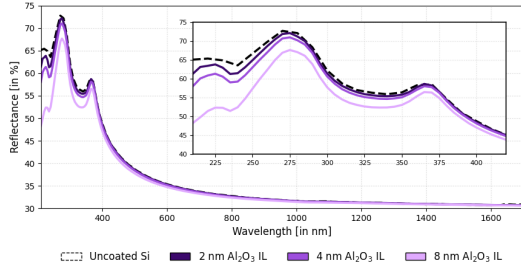
(b) 2 nm, 4 nm and 8 nm Al_2O_3 interlayers on silver substrate without O_2 plasma exposure.



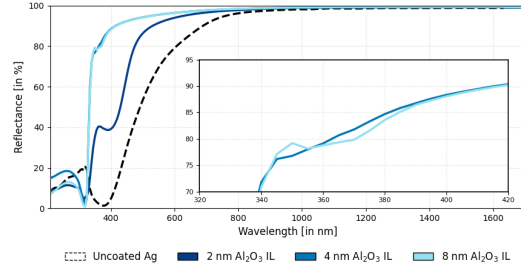
(c) 2 nm, 4 nm and 8 nm Al_2O_3 interlayers on silicon substrate after 50 W O_2 plasma exposure.



(d) 2 nm, 4 nm and 8 nm Al_2O_3 interlayers on silver substrate after 50 W O_2 plasma exposure.



(e) 2 nm, 4 nm and 8 nm Al_2O_3 interlayers on silicon substrate after 150 W O_2 plasma exposure.



(f) 2 nm, 4 nm and 8 nm Al_2O_3 interlayers on silver substrate after 150 W O_2 plasma exposure.

Figure 4.8: Comparison of thermally deposited Al_2O_3 interlayer thicknesses on silicon (left column) and silver (right column). Each subplot compares 2 nm, 4 nm and 8 nm Al_2O_3 interlayers with the corresponding uncoated substrate under identical plasma conditions: without O_2 plasma exposure (a, b), after 50 W O_2 plasma exposure (c, d), and after 150 W O_2 plasma exposure (e, f). The figure illustrates the influence of interlayer thickness on the optical response and allows identification of the optimum compromise between minimizing interlayer-induced optical losses and maximizing protection against oxygen-plasma-induced reflectance degradation.

The effectiveness of the selected interlayer thicknesses is further confirmed after exposure

to a 150 W oxygen plasma, where the 2 nm interlayer still exhibits noticeable reflectance losses, whereas the spectra obtained for the 4 nm and 8 nm interlayers remain almost identical to those measured after the 50 W plasma exposure. However, the increased oscillation amplitude observed for the 8 nm interlayer demonstrates that this thickness introduces additional optical modulation without providing a measurable improvement in protection compared to the 4 nm interlayer.

Overall, this evaluation demonstrates that a 4 nm Al_2O_3 interlayer provides the most appropriate compromise between preserving the optical reflectance and protecting the silver substrate against oxygen plasma. Consequently, this thickness was selected for all subsequent interlayer investigations.

4.3.2 Comparison of Interlayer Materials

After selecting an interlayer thickness of 4 nm, the next step was to determine the most appropriate interlayer material. The thermally deposited 4 nm Al_2O_3 interlayer, which had been used throughout the thickness optimization, was compared with a 4 nm AlN interlayer deposited by PEALD. Although AlN exhibits optical properties comparable to those of Al_2O_3 , it differs fundamentally in its deposition process. In contrast to PEALD of Al_2O_3 , where the plasma is based on oxygen, AlN deposition employs an ammonia (NH_3) plasma. This difference in the process recipe allows the use of PEALD instead of TALD without causing oxidation of the substrate.

As an initial comparison, this study was again limited to the silicon and silver substrates in order to accurately determine the deposited film thickness by ellipsometry on silicon while evaluating the protective effect of the interlayers on the silver substrate. Both interlayer materials were first evaluated by optical reflectance measurements to determine whether significant optical differences would arise.

On the silicon substrate, the presence of the interlayer introduces the expected reduction in reflectance, which is slightly more pronounced for AlN due to its higher refractive index. In contrast, almost no difference is observed on the silver substrate. This is particularly evident in the enlarged view, where the spectra of the Al_2O_3 and AlN interlayers almost completely overlap, differing only by minor local deviations. Since reflectance alone did not provide sufficient evidence to distinguish between the two candidate interlayer materials, an additional comparison was made by considering the surface morphology.

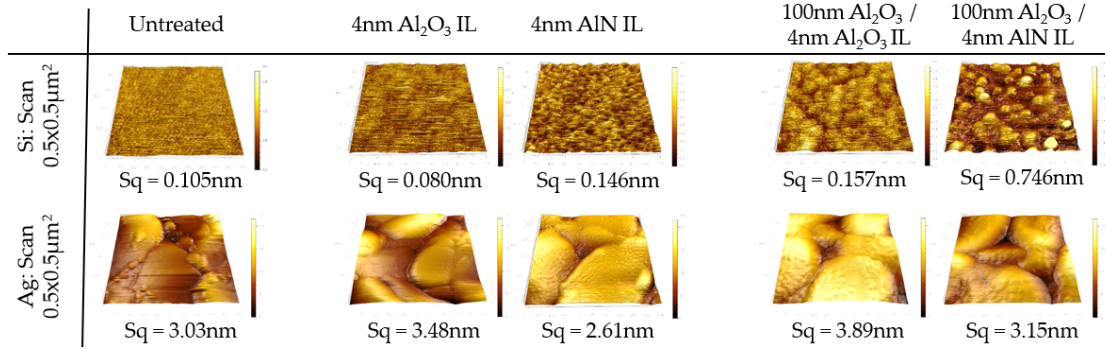


Figure 4.9: AFM topography comparison of the investigated interlayer systems. The untreated substrates are compared with substrates coated with a 4 nm Al₂O₃ interlayer, a 4 nm AlN interlayer, and the complete coating stacks consisting of 100 nm Al₂O₃ deposited on top of each interlayer. The comparison allows evaluation of the influence of the interlayer material on the surface morphology before mechanical adhesion testing.

The AFM measurements reveal that both interlayer materials modify the surface morphology compared to the untreated substrate. A further comparison was performed after deposition of a 100 nm Al₂O₃ single layer on top of the two different interlayers. Following deposition, the surface roughness increases for both coating systems. Nevertheless, the coating stack employing the Al₂O₃ interlayer consistently exhibits a smoother and more homogeneous surface than the corresponding AlN system. Although the Sq values do not fully support this observation, the qualitative comparison of the topography images provides a more meaningful assessment, since isolated features may strongly influence the numerical roughness values. While these observations favor the Al₂O₃ interlayer, they are not sufficiently conclusive to select the material based on morphology alone.

Since the 100 nm Al₂O₃ single layer had been deposited on all substrate types using both interlayer materials, two coating stacks were available for adhesion evaluation:

- 100 nm Al₂O₃/4 nm Al₂O₃ Interlayer (IL)/substrate
- 100 nm Al₂O₃/4 nm AlN Interlayer (IL)/substrate.

The interlayer materials were therefore further evaluated based on their adhesion performance, as this represents an important factor for subsequent coating depositions and the overall stability of the multilayer stack. A Scotch tape test was first performed as a rapid qualitative screening method. Adhesive tape was firmly applied to approximately half of each coated sample before being removed with a rapid pull. No visible coating damage or delamination was observed for either interlayer material on any substrate. Consequently, the tape test confirmed that all investigated coating systems exhibit satisfactory adhesion, but it did not allow further differentiation between the two interlayer candidates.

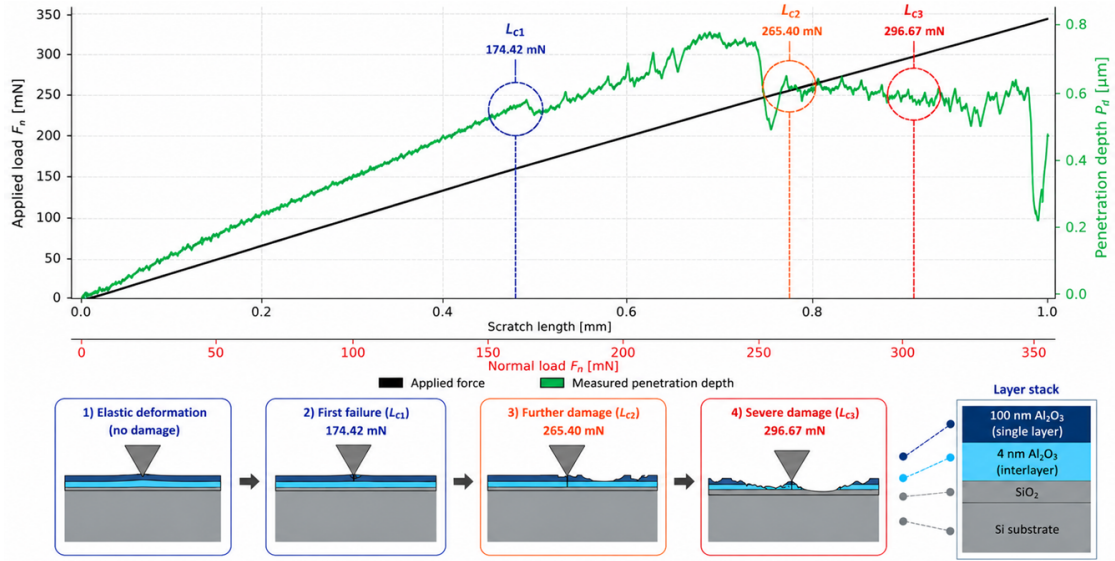


Figure 4.10: Representative nanoscratch measurement for the coating stack employing a 4 nm Al_2O_3 interlayer. The applied load increases continuously from 3 mN to 350 mN over a scratch length of 1 mm. The identified critical loads are highlighted and correspond to distinct failure events occurring during scratching.

Since the Scotch tape test did not reveal measurable differences, nanoscratch testing was employed as a quantitative adhesion evaluation. During the measurement, a diamond wedge indenter was drawn across the sample surface while the applied normal load increased continuously from 3 mN to 350 mN over a scratch length of 1 mm. Failure events were identified from changes in penetration depth together with optical inspection of the scratch track. Figure 4.10 shows a representative measurement together with the identified critical loads, which are highlighted by circles. The first critical load, L_{c1} , was selected as the most relevant comparison parameter, since it corresponds to the onset of failure at the coating–substrate interface, whereas the subsequent critical loads are less suitable for evaluating interlayer adhesion because they are increasingly influenced by failure mechanisms occurring within the coating or the bulk substrate.

Table 4.1 summarizes the critical loads obtained for all investigated substrates. For every substrate, the coating stack containing the Al_2O_3 interlayer exhibits a higher first critical load than the corresponding AlN system. The improvement is particularly pronounced for the aluminium and gold substrates, while silicon and silver likewise show consistently higher L_{c1} values when employing the Al_2O_3 interlayer. In contrast, the subsequent critical loads L_{c2} and L_{c3} do not exhibit a similarly consistent trend between the two interlayer materials across all substrates. Since these later failure events are increasingly influenced by cohesive coating failure and substrate deformation, they were considered supplementary information rather than primary indicators of interlayer adhesion.

Table 4.1: Critical loads obtained from nanoscratch measurements for coating stacks employing either a 4 nm Al_2O_3 or a 4 nm AlN interlayer. The first critical load L_{c1} is used as the main comparison parameter for evaluating adhesion at the coating–substrate interface.

Critical loads measured by application of force through nanoscratch test								
Substrate	Si		Ag		Al		Au	
Interlayer material	Al_2O_3	AlN	Al_2O_3	AlN	Al_2O_3	AlN	Al_2O_3	AlN
L_{c1} (mN)	174.42	156.57	14.36	8.23	26.04	15.87	46.42	27.08
L_{c2} (mN)	265.40	240.25	142.50	95.08	231.04	228.72	91.35	167.68
L_{c3} (mN)	296.67	268.24	292.41	295.56	269.21	252.53	237.45	182.29

Overall, the combined optical and topographical investigations demonstrate that optical reflectance alone is insufficient for selecting the optimum interlayer material. While AFM already indicates a slight advantage for Al_2O_3 , the quantitative nanoscratch measurements clearly identify the thermally deposited 4 nm Al_2O_3 interlayer as the mechanically superior solution.

4.4 Single-Layer Protective Coatings

Following the optimization of the pre-deposition procedure, including the Ar/H_2 plasma pretreatment and the selection of the interlayer thickness and material, the research moved towards protective single-layer coatings deposited by PEALD.

Unless stated otherwise, all coating systems discussed in the following sections were deposited following the optimized process route consisting of substrate cleaning with a 50 W, 2% H_2 Ar/H_2 plasma pretreatment for 60 s and deposition of a 4 nm thermally deposited Al_2O_3 interlayer. Since these process steps remained identical for all investigated coatings, they are not explicitly mentioned for every deposition. Any deviations from this standard process flow are highlighted.

As discussed in both the methods and results sections of the preliminary etching study, only substrates exhibiting measurable degradation were considered for single-layer coating evaluation. Consequently, HCl resistance was investigated only on silver and aluminium substrates, whereas KOH resistance was evaluated on silicon and aluminium. Therefore, only these three substrates were coated and subsequently etched for each single-layer material. This process was carried out for 30 and 90 min exposure times, after which two complementary methods were used to evaluate the results.

Reflectance measurements before and after chemical exposure provided a first screen-

ing evaluation of the protective performance of the investigated single-layer coatings. Since many coating systems exhibited no changes or only minor spectral variations, the complete reflectance spectra are provided in the Appendix. The main results are summarized using the grading system shown in Table 4.2. Hereby, the grading system consists of scores ranging from zero to three, with a score of three corresponding to no measurable degradation, whereas a score of zero indicates complete coating failure, with the substrate itself eventually being etched. One example is the aluminium mirror, where complete removal of the alumina layer leaves only the underlying silicon substrate exposed.

Table 4.2: Reflectance-based grading of 50 nm single-layer coatings after chemical exposure. A score of 3 indicates no measurable degradation, while 0 indicates complete coating failure or substrate exposure.

	50 nm Al_2O_3		50 nm SiO_2		50 nm TiO_2		50 nm HfO_2		50 nm Ta_2O_5	
	HCl	KOH	HCl	KOH	HCl	KOH	HCl	KOH	HCl	KOH
Si	–	0	–	2	–	3	–	3	–	3
Ag	1	–	3	–	3	–	3	–	2	–
Al	1	0	3	3	2	2	2	2	2	1
Total	2	0	6	5	5	5	5	5	4	4

This allowed a first reduction of suitable coating materials, whereby SiO_2 , TiO_2 , and HfO_2 exhibited the most favorable overall behaviour and were therefore highlighted in green in the summary table. Due to the broad outcome of the reflectance evaluation, a further method was combined to filter the candidates even further. An additional visual inspection was therefore performed after etching, allowing effective protection against the aggressive chemical environments to be evaluated by observing the amount of delamination occurring on the deposited single layers. Hereby, this may range from smaller isolated spots to larger flakes. In order to make this evaluation more tangible, the top right corner of the samples was never taken into consideration during the evaluation, as this was the location where the sample was handled with tweezers and the resulting mechanical force in combination with the chemical environments would represent an additional external influence.

Table 4.3: Visual inspection of 50 nm single-layer coatings after chemical exposure. Green cells indicate coating systems that showed no visible degradation or delamination after etching.

	50 nm Al_2O_3		50 nm SiO_2		50 nm TiO_2		50 nm HfO_2		50 nm Ta_2O_5	
	HCl	KOH	HCl	KOH	HCl	KOH	HCl	KOH	HCl	KOH
Si										
Ag										
Al										

The visual inspection confirmed the trends observed from the reflectance analysis while additionally revealing localized degradation mechanisms that were not always apparent from optical measurements alone. For acidic environments, Al_2O_3 and TiO_2 exhibited the most favorable behaviour. Under alkaline conditions, SiO_2 , TiO_2 , and Ta_2O_5 showed the most favorable visual appearance after KOH exposure.

Since the final material selection aimed to balance both optical performance and chemical stability, combining both evaluations allowed the material selection for the subsequent nanolaminate study to be reduced to SiO_2 , TiO_2 , and HfO_2 . In addition, the testing environments for the subsequent nanolaminate evaluation were reduced to 10 wt% HCl, due to the too mild effects observed at lower concentrations, and because the most relevant results for future company projects originated from the evaluation of silver and aluminium substrates.

4.5 Nanolaminate Protective Coatings

Following the single-layer evaluation, the materials selected for nanolaminate fabrication were SiO_2 , TiO_2 and HfO_2 . Since TiO_2 and SiO_2 showed the most favorable overall behaviour during both the reflectance and visual evaluations, they were selected as the primary nanolaminate candidate, while HfO_2 and SiO_2 were selected as the second nanolaminate combination.

Unless stated otherwise, all coating systems discussed in the following sections were deposited following the optimized process route consisting of substrate cleaning with a 50 W, 2% H_2 Ar/ H_2 plasma pretreatment for 60 s and deposition of a 4 nm thermally deposited Al_2O_3 interlayer. Since these process steps remained identical for all investigated coatings, they are not explicitly mentioned for every deposition. Any deviations from this standard process flow are highlighted.

The investigated nanolaminate architectures consisted of alternating oxide layers repeated until a total thickness of 50 nm was reached. Four different layer thickness ra-

tios were investigated for both material systems: 1 nm:1 nm, 5 nm:5 nm, 4 nm:1 nm and 1 nm:4 nm. By controlling the material contribution within a pair, these ratios require a different number of supercycles to reach the final coating thickness.

A first evaluation of the nanolaminate deposition was performed directly after coating using ellipsometry. In addition to determining the deposited thickness, the measured refractive index was compared with a theoretical effective refractive index estimated from the relative contributions of the two constituent oxides. The theoretical single-layer refractive indices used for this comparison were $n_{\text{SiO}_2} = 1.46$, $n_{\text{TiO}_2} = 2.40$, and $n_{\text{HfO}_2} = 2.02$. at 632 nm.

For a layered medium with a periodicity much smaller than the wavelength of the incident light, the optical response can be described using an effective-medium approximation. Rather than averaging the refractive indices directly, the dielectric functions of the constituent materials are combined. The resulting layered medium is uniaxially birefringent, with the ordinary and extraordinary refractive indices given by

$$n_o^2 = f_A n_A^2 + f_B n_B^2 \quad (4.1)$$

$$\frac{1}{n_e^2} = \frac{f_A}{n_A^2} + \frac{f_B}{n_B^2} \quad (4.2)$$

where f_A and f_B represent the relative thickness contributions of the two oxides within one supercycle, and n_A and n_B their respective refractive indices. For the symmetric 1 nm:1 nm and 5 nm:5 nm architectures, both oxides contribute equally, whereas for the asymmetric 4 nm:1 nm and 1 nm:4 nm architectures, the contributions are 80% and 20%.

Table 4.4 compares the calculated ordinary and extraordinary refractive indices with the refractive index and coating thickness obtained from the isotropic ellipsometric fit. Since an isotropic optical model was employed, the fitted refractive index is expected to lie between the calculated n_e and n_o values. This is the case for six of the eight investigated nanolaminate architectures. The two exceptions correspond to the 5 nm:5 nm architectures, which also exhibit the largest deviations from the targeted coating thickness. This behaviour is likely related to the correlation between refractive index and thickness in the ellipsometric fit rather than to a physical refractive-index shift. The comparison constrains the average optical composition of the coatings but does not confirm the presence, continuity, or internal structure of the individual nanolaminate layers.

Table 4.4: Comparison between the coating thickness and refractive index obtained from ellipsometric fitting and the calculated ordinary (n_o) and extraordinary (n_e) refractive indices of the investigated nanolaminate architectures. The calculated values were obtained using $n_{\text{SiO}_2} = 1.46$, $n_{\text{TiO}_2} = 2.40$, and $n_{\text{HfO}_2} = 2.02$ at $\lambda = 632$ nm. The ellipsometric spectra were fitted using an Isotropic Cauchy model.

	Ratio	d [nm]	Δd [nm]	n_e	n_o	n_{measured}
TiO₂/SiO₂	1 nm:1 nm	53.13	+3.13	1.764	1.986	1.960
	5 nm:5 nm	46.46	-3.54	1.764	1.986	2.020
	4 nm:1 nm	51.69	+1.69	2.073	2.244	2.259
	1 nm:4 nm	51.63	+1.63	1.562	1.690	1.641
HfO₂/SiO₂	1 nm:1 nm	50.04	+0.04	1.673	1.762	1.734
	5 nm:5 nm	42.32	-7.68	1.673	1.762	1.773
	4 nm:1 nm	48.64	-1.36	1.857	1.921	1.929
	1 nm:4 nm	54.13	+4.13	1.535	1.588	1.564

Like for the single-layer coatings, reflectance measurements and visual inspection were selected as the primary evaluation methods. However, compared to the single-layer coatings, the nanolaminates resulted in significantly smaller reflectance changes, making the evaluation considerably more challenging. In several cases, no measurable degradation could be identified after 30 minutes exposure and only minor spectral variations were observed even after 90 minutes. Consequently, the evaluation was performed at multiple time points, allowing for a more detailed evaluation of degradation progression. Comparison between the two nanolaminate systems was first performed to identify the more suitable material combination overall,, followed then by comparing the individual layer thickness ratios within the same material combination.

A particularly important observation concerns the aluminium substrates. During the single-layer evaluation, severe bubbling and localized coating detachment occurred rapidly after HCl exposure. The nanolaminate architectures substantially delayed the onset of this behaviour and reduced the spatial extent of the affected regions. Depending on the investigated architecture, bubbling was either completely suppressed during the investigated immersion period or reduced both in density and size. This observation strongly suggests that the nanolaminate architecture improves the barrier properties of the coating system beyond what can be achieved by the corresponding single-layer coatings alone.

Table 4.5: Reflectance-based grading of 50 nm $\text{TiO}_2/\text{SiO}_2$ nanolaminates with different ratios of $\text{TiO}_2:\text{SiO}_2$ layer thickness on different substrates after 30 min exposure to 10 wt% HCl, evaluated with a grading system from 0 for drastic changes to 3 for no/minimum changes.

	1 nm:1 nm	5 nm:5 nm	4 nm:1 nm	1 nm:4 nm
Si	3	3	3	3
Ag	3	3	3	3
Al	2	2	3	2
Au	3	3	3	3
Total	11	11	12	11

Table 4.6: Reflectance-based grading of 50 nm $\text{TiO}_2/\text{SiO}_2$ nanolaminates with different ratios of $\text{TiO}_2:\text{SiO}_2$ layer thickness on different substrates after 90 min exposure to 10 wt% HCl, evaluated with a grading system from 0 for drastic changes to 3 for no/minimum changes.

	1 nm:1 nm	5 nm:5 nm	4 nm:1 nm	1 nm:4 nm
Si	3	3	3	3
Ag	3	3	2	3
Al	2	1	3	2
Au	3	3	3	3
Total	11	10	11	11

The reflectance evaluation already reveals clear differences between the two investigated nanolaminate systems. For the $\text{TiO}_2/\text{SiO}_2$ nanolaminates, almost no measurable degradation is observed after 30 min exposure to 10 wt% HCl. Independent of the selected layer ratio, all substrate-coating combinations are associated with the maximum score of three, while only minor reductions were observed on the aluminium substrate for three of the four investigated architectures. Even after extending the immersion time to 90 min, the overall behaviour remains largely unchanged, as most issues are still connected to the aluminum substrate, and only one additional substrate-coating combination exhibited measurable degradation compared to the 30 min evaluation. This indicates that the coating system provides stable protection over prolonged exposure times.

Table 4.7: Reflectance-based grading of 50 nm HfO₂/SiO₂ nanolaminates with different ratios of HfO₂:SiO₂ layer thickness on different substrates after 30 min exposure to 10 wt% HCl, evaluated with a grading system from 0 for drastic changes to 3 for no/minimum changes.

	1 nm:1 nm	5 nm:5 nm	4 nm:1 nm	1 nm:4 nm
Si	3	3	3	3
Ag	3	2	1	2
Al	0	3	3	3
Au	3	1	3	3
Total	9	9	10	11

Table 4.8: Reflectance-based grading of 50 nm HfO₂/SiO₂ nanolaminates with different ratios of HfO₂:SiO₂ layer thickness on different substrates after 90 min exposure to 10 wt% HCl, evaluated with a grading system from 0 for drastic changes to 3 for no/minimum changes.

	1 nm:1 nm	5 nm:5 nm	4 nm:1 nm	1 nm:4 nm
Si	3	3	3	3
Ag	3	2	1	0
Al	0	2	0	3
Au	1	0	0	3
Total	7	7	4	9

In contrast, the HfO₂/SiO₂ nanolaminates exhibit significant degradation already after 30 min exposure. Reflectance losses become visible on all metallic substrates and are particularly pronounced for aluminium, where scores of zero or one are assigned already after shorter times, indicating severe coating degradation or complete coating failure. The prolonged immersion time of 90 min further confirms this trend and highlights the inferior protective behaviour of this material combination. In several cases the measured reflectance approaches that of the uncoated metallic substrate, indicating that the coating was fully removed during the etching process.

Although the TiO₂/SiO₂ nanolaminate clearly outperforms the HfO₂/SiO₂ system, Although the reflectance evaluation already identifies TiO₂/SiO₂ as the superior material combination, it does not allow a definitive selection of the optimal layer ratio within this system., as reflectance is always averaged over a wider surface. The total scores differ only slightly between the investigated architectures and several ratios achieve nearly identical results even after prolonged exposure. Since the differences remain sufficiently

small, an additional evaluation criterion becomes necessary, allowing to get further information to conclude the study more specifically. The visual inspection provided a substantially stronger differentiation between the investigated architectures than the reflectance measurements, as the whole surface can be taken into consideration using a grading system based on the spatial extent and severity of visible degradation. Localized delamination, flaking and substrate bubbling become visible even in cases where the reflectance spectra remain largely unchanged, providing a more complete and detailed full-picture.

Table 4.9: Visual grading of 50 nm TiO₂/SiO₂ nanolaminates after 30 min exposure to 10 wt% HCl. The scores account for visible degradation such as delamination, localized failure and substrate bubbling.

	1 nm:1 nm	5 nm:5 nm	4 nm:1 nm	1 nm:4 nm
Si	3	3	3	3
Ag	2	3	2	3
Al	2	2	3	2
Au	2	2	1	3
Total	9	10	9	11

Table 4.10: Visual grading of 50 nm TiO₂/SiO₂ nanolaminates after 90 min exposure to 10 wt% HCl.

	1 nm:1 nm	5 nm:5 nm	4 nm:1 nm	1 nm:4 nm
Si	3	3	3	3
Ag	2	2	1	3
Al	1	1	2	1
Au	0	1	0	3
Total	7	7	6	10

A first comparison for the material combinations confirms the evaluations made based on the reflectance. Overall scores are better when comparing 30 minutes of the two material systems, as well as after 90 minutes etching time. Going into further analysis, the visual evaluation confirms the excellent behaviour of the 1 nm:4 nm architecture of the TiO₂/SiO₂ nanolaminate system, as the score assigned after 30 minutes is repeated also after 90 minute etching, keeping a stable grading over the whole evaluated immersion period. The 5 nm:5 nm architecture showed comparable behaviour during short exposure times but exhibited increased degradation after prolonged immersion, particularly on aluminium substrates. The 1 nm:1 nm and 4 nm:1 nm architectures likewise showed good

overall protection performance but experienced major delamination after 90 minutes of etching, as the coating on the gold mirror was fully removed.

Table 4.11: Visual grading of 50 nm HfO₂/SiO₂ nanolaminates after 30 min exposure to 10 wt% HCl.

	1 nm:1 nm	5 nm:5 nm	4 nm:1 nm	1 nm:4 nm
Si	3	3	3	3
Ag	3	2	3	2
Al	2	2	2	3
Au	1	1	2	2
Total	9	8	10	10

Table 4.12: Visual grading of 50 nm HfO₂/SiO₂ nanolaminates after 90 min exposure to 10 wt% HCl.

	1 nm:1 nm	5 nm:5 nm	4 nm:1 nm	1 nm:4 nm
Si	3	3	3	3
Ag	2	1	2	2
Al	1	1	0	2
Au	1	0	0	1
Total	7	5	5	8

The overall evaluation confirms also here less effective protection from the HfO₂/SiO₂ nanolaminates, as overall more severe degradation occurred on multiple samples and it becomes more difficult to identify good substrate-coating combinations. For the HfO₂/SiO₂ nanolaminates, a similar trend can be observed when going into further analysis, with the 1 nm:4 nm architecture again producing the highest overall scores after the full etching period, while being evaluated similar to other ratio systems after shorter times. Severe delamination is also here found on the gold mirror, but also on the alumina, with major delamination occurring.

Overall, both evaluation methods consistently identify the TiO₂/SiO₂ nanolaminates as the superior material combination. Furthermore, increasing the relative SiO₂ fraction within the stack generally improves the protection performance, with the 1 nm TiO₂ : 4 nm SiO₂ architecture exhibiting the best overall behaviour. Consequently, the TiO₂/SiO₂ nanolaminate employing the 1 nm:4 nm layer ratio was selected as the most promising coating architecture and was therefore carried forward for the subsequent optimization of total nanolaminate thickness.

4.6 Electrochemical Characterization

Following the optical and visual evaluation of the investigated coating systems, electrochemical characterization was performed as an add-on validation of the selected nanolaminate architectures. Unlike the previous characterization techniques, which primarily evaluate optical performance and surface delamination, electrochemical measurements provide direct information on the barrier properties of the coatings against electrolyte penetration and corrosion. Since these measurements were intended to complement the previous results rather than to establish the coating selection, only the most promising material combination ($\text{TiO}_2/\text{SiO}_2$) was investigated. The electrochemical evaluation first compares the influence of the nanolaminate layer ratio at a constant total thickness of 50 nm, followed by the influence of the total coating thickness for the selected 1 nm TiO_2 : 4 nm SiO_2 architecture.

4.6.1 Influence of the Nanolaminate Layer Ratio

The potentiodynamic polarization curves of the investigated single-layer and nanolaminate coatings are presented in Figure 4.11. The measurements were carried out in 0.1 M HCl in order to maintain a chemically comparable acidic and chloride-containing environment to the HCl corrosion experiments previously used for coating evaluation, while a lower HCl concentration was selected for the electrochemical measurements in order to avoid damage to the electrochemical setup and reference electrode.

Among the investigated nanolaminate architectures, 1 nm TiO_2 : 4 nm SiO_2 (Mix 4) exhibits the lowest current densities over the measured potential range and therefore the most protective behaviour among the investigated coating systems. 1 nm TiO_2 : 1 nm SiO_2 (Mix 2) likewise exhibits lower current densities than Mix 1 and Mix 3, although its current increases more strongly with applied potential. 5 nm TiO_2 : 5 nm SiO_2 (Mix 1) and 4 nm TiO_2 : 1 nm SiO_2 (Mix 3) show comparable behaviour to the TiO_2 single layer, with a sharp increase in current density occurring relatively close to the OCP.

The SiO_2 single-layer coating exhibits a continuous increase in current density with increasing applied potential, indicating active dissolution under the investigated HCl conditions. The TiO_2 coating similarly loses its protective behaviour at relatively low polarization potentials. Although Mix 4 still shows an increase in current density and therefore does not remain completely passive in the aggressive environment, its lower electrochemical activity compared to the remaining coatings indicates the highest resistance among the investigated systems.

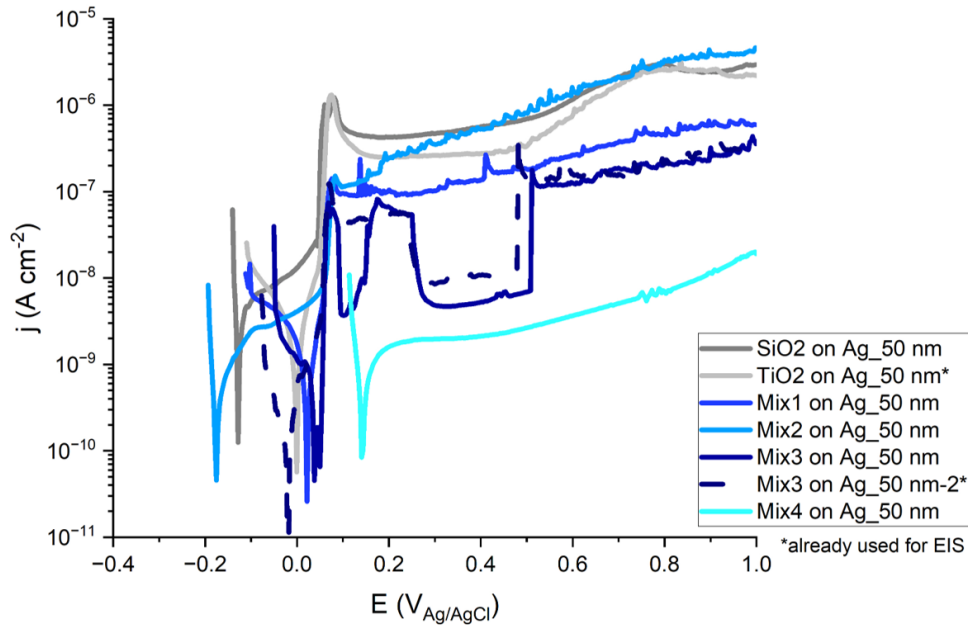


Figure 4.11: Potentiodynamic polarization curves of the investigated 50 nm single-layer and nanolaminate coatings measured in 0.1 M HCl. Lower current densities indicate reduced electrochemical activity and improved corrosion resistance. Measurements were performed at OST.

The E-j measurements therefore support the previous optical and visual evaluation, where the 1 nm TiO₂/4 nm SiO₂ nanolaminate was likewise identified as the most promising coating architecture. Notably, the 1 nm TiO₂:4 nm SiO₂ nanolaminate also exhibits lower current densities than the SiO₂ single-layer coating, indicating that its improved electrochemical performance cannot be attributed solely to the high SiO₂ fraction, but is also associated with the nanolaminate architecture. To further evaluate whether the corresponding electrochemical barrier response follows the same trend, the coatings were subsequently compared by EIS under the milder conditions of 0.1 M citric acid at pH 5.2.

The corresponding Bode plots are presented in Figure 4.12. All investigated 50 nm coating systems exhibit comparatively high impedance magnitudes, approximately between $3.0 \times 10^7 \Omega$ and $2.0 \times 10^8 \Omega$, indicating generally favourable barrier properties. The principal differences between the coatings are therefore observed in the phase-angle response rather than in the absolute impedance magnitude. A phase angle approaching 90° over a broad frequency range corresponds to a predominantly capacitive response and therefore to a coating behaving more closely as an insulating dielectric barrier. The TiO₂ single-layer coating exhibits the broadest capacitive region and approaches ideal dielectric behaviour more closely than the remaining investigated systems. In contrast, the SiO₂ coating exhibits two distinguishable time constants together with lower phase

angles, indicating a less ideal capacitive response. According to the EIS analysis, this behaviour may be associated with a higher defect density, increased porosity, or greater dielectric heterogeneity within the coating. Since EIS cannot distinguish between these contributions, complementary characterization is required to correlate the electrochemical response with specific structural features. The nanolaminates likewise exhibit two characteristic time constants. Their high-frequency response remains relatively constant between the different nanolaminates and can be attributed to the barrier response of the coating. In contrast, the low-frequency time constant varies depending on the investigated nanolaminate architecture.

Mix 1 and Mix 3 show similar phase responses, including a phase minimum around 1 Hz, whereas Mix 2 exhibits a more homogeneous response approaching a single-time-constant system. Mix 4 exhibits a shifted and more pronounced low-frequency response. According to the EIS analysis, this behaviour may be associated with increased electrochemical heterogeneity arising from defect-related processes, electrolyte/substrate charge transfer, or a broader distribution of relaxation times associated with the repeated $\text{TiO}_2/\text{SiO}_2$ interfaces. Since EIS cannot distinguish between these contributions, the exact origin of the low-frequency response cannot be identified from the impedance measurements alone. Detailed structural characterization of the individual layers and interfaces would further help determine whether this response is primarily governed by the local layer composition or by the interfaces within the nanolaminate.

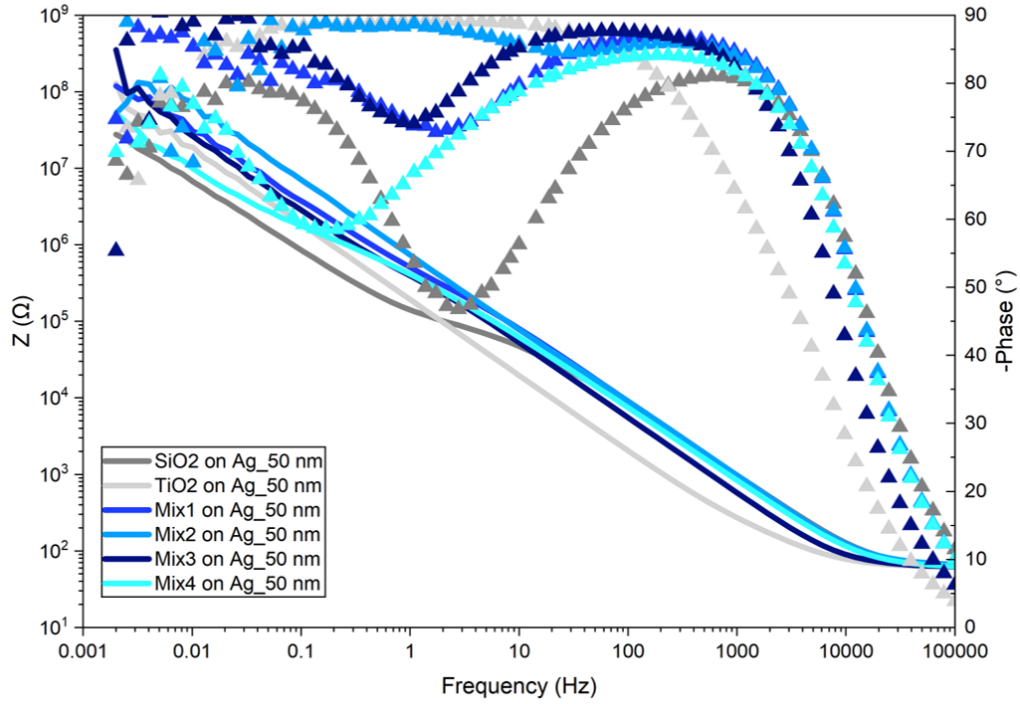


Figure 4.12: Bode plots of the investigated 50 nm single-layer and nanolaminate coatings measured in 0.1 M citric acid at pH 5.2. The impedance magnitude (lines) and phase angle (triangles) are shown as a function of frequency. Measurements were performed at OST.

While EIS alone does not identify the structural origin of the different phase responses, the high impedance values confirm that all investigated coatings provide substantial barrier resistance. Considered together with the potentiodynamic polarization results, EIS therefore provides complementary information on the barrier behaviour of the investigated coatings rather than an independent ranking of their corrosion resistance.

4.6.2 Influence of the Total Nanolaminate Thickness

Following the comparison of the different layer ratios, the influence of total coating thickness was investigated for the selected 1 nm TiO₂:4 nm SiO₂ architecture at total thicknesses of 25, 50, and 100 nm.

The potentiodynamic polarization curves are presented in Figure 4.13. The 25 nm coating exhibits an early increase in current density, indicating active dissolution at relatively low polarization potentials. The 50 nm coating shows the most favourable polarization response. In contrast, the 100 nm coating also exhibits a continuous increase in current

density and fails earlier than expected from its greater thickness alone.

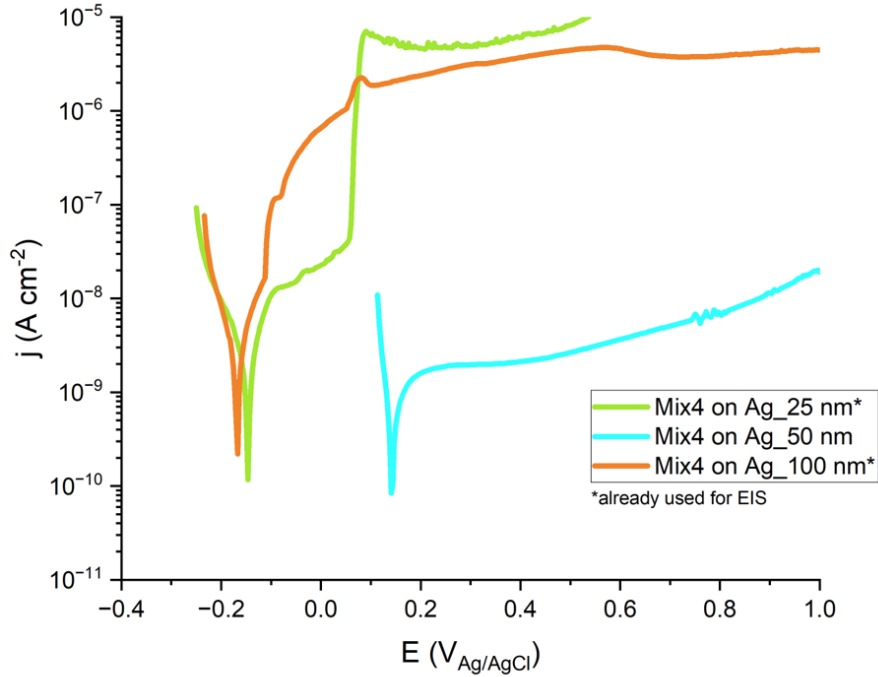


Figure 4.13: Potentiodynamic polarization curves of the selected 1 nm TiO₂:4 nm SiO₂ nanolaminate for total coating thicknesses of 25, 50, and 100 nm measured in 0.1 M HCl. Measurements were performed at OST.

The thickness-dependent polarization results must, however, be interpreted with care. The 25 nm and 100 nm samples had previously undergone EIS measurements, whereas the 50 nm sample used for polarization had not, although no major changes are assumed due to this. The lower OCPs measured for the 25 nm and 100 nm coatings indicate that interaction with the electrolyte had already occurred during the preceding EIS measurements. Consequently, the poorer polarization response of the 100 nm coating cannot be attributed exclusively to coating thickness, and fresh, previously unexposed samples would be required for a fully equivalent comparison.

The EIS measurements provide additional information on the barrier response as a function of coating thickness. The corresponding Bode plots are shown in Figure 4.14. Increasing the coating thickness shifts the phase response towards higher frequencies together with a small increase in impedance magnitude. This is expected, since impedance is inversely proportional to coating capacitance, which decreases with increasing film thickness.

All investigated coatings maintain comparatively high impedance values at low frequencies, around $6 \times 10^7 \Omega$, indicating good barrier properties with limited electrolyte access to the underlying silver substrate. However, the phase response shows that the coatings do not behave as ideal dielectric barriers. Two characteristic time constants can be distinguished, one around 300 Hz and a second in the low-frequency region around 10 mHz. Although the maximum phase angle approaches approximately 85° , the relatively narrow capacitive region indicates a finite coating response rather than purely capacitive blocking over the complete frequency range.

The low-frequency response further changes with total coating thickness. The 25 nm coating exhibits the broadest low-frequency peak, whereas the 100 nm coating shows the most pronounced decrease in phase angle. Consequently, increasing the coating thickness does not simply produce a thicker barrier layer. Instead, the observed differences suggest that increasing thickness may also introduce changes in the coating microstructure, such as differences in defect density or grain-boundary structure. More detailed microstructural investigations would be required to confirm these observations.

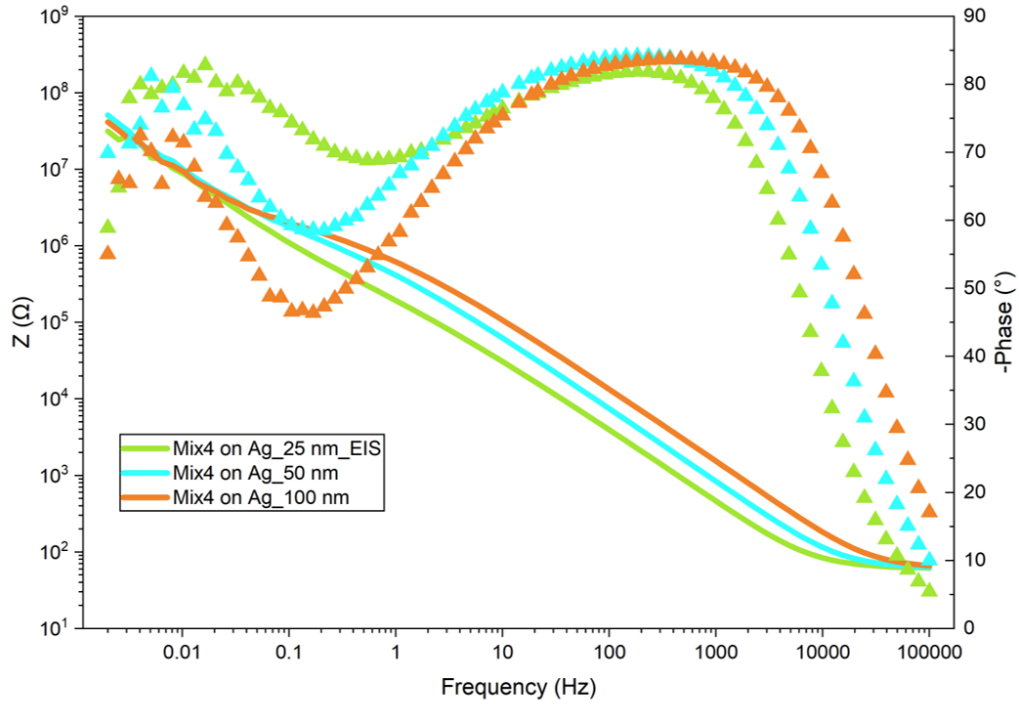


Figure 4.14: Bode plots of the selected 1 nm TiO_2 :4 nm SiO_2 nanolaminate for total coating thicknesses of 25, 50, and 100 nm measured in 0.1 M citric acid at pH 5.2. Measurements were performed at OST.

Overall, the electrochemical characterization complements the coating evaluation obtained from reflectance measurements and visual inspection. The potentiodynamic polarization measurements provide direct comparison of the corrosion resistance under an aggressive HCl environment, whereas EIS evaluates the electrochemical barrier response under milder conditions without intentionally driving the coatings towards degradation. For the layer-ratio comparison, the electrochemical measurements support the favourable performance of the SiO₂-rich 1 nm TiO₂/4 nm SiO₂ nanolaminate. For the total thickness comparison, the results indicate that coating thickness influences both corrosion resistance and barrier response, while also highlighting the importance of identical sample histories when comparing electrochemical measurements. Considering the combined optical, visual, and electrochemical characterization, the 50 nm 1 nm TiO₂:4 nm SiO₂ nanolaminate remains the most favourable overall coating architecture investigated in this work.

5 Discussion

5.1 Development of an Optimized Protective Coating Process

The development of protective coatings for metallic mirrors requires balancing two equally important requirements: corrosion resistance and preservation of optical performance. Unlike many conventional protective coatings, a coating providing excellent chemical stability alone is insufficient if it significantly alters the reflectance of the mirror. This trade-off strongly influenced the experimental strategy. Increasing the coating thickness generally improves the barrier against corrosive environments, but a thicker coatings also modifies the optical response through interference effects and may increase the residual stress within the coating stack. Excessive stress can reduce coating adhesion and promote delamination, ultimately compromising both the mechanical integrity and the optical performance of the system. Rather than maximizing the coating thickness, the objective was therefore to identify the compromise between thickness capable of providing sufficient protection while preserving the characteristic reflectance of the metallic mirrors.

Before investigating protective coating materials, the preparation process itself had to be optimized. The Ar/H₂ plasma pretreatment was introduced to remove surface contamination while minimizing unwanted modification of the substrate surface. Compared with oxygen-based plasmas, the inert Ar/H₂ atmosphere successfully preserved the optical properties of all investigated substrates while providing suitable surface conditions for subsequent ALD deposition.

The largest challenge for PEALD was already known prior to deposition of oxide materials. Among the investigated substrates, silver exhibited by far the highest sensitivity to oxygen exposure, showing a pronounced decrease in reflectance even under the mildest plasma conditions. Since silver represents one of the most important mirror materials for optical applications, preventing oxygen-induced degradation became a prerequisite for the subsequent coating development. This challenge was addressed through the introduction of a thin thermally deposited Al₂O₃ interlayer. Depositing the interlayer by thermal ALD prevented the substrate from being exposed to oxygen plasma during the initial growth cycles while simultaneously providing a continuous protective barrier for all subsequent PEALD depositions. Al₂O₃ was selected for the initial investigation due to its well-established ALD process and its ability to form uniform and conformal films already at very small thicknesses. The optimization of the interlayer thickness demonstrated that 2 nm did not provide sufficient protection against oxygen plasma, whereas 4 nm and 8 nm resulted in comparable protection of the silver substrate. Since the thicker interlayer introduced a greater influence on the optical properties without providing additional protection, 4 nm represented the optimum compromise between maintaining reflectance and ensuring sufficient barrier performance. Finally, comparison

between Al_2O_3 and AlN interlayers showed that both materials produced comparable optical behaviour. However, the superior adhesion observed for coating systems employing the Al_2O_3 interlayer after deposition of a 100 nm single-layer coating identified Al_2O_3 as the more appropriate solution.

Consequently, the optimized process established throughout this work consists of a 50 W Ar/ H_2 plasma pretreatment with 2% H_2 for 60 s, followed by a 4 nm thermally deposited Al_2O_3 interlayer prior to deposition of the functional protective coating. This optimized process formed the foundation for the subsequent evaluation of single-layer and nanolaminate coating architectures.

Several limitations should nevertheless be considered when interpreting the results of this work. The internal structure of the nanolaminate coatings was not directly validated by structural characterization such as TEM, and the presence and continuity of the nominal individual layers therefore remain to be confirmed. Furthermore, the electrochemical measurements were performed under different measurement conditions, limiting direct quantitative comparison between the different data sets. The S_q values obtained for the different substrate materials cannot be directly compared because different AFM scan areas were used. Finally, although silver exhibited pronounced degradation during oxygen-plasma exposure, the underlying chemical nature and degradation mechanism of this response were not investigated.

5.2 From Single-Layer Coatings to Nanolaminate Architectures

The single-layer coating study demonstrated that none of the investigated oxides simultaneously fulfilled all the requirements for the protection of metallic mirrors. Although several materials exhibited excellent performance under specific conditions, each coating also presented limitations when evaluated from both an optical and a visual perspective. Consequently, the transition from single-layer coatings to nanolaminates was not only motivated by the existing literature, but also by the experimental observations obtained throughout this work.

An important outcome of the single-layer evaluation was that reflectance measurements alone were insufficient to identify the most suitable protective coating. Since reflectance measurements evaluate only the optical response along the illuminated measurement area, localized coating degradation or delamination may remain undetected when the overall optical response is only slightly affected. The complementary visual inspection therefore proved essential, allowing localized failure mechanisms to be identified over the entire sample surface. Combining both characterization techniques enabled a more reliable ranking of the investigated materials and ultimately led to the selection of SiO_2 , TiO_2 , and HfO_2 for the subsequent nanolaminate investigation. While SiO_2 , TiO_2 , and HfO_2 exhibited the most favourable overall performance, none of them consistently

provided the highest resistance under all investigated conditions. Similarly, Al_2O_3 and Ta_2O_5 were excluded despite exhibiting favourable behaviour in specific cases, as both materials showed pronounced optical losses after chemical exposure. These observations demonstrate that selecting a single oxide inevitably represents a compromise between competing material properties.

Rather than searching for a single material capable of satisfying all requirements, nanolaminates offer the possibility of combining the properties of different oxides within one coating architecture. As discussed in the theoretical background, the introduction of multiple interfaces interrupts the continuous propagation of defects and pinholes that may form during thin-film growth. Consequently, direct pathways for electrolyte penetration become less probable, while the alternating layers increase the effective diffusion path through the coating. In addition, combining materials with different optical, chemical, and mechanical characteristics allows the overall coating performance to be tailored beyond the capabilities of the individual constituent oxides.

The single-layer screening therefore demonstrated that the investigated oxides should not be regarded as competing alternatives, but rather as complementary materials with different strengths and limitations. This observation is consistent with the concept of nanolaminate coatings introduced in the theoretical background, where alternating materials are expected to compensate for the shortcomings of the individual oxides while combining their favourable properties. Consequently, the subsequent stage of this work focused on optimizing the nanolaminate architecture through systematic variation of the layer thickness ratio and the total coating thickness.

5.3 Optimization of the Nanolaminate Architecture

Following the selection of the most promising oxide materials, the influence of the nanolaminate architecture was investigated by varying both the individual layer thickness ratio and the total coating thickness. Unlike single-layer coatings, nanolaminates introduce additional design parameters, allowing the contribution of each constituent material to be adjusted while maintaining the overall coating thickness.

The investigated layer thickness ratios (1 nm:1 nm, 5 nm:5 nm, 4 nm:1 nm, and 1 nm:4 nm) were selected to evaluate how the relative contribution of each oxide influences the overall coating performance. While the symmetric architectures provide an equal contribution from both materials, the asymmetric ratios allow one material to dominate the coating behaviour while still benefiting from the complementary properties introduced by the second oxide. This approach enabled the influence of both the material combination and the relative layer thickness to be assessed systematically.

Among the investigated architectures, the SiO_2 -rich nanolaminates consistently provided the best overall performance. This observation agrees with the excellent behaviour of

SiO₂ during the single-layer screening and indicates that the favourable barrier properties of SiO₂ remain dominant within the nanolaminate architecture. At the same time, the addition of TiO₂ or HfO₂ further improved the coating performance by combining the advantageous properties of both materials. This role of the architecture is particularly evident in the electrochemical characterization, where the 1 nm TiO₂:4 nm SiO₂ nanolaminate exhibited lower current densities than the SiO₂ single-layer coating despite containing a smaller overall fraction of SiO₂. In particular, the 1 nm TiO₂:4 nm SiO₂ architecture achieved the most favourable balance between maintaining the optical properties, limiting delamination, and improving the resistance against chemical attack.

A likely explanation for the superior performance of the SiO₂-rich architectures is related to the different microstructural behaviour of the constituent oxides. PEALD SiO₂ is expected to remain predominantly amorphous, whereas TiO₂ can develop crystalline regions, for example anatase, under the applied deposition conditions. Grain boundaries associated with crystalline TiO₂ may act as preferential diffusion pathways for aggressive species through the coating. In SiO₂-rich nanolaminates, the TiO₂ layers are thinner and are repeatedly interrupted by amorphous SiO₂, which may suppress the formation of continuous crystalline regions and therefore reduce the probability of continuous grain-boundary diffusion paths. This provides a plausible explanation for why the 1 nm TiO₂:4 nm SiO₂ architecture outperformed the 4 nm:1 nm and 5 nm:5 nm architectures. More generally, this behaviour is consistent with the classical nanolaminate barrier concept, in which repeated interfaces interrupt continuous transport pathways through the coating.

The total coating thickness was likewise found to influence the coating performance. While thinner coatings reduce optical interference effects, they may not provide sufficient protection against aggressive environments. Conversely, increasing the coating thickness beyond 50 nm did not result in a clear improvement in the optical or visual evaluation, while simultaneously increasing the likelihood of stress accumulation within the coating stack. Although the electrochemical characterization suggested improved barrier properties for thicker coatings, these improvements were not reflected by the optical and visual assessments. Since preserving the optical performance represents one of the principal objectives of this work, the 50 nm nanolaminate was identified as the most suitable compromise between protection and optical preservation.

The electrochemical measurements further supported the conclusions obtained from the optical characterization. Although EIS was primarily employed as a complementary validation technique, the investigated nanolaminates exhibited trends consistent with the reflectance and visual evaluations. In particular, the TiO₂-rich and SiO₂-rich architectures could be differentiated based on their impedance response, with the 1 nm TiO₂:4 nm SiO₂ nanolaminate again exhibiting the most favourable overall behaviour. The agreement between the optical, morphological, and electrochemical characterization techniques therefore increases the confidence in the selected coating architecture.

Overall, the results demonstrate that the optimization of nanolaminates extends beyond the selection of suitable materials alone. The relative layer thickness and the total coating thickness both play an important role in determining the final coating performance. By systematically optimizing these parameters, a SiO_2 -rich $\text{TiO}_2/\text{SiO}_2$ nanolaminate with a total thickness of 50 nm was identified as the most promising protective coating investigated within this work.

5.4 Limitations

Although the developed coating process and nanolaminate architecture showed promising performance, several limitations of the present study should be considered when interpreting the results.

A principal limitation concerns the structural characterization of the nanolaminate coatings. The individual layer thicknesses and sequences discussed throughout this work represent the nominal deposition architecture and were not directly verified by structural techniques such as transmission electron microscopy (TEM) or X-ray reflectometry (XRR). Ellipsometry provides information on the total coating thickness and average optical response, but cannot confirm the presence, continuity, or sharpness of the individual layers and interfaces. Consequently, interpretations relating the improved barrier performance to the nanolaminate interfaces or microstructure remain hypotheses until the internal coating structure is directly characterized.

A further limitation arises from the ellipsometric and AFM characterization. Because reliable ellipsometric modelling of the metallic mirror stacks was not possible, coating thickness and refractive index were determined from simultaneously coated silicon reference samples and assumed to be representative of the corresponding coatings on the metallic substrates. In addition, different AFM scan areas were employed for silicon and the metallic mirrors. The resulting S_q values can therefore be used to evaluate changes within a given substrate system, but should not be directly compared between all substrate materials.

The electrochemical characterization also contains limitations regarding direct comparability. Different scan rates were used for the potentiodynamic polarization measurements performed for the layer-ratio and total-thickness comparisons, and these data sets should therefore not be quantitatively compared with each other. Furthermore, the 25 and 100 nm samples used for the thickness-dependent polarization measurements had previously undergone EIS measurements, whereas the 50 nm sample had not. Differences in sample history may consequently contribute to the observed response. EIS and potentiodynamic polarization were additionally performed using different electrolytes and should therefore be regarded as complementary evaluations of barrier performance rather than directly equivalent measurements.

Finally, the mechanisms responsible for some of the observed degradation remain unresolved. In particular, oxygen-plasma exposure produced pronounced optical and morphological changes on silver, but the chemical nature of this degradation was not investigated directly. Similarly, changes in electrochemical response with nanolaminate architecture and thickness cannot yet be related unambiguously to specific microstructural features. Dedicated chemical and structural characterization would therefore be required to establish these mechanisms. Moreover, the durability evaluation was based primarily on accelerated chemical exposure and selected electrochemical conditions. The long-term stability of the optimized coating under representative service environments therefore remains to be demonstrated.

6 Conclusions

6.1 Key Findings

This work developed and optimized PEALD oxide coatings for the protection of metallic mirror substrates while preserving their optical performance. The first step was the optimization of the surface preparation, where an Ar/H₂ plasma treatment at 50 W, 2% H₂, and 60 s was identified as the most suitable condition, introducing only minor optical and morphological changes.

Silver was found to be by far the most oxygen-sensitive substrate, with its reflectance at 532 nm decreasing by more than 25% after only 30 s exposure to a 50 W O₂ plasma. To mitigate this effect, a thermally deposited Al₂O₃ interlayer was introduced. A thickness of 4 nm provided protection, causing less optical interference. Furthermore, nanoscratch measurements showed higher first critical loads for Al₂O₃ than for AlN on all investigated substrates.

The subsequent coating screening showed that SiO₂, TiO₂, and HfO₂ were the most promising single-layer materials. Their combination into nanolaminates further improved the coating performance. TiO₂/SiO₂ nanolaminates outperformed the corresponding HfO₂/SiO₂ systems, with the SiO₂-rich 1 nm TiO₂:4 nm SiO₂ architecture showing the most favourable overall behaviour. Considering chemical resistance, optical preservation, and electrochemical performance together, a total coating thickness of 50 nm provided the best overall compromise. Potentiodynamic polarization and EIS measurements supported this ranking and further indicated that the improved performance is related not only to composition, but also to the nanolaminate architecture.

Overall, the optimized process consists of a 50 W Ar/H₂ pretreatment, a 4 nm thermally deposited Al₂O₃ interlayer, and a 50 nm nanolaminate composed of 1 nm TiO₂:4 nm SiO₂. This coating architecture represents the most promising protective system identified within the scope of this work.

6.2 Possible Future Work

Further work should first focus on validating the internal structure of the nanolaminates. XRR and cross-sectional TEM are required to confirm the periodicity, continuity, and interface quality of the nominally 1 nm layers, while XRD would help establish the crystallinity of the constituent oxides. This is particularly important for verifying whether suppression of continuous TiO₂ grain-boundary pathways contributes to the improved performance of the SiO₂-rich architectures.

The degradation mechanism of silver under O₂ plasma should also be investigated in more detail, for example by XPS. In addition, repeated nanoscratch measurements would

improve the statistical reliability of the adhesion comparison, while quantitative extraction of E_{corr} and j_{corr} from the polarization data would provide a more complete electrochemical evaluation.

Finally, the optimized coating should be tested under more application-relevant conditions, including representative mirror geometries, thermal cycling, damp-heat exposure, and laser-induced damage threshold (LIDT) measurements. These investigations would provide the structural and long-term validation required for practical optical applications.

Appendix

Table A.1: Measurement parameters used for all reflectance measurements performed with the PHOTON RT Spectrophotometer Model 0252 (EssentOptics).

Parameter	Value
Measurement mode	Reflectance
Start wavelength	210 nm
End wavelength	1700 nm
Sampling pitch	5 nm
Averaging count	20
Smoothing mode	0
Manual mode	0
Sample stage angle	8°
Detector angle	16°
Detector auto displacement	Flat
Detector displacement	0.20 mm
Sample thickness	1.10 mm
Refractive index (n)	1.52
Slit width	170 μm / 120 μm
Spot size	6.0 mm
Polarization	Averaged (P+S)
Deuterium light source	Enabled

Silicon

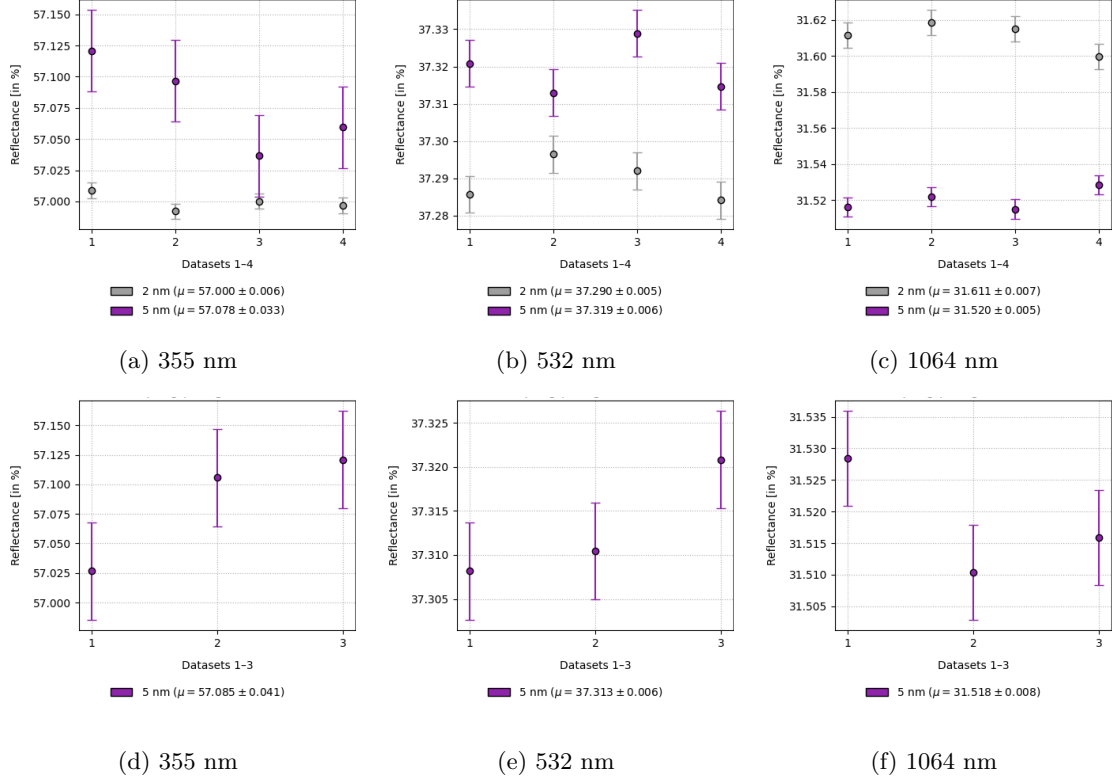


Figure A.1: Reflectance reproducibility of the silicon substrate. Subfigures (a)–(c) show short-term repeated measurements, while (d)–(f) show long-term measurements performed at one-week intervals on different samples from the same wafer. Error bars are based on the standard deviation.

Silver

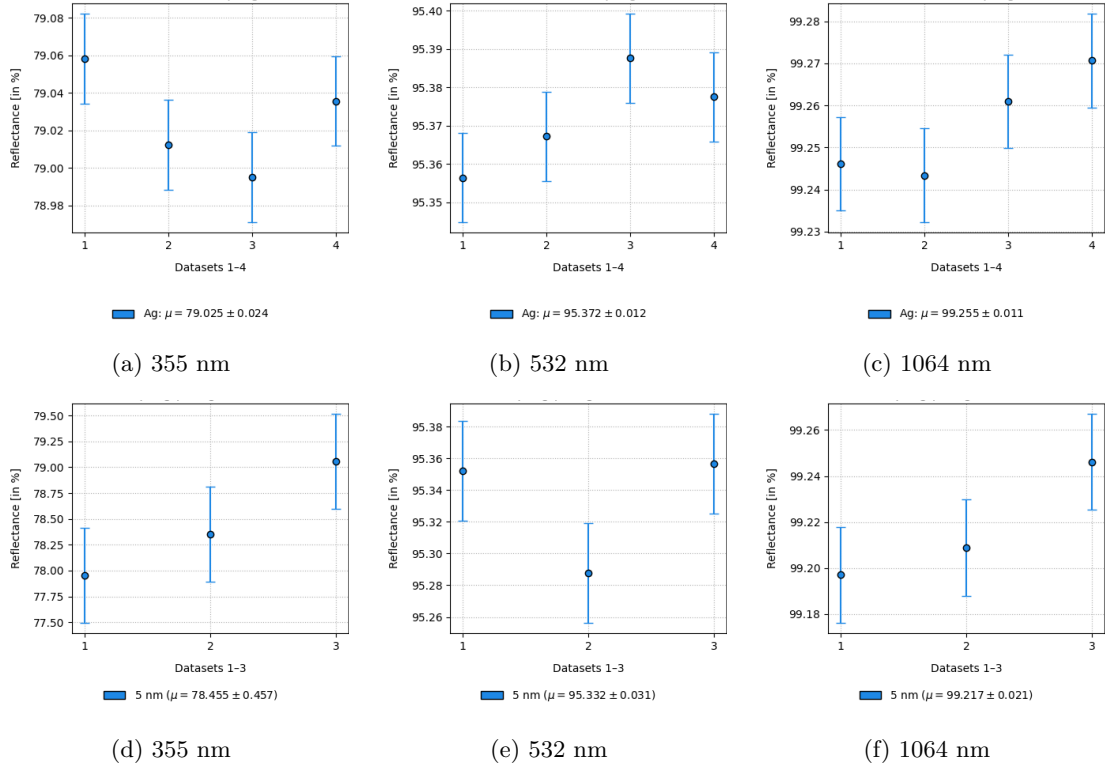


Figure A.2: Reflectance reproducibility of the silver-coated substrate. Subfigures (a)–(c) show short-term repeated measurements, while (d)–(f) show long-term measurements performed at one-week intervals on different samples from the same wafer. Error bars represent one standard deviation.

Aluminium

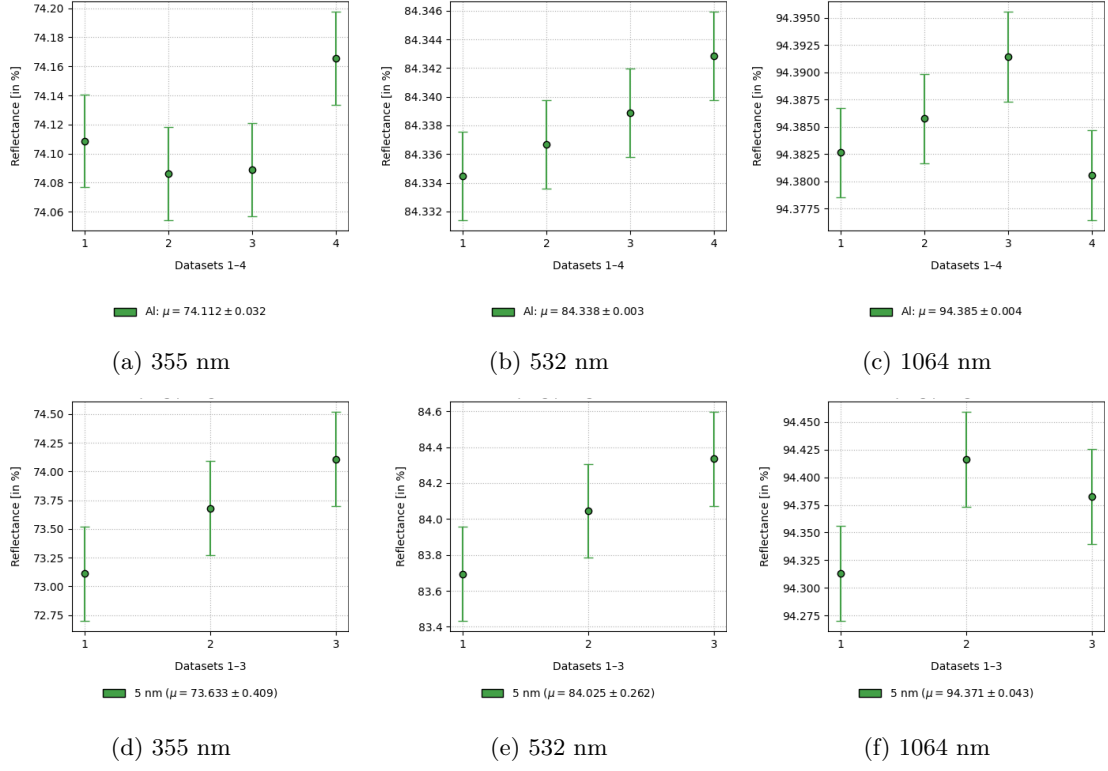


Figure A.3: Reflectance reproducibility of the aluminum-coated substrate. Subfigures (a)–(c) show short-term repeated measurements, while (d)–(f) show long-term measurements performed at one-week intervals on different samples from the same wafer. Error bars represent one standard deviation.

Gold

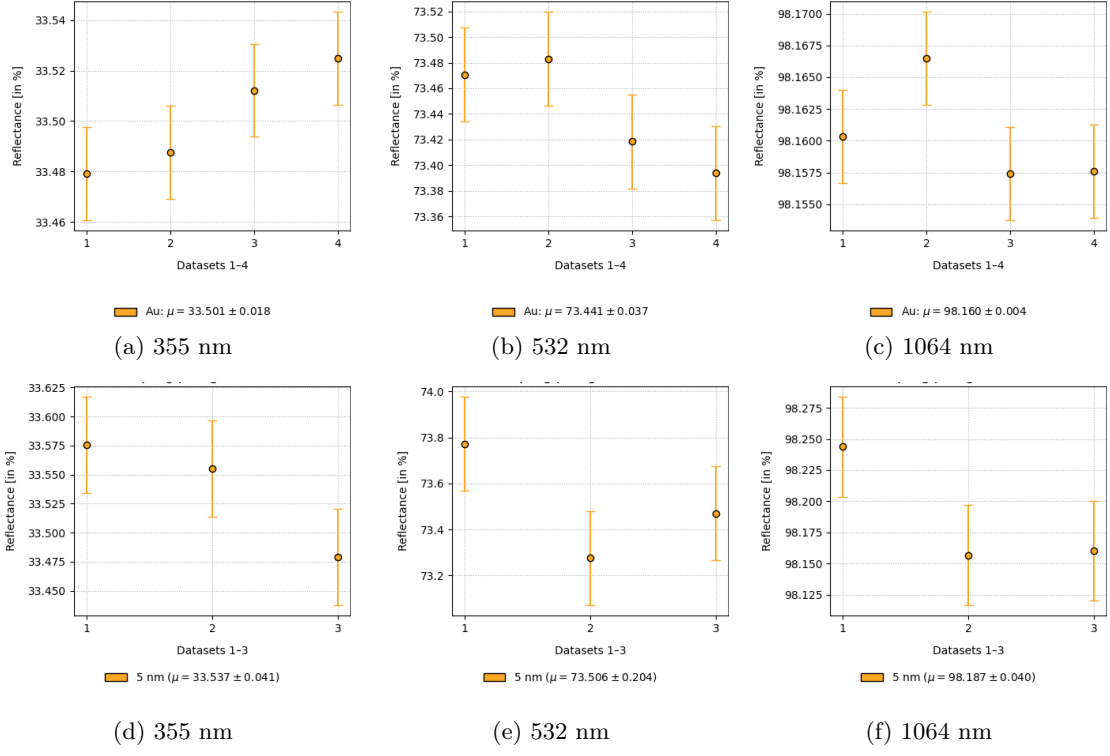
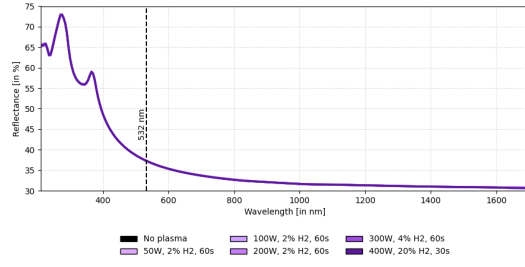
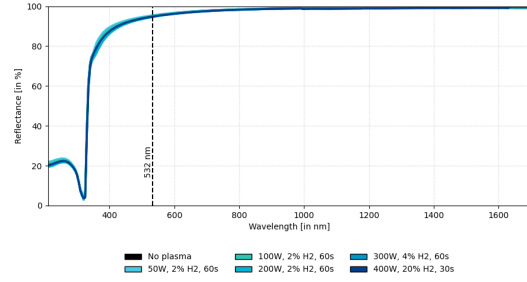


Figure A.4: Reflectance reproducibility of the gold-coated substrate. Subfigures (a)–(c) show short-term repeated measurements, while (d)–(f) show long-term measurements performed at one-week intervals on different samples from the same wafer. Error bars represent one standard deviation.

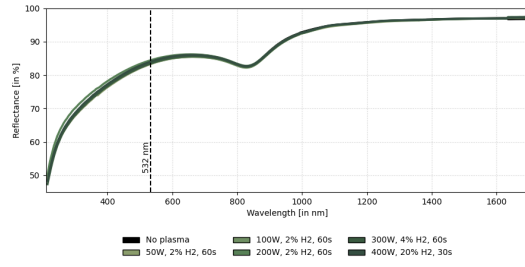
Reflectance Spectra per Substrate after Different Ar/H₂ Plasmas



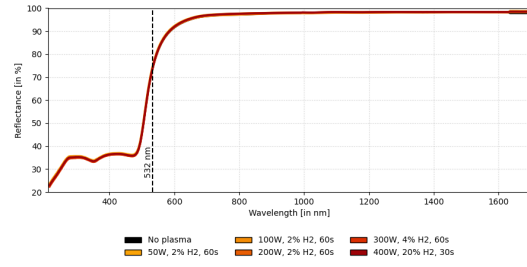
(a) Si substrate



(b) Ag substrate



(c) Al substrate



(d) Au substrate

Figure A.5: Reflectance spectra of Si, Ag, Al, and Au substrates after Ar/H₂ plasma treatment under varying process conditions, including power, hydrogen concentration, and exposure time.

Table A.2: Surface roughness S_q of Si, Ag, Al, and Au substrates as a function of Ar/H₂ plasma power. The untreated values correspond to the reference surface roughness measurements, while all plasma-treated samples were exposed using 2% H₂ for 60 s.

Plasma power [W]	Surface roughness S_q [nm]			
	Si	Ag	Al	Au
0	0.105	4.68	36.31	2.56
50	0.859	12.96	31.79	2.88
100	0.136	7.11	23.58	4.82
200	0.129	10.08	38.07	4.90
300	0.157	12.17	37.70	4.77
400	0.149	6.49	28.63	5.08

Table A.3: Surface roughness S_q of Si, Ag, Al, and Au substrates as a function of O₂ plasma power. Plasma-treated samples were exposed for 30 s at 150 °C.

Plasma power [W]	Surface roughness S_q [nm]			
	Si	Ag	Al	Au
0	1.675	1.68	7.93	2.56
50	0.136	9.99	27.60	2.58
100	0.179	10.89	21.53	4.80
150	0.277	11.05	37.99	5.48

Reflectance Comparison of Interlayer Materials

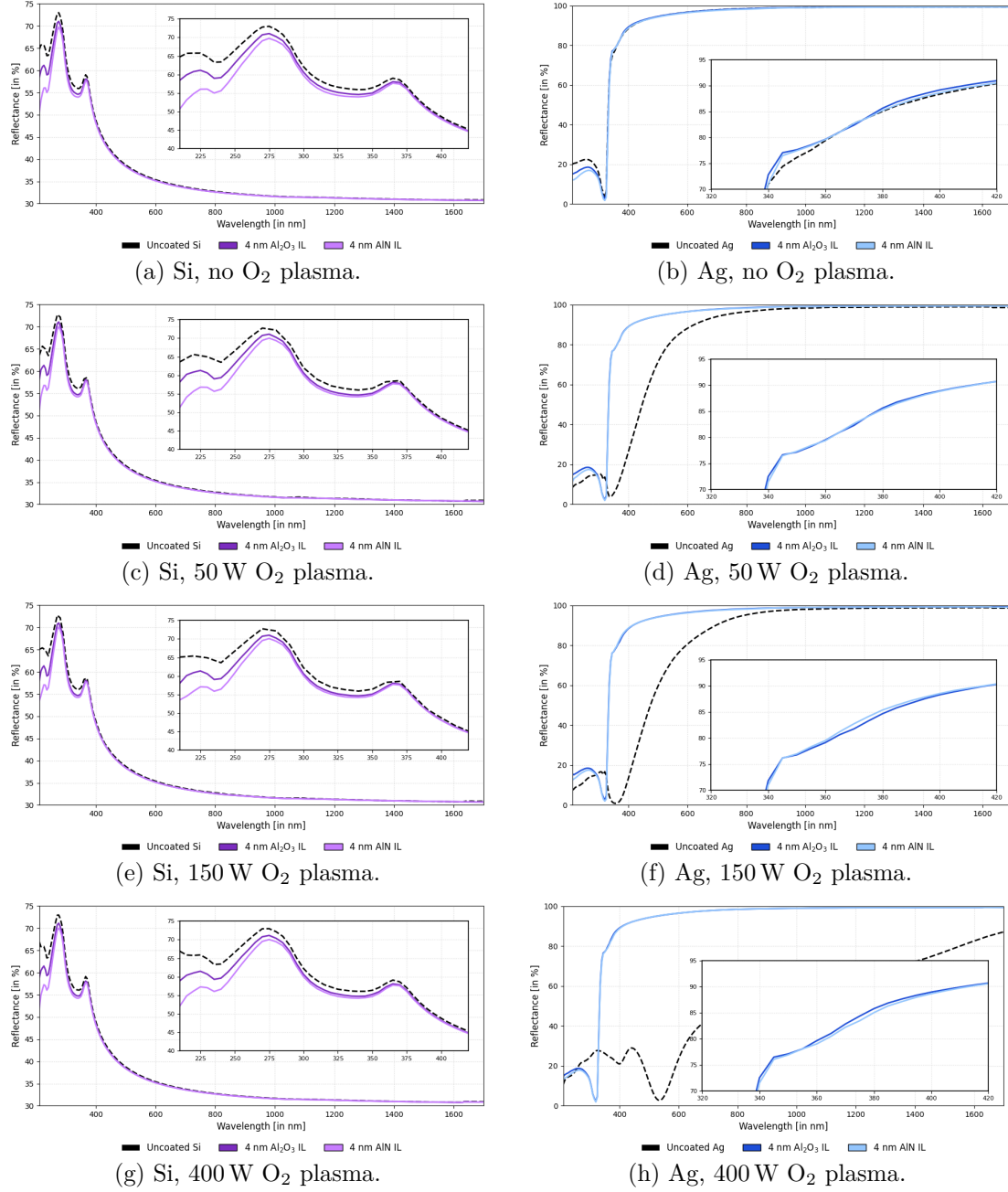
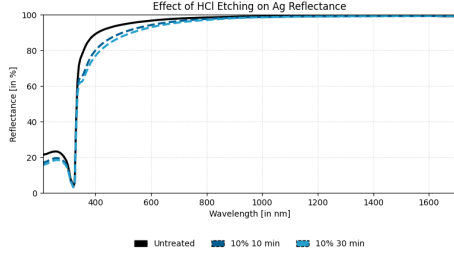
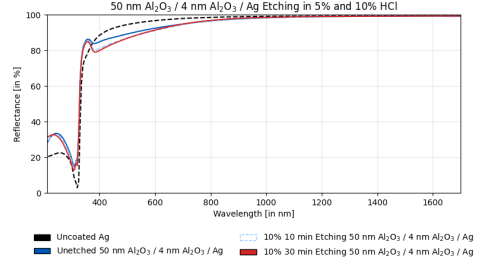


Figure A.6: Reflectance comparison of 4 nm Al₂O₃ and 4 nm AlN interlayers on silicon and silver substrates under different oxygen plasma exposure conditions. The rows correspond to no O₂ plasma exposure, 50 W, 150 W, and 400 W O₂ plasma exposure, respectively.

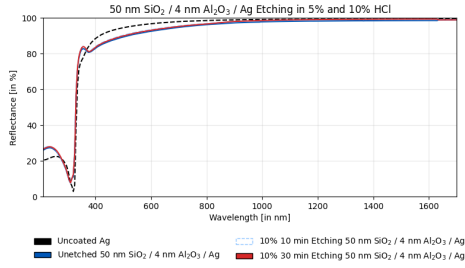
Protection Screening from HCl by Single-Layer Coatings on Ag



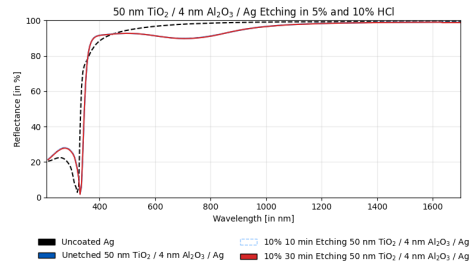
(a) Uncoated Ag substrate.



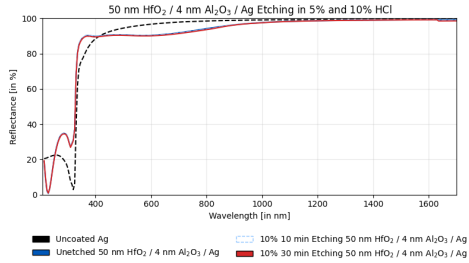
(b) Ag with 50 nm Al_2O_3 .



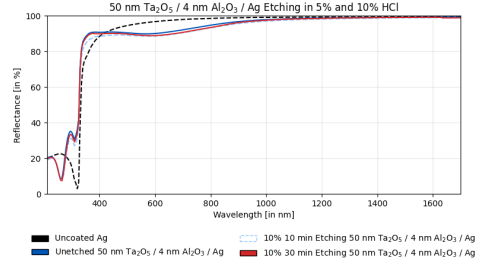
(c) Ag with 50 nm SiO_2 .



(d) Ag with 50 nm TiO_2 .



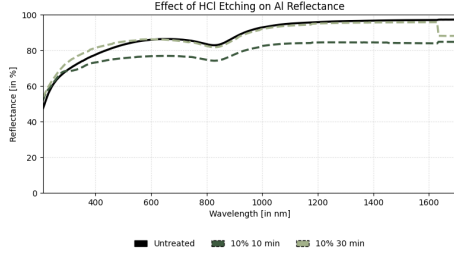
(e) Ag with 50 nm HfO_2 .



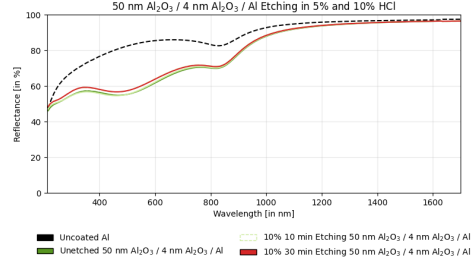
(f) Ag with 50 nm Ta_2O_5 .

Figure A.7: Reflectance-based protection screening of the silver substrate protected by different 50 nm single-layer oxide coatings during HCl exposure. The uncoated Ag substrate provides the reference response to HCl, while the Al_2O_3 , SiO_2 , TiO_2 , HfO_2 , and Ta_2O_5 coatings illustrate the influence of the individual oxide materials on the preservation of the optical properties of the silver mirror.

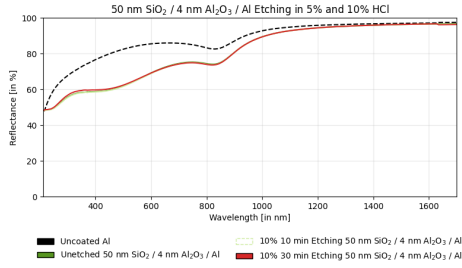
Protection Screening from HCl by Single-Layer Coatings on Al



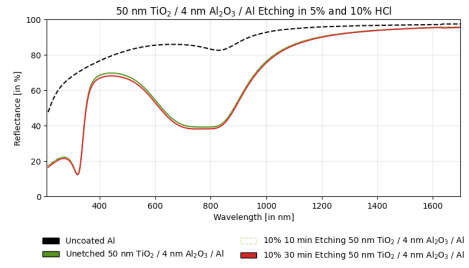
(a) Uncoated Al substrate.



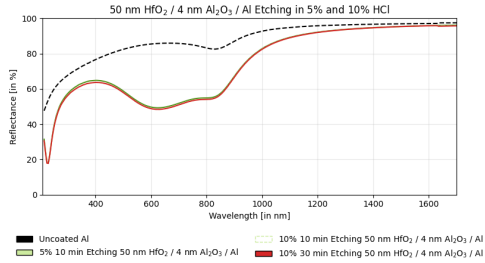
(b) Al with 50 nm Al_2O_3 .



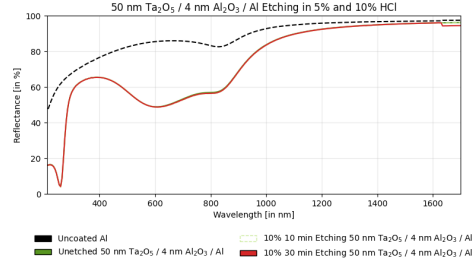
(c) Al with 50 nm SiO_2 .



(d) Al with 50 nm TiO_2 .



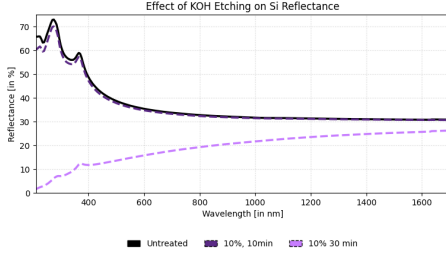
(e) Al with 50 nm HfO_2 .



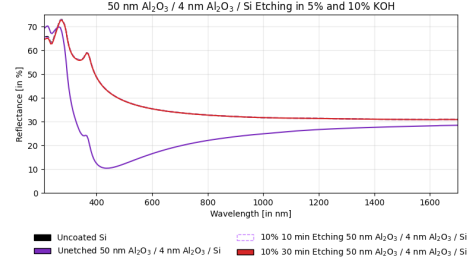
(f) Al with 50 nm Ta_2O_5 .

Figure A.8: Reflectance-based protection screening of the aluminium substrate protected by different 50 nm single-layer oxide coatings during HCl exposure. The uncoated Al substrate provides the reference response to HCl, while the Al_2O_3 , SiO_2 , TiO_2 , HfO_2 , and Ta_2O_5 coatings illustrate the influence of the individual oxide materials on the preservation of the optical properties of the aluminium mirror.

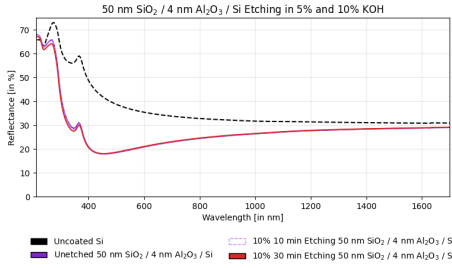
Protection Screening from KOH by Single-Layer Coatings on Si



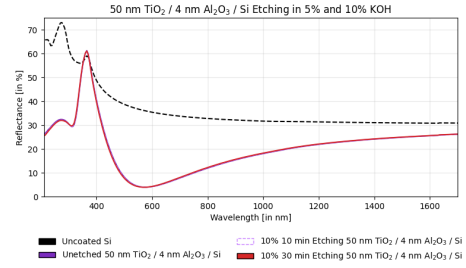
(a) Uncoated Si substrate.



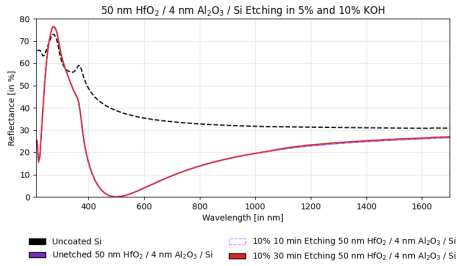
(b) Si with 50 nm Al_2O_3 .



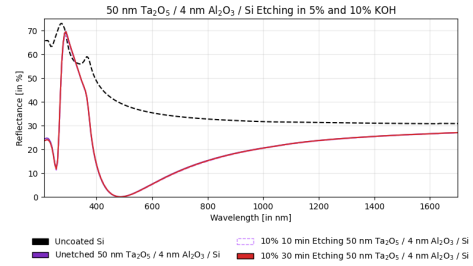
(c) Si with 50 nm SiO_2 .



(d) Si with 50 nm TiO_2 .



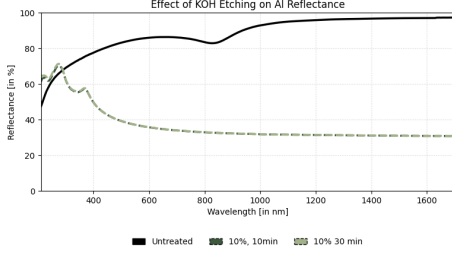
(e) Si with 50 nm HfO_2 .



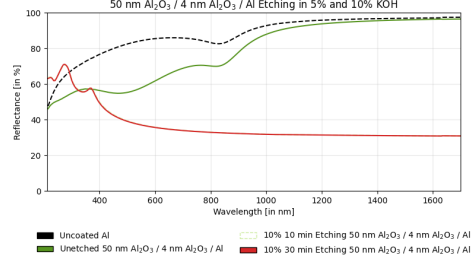
(f) Si with 50 nm Ta_2O_5 .

Figure A.9: Reflectance-based protection screening of the silicon substrate protected by different 50 nm single-layer oxide coatings during KOH exposure. The uncoated Si substrate provides the reference response to KOH, while the Al_2O_3 , SiO_2 , TiO_2 , HfO_2 , and Ta_2O_5 coatings illustrate the influence of the individual oxide materials on the preservation of the optical properties of the silicon mirror.

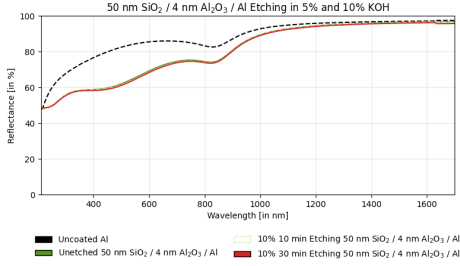
Protection Screening from KOH by Single-Layer Coatings on Al



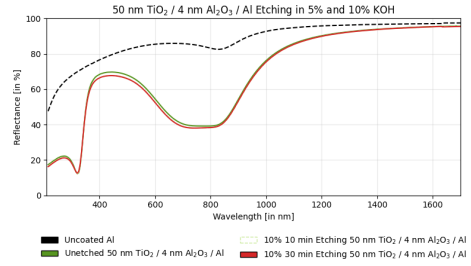
(a) Uncoated Al substrate.



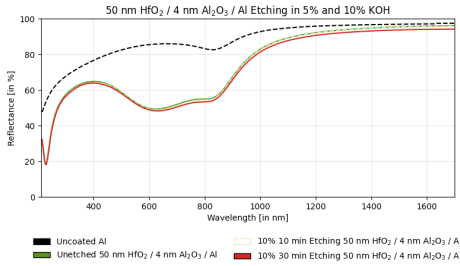
(b) Al with 50 nm Al_2O_3 .



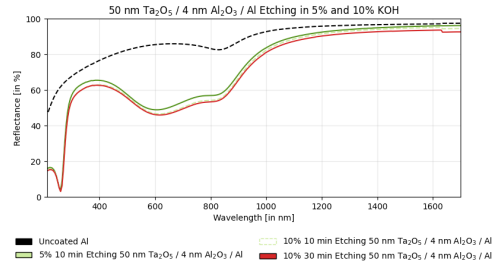
(c) Al with 50 nm SiO_2 .



(d) Al with 50 nm TiO_2 .



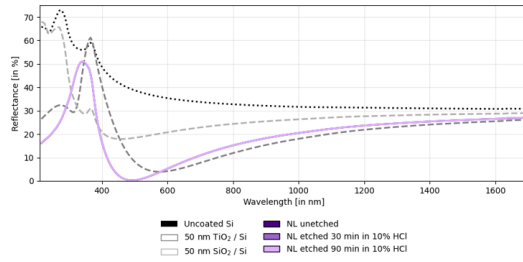
(e) Al with 50 nm HfO_2 .



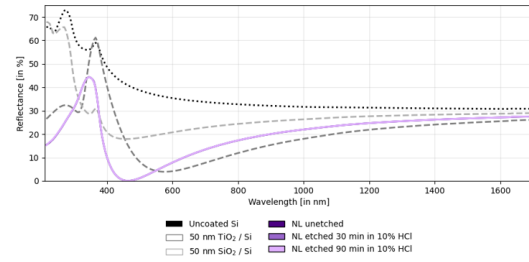
(f) Al with 50 nm Ta_2O_5 .

Figure A.10: Reflectance-based protection screening of the aluminium substrate protected by different 50 nm single-layer oxide coatings during KOH exposure. The uncoated Al substrate provides the reference response to KOH, while the Al_2O_3 , SiO_2 , TiO_2 , HfO_2 , and Ta_2O_5 coatings illustrate the influence of the individual oxide materials on the preservation of the optical properties of the aluminium mirror.

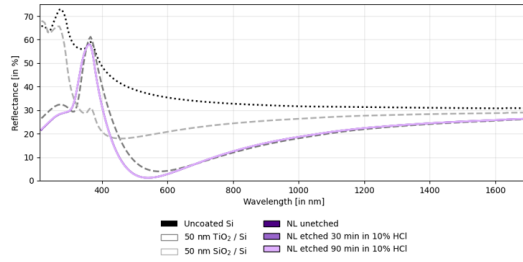
Protection Screening against HCl by $\text{TiO}_2/\text{SiO}_2$ Nanolaminate Coatings on Si



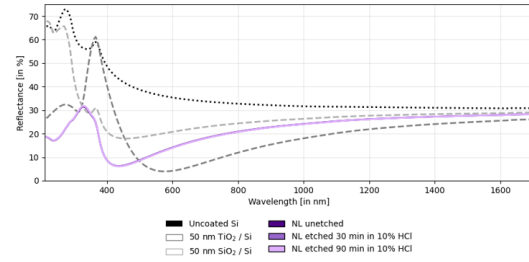
(a) 1 nm TiO_2 / 1 nm SiO_2 .



(b) 5 nm TiO_2 / 5 nm SiO_2 .



(c) 4 nm TiO_2 / 1 nm SiO_2 .



(d) 1 nm TiO_2 / 4 nm SiO_2 .

Figure A.11: Reflectance-based HCl protection screening of 50 nm $\text{TiO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on silicon. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.

Protection Screening against HCl by $\text{TiO}_2/\text{SiO}_2$ Nanolaminate Coatings on Ag

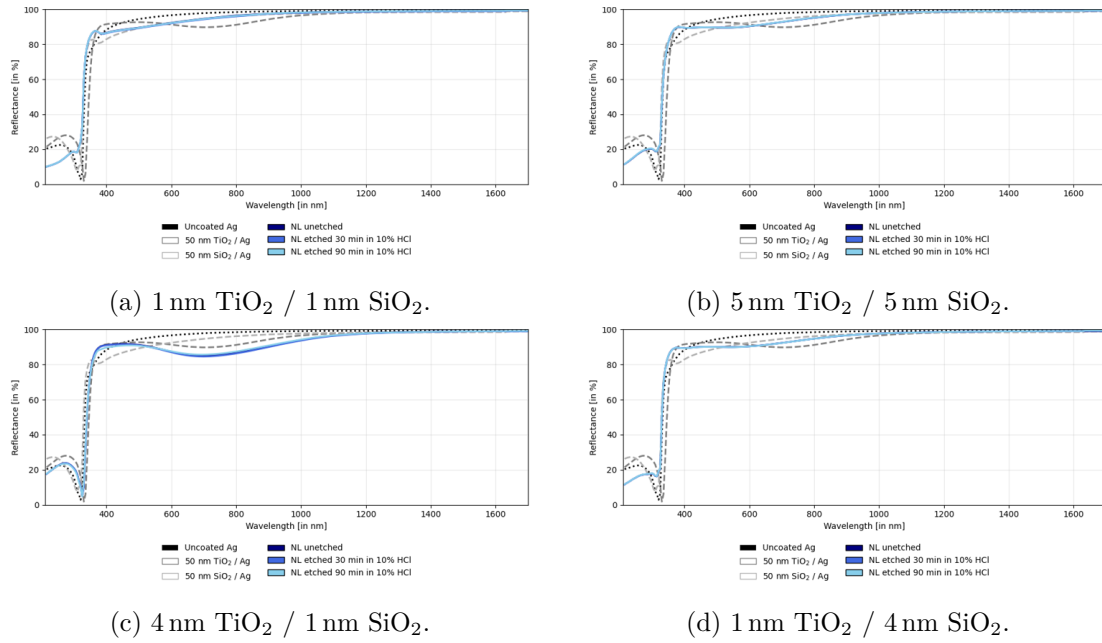


Figure A.12: Reflectance-based HCl protection screening of 50 nm $\text{TiO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on silver. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.

Protection Screening against HCl by $\text{TiO}_2/\text{SiO}_2$ Nanolaminate Coatings on Al

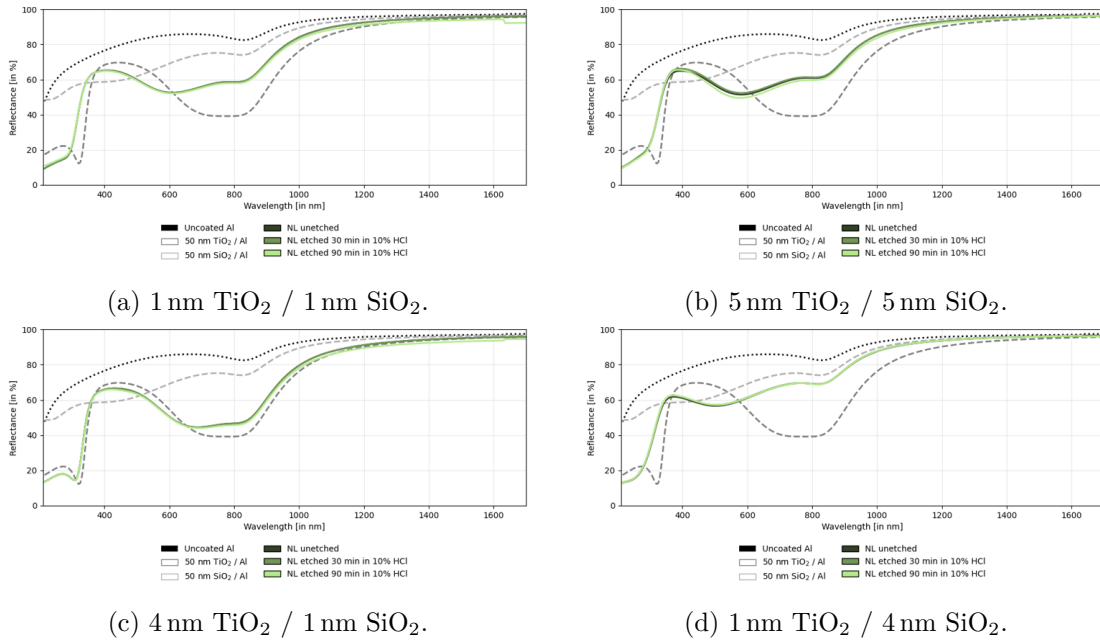


Figure A.13: Reflectance-based HCl protection screening of 50 nm $\text{TiO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on aluminium. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.

Protection Screening against HCl by $\text{TiO}_2/\text{SiO}_2$ Nanolaminate Coatings on Au

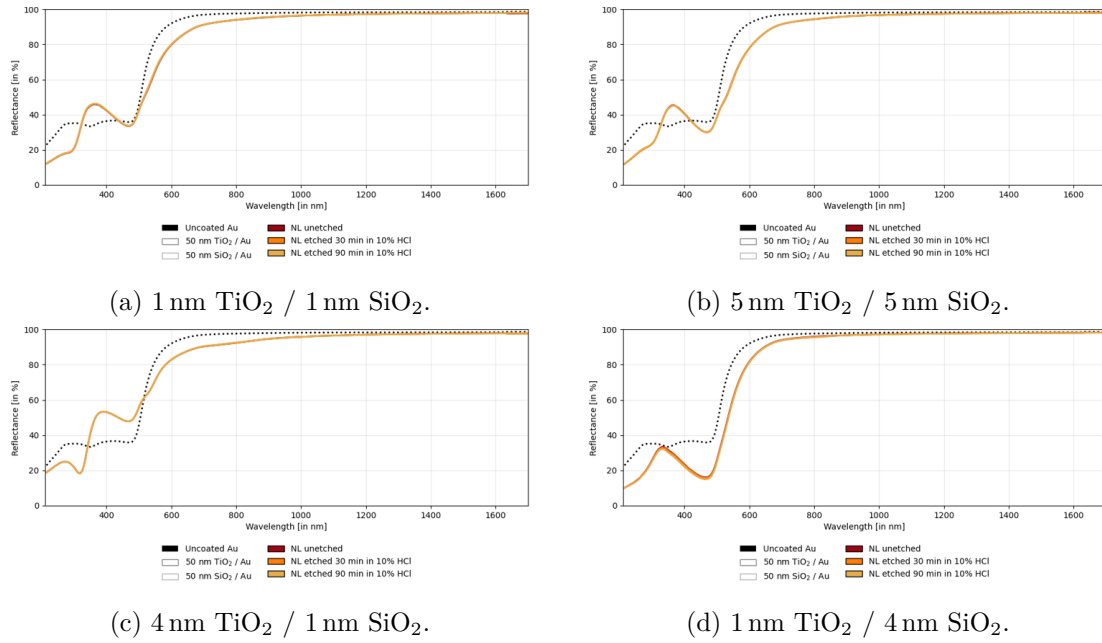


Figure A.14: Reflectance-based HCl protection screening of 50 nm $\text{TiO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on gold. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.

Protection Screening against HCl by $\text{HfO}_2/\text{SiO}_2$ Nanolaminate Coatings on Si

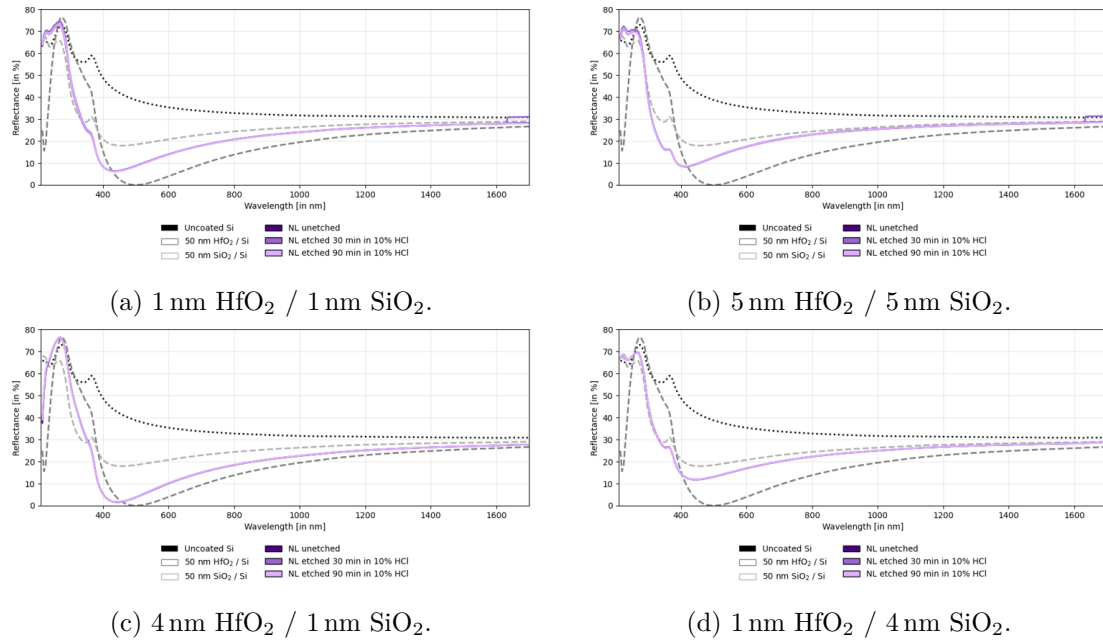


Figure A.15: Reflectance-based HCl protection screening of 50 nm $\text{HfO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on silicon. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.

Protection Screening against HCl by $\text{HfO}_2/\text{SiO}_2$ Nanolaminate Coatings on Ag

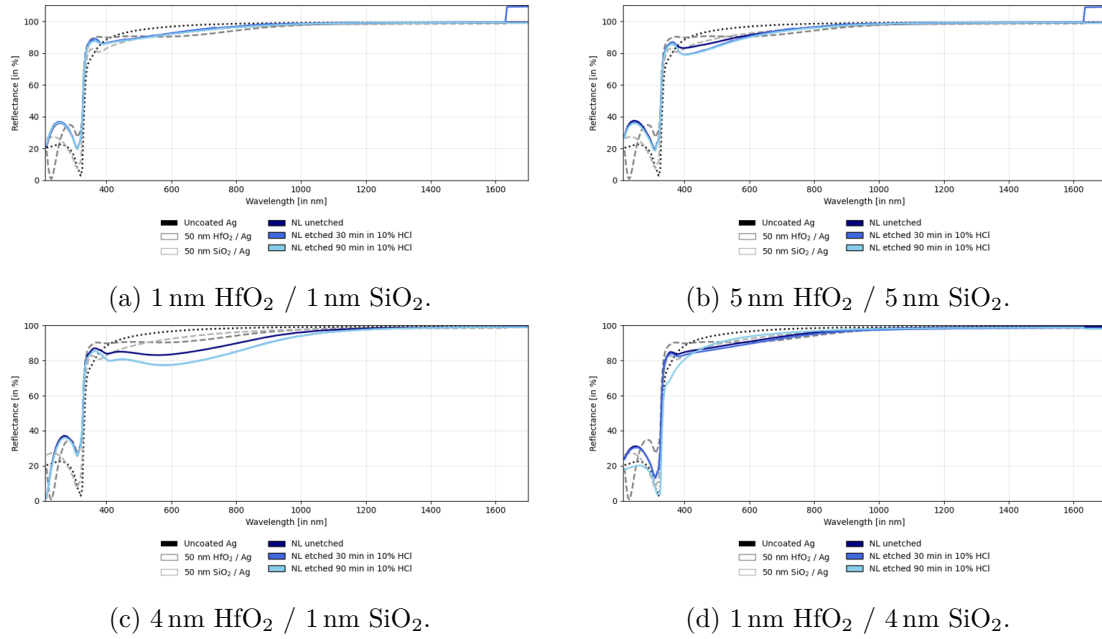


Figure A.16: Reflectance-based HCl protection screening of 50 nm $\text{HfO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on silver. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.

Protection Screening against HCl by $\text{HfO}_2/\text{SiO}_2$ Nanolaminate Coatings on Al

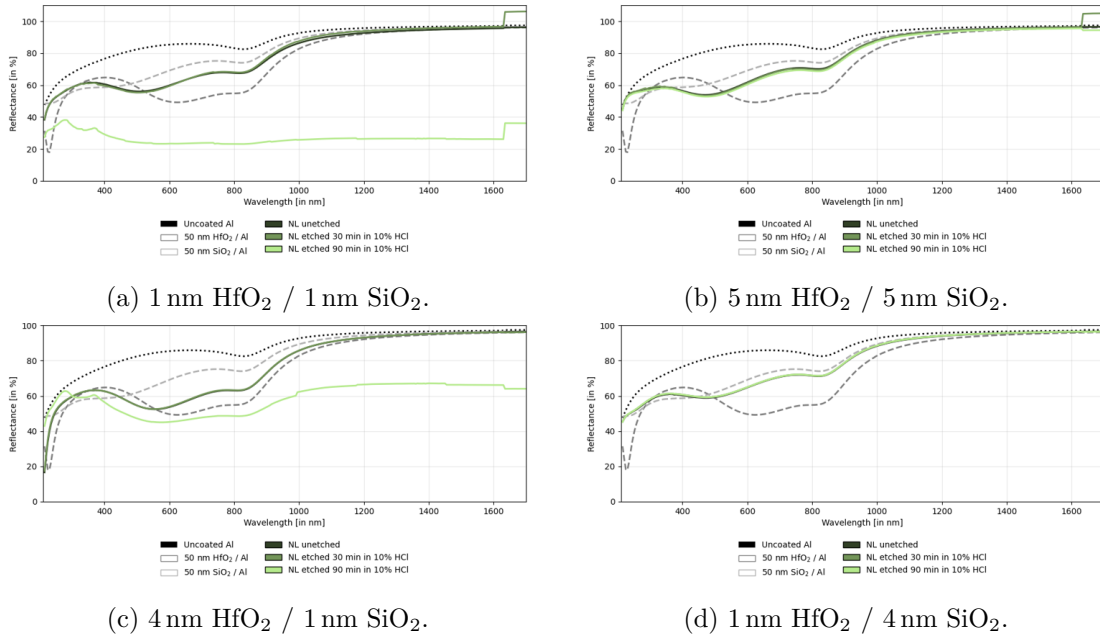


Figure A.17: Reflectance-based HCl protection screening of 50 nm $\text{HfO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on aluminium. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.

Protection Screening against HCl by $\text{HfO}_2/\text{SiO}_2$ Nanolaminate Coatings on Au

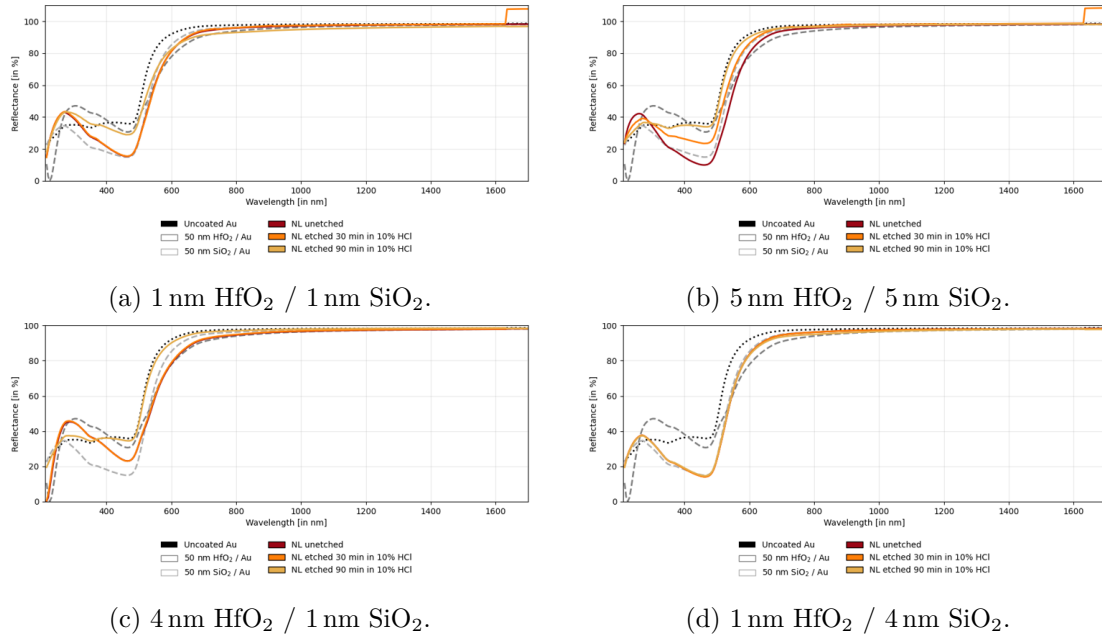


Figure A.18: Reflectance-based HCl protection screening of 50 nm $\text{HfO}_2/\text{SiO}_2$ nanolaminate coatings with different individual layer thickness ratios on gold. All nanolaminates were deposited on a 4 nm Al_2O_3 interlayer.

Bibliography

- [1] Erwin Kessels, Anjana Devi, Jin-Seong Park, Mikko Ritala, Angel Yanguas-Gil, and Claudia Wiemer. Atomic layer deposition. *Nature Reviews Methods Primers*, 5(1): 66, 2025. doi: 10.1038/s43586-025-00435-6.
- [2] Xiaohua Du, Kevin Zhang, Kathy Holland, Thomas Tomblor, and Martin Moskovits. Chemical corrosion protection of optical components using atomic layer deposition. *Applied Optics*, 48(33):6470–6474, 2009. doi: 10.1364/AO.48.006470.
- [3] H.-J. Chen, Y.-C. Chen, P.-C. Lin, et al. Study of atomic layer deposition nano-oxide films on corrosion protection of Al-SiC composites. *Materials*, 16:6149, 2023. doi: 10.3390/ma16186149.
- [4] David M. Fryauf, Andrew C. Phillips, and Nobuhiko P. Kobayashi. Critical processing temperature for high-performance protected silver mirrors. *Journal of Astronomical Telescopes, Instruments, and Systems*, 7(3):034002, 2021. doi: 10.1117/1.JATIS.7.3.034002.
- [5] A. I. Abdulagatov, Y. Yan, J. R. Cooper, et al. Al₂O₃ and TiO₂ atomic layer deposition on copper for water corrosion resistance. *ACS Applied Materials & Interfaces*, 3(12):4593–4601, 2011. doi: 10.1021/am2009579.
- [6] Lae Ho Kim, K. Kim, S. Park, Y. J. Jeong, H. Kim, D. S. Chung, S. H. Kim, and C. E. Park. Al₂O₃/TiO₂ nanolaminate thin film encapsulation for organic thin film transistors via plasma-enhanced atomic layer deposition. *ACS Applied Materials & Interfaces*, 6(9):6731–6738, 2014. doi: 10.1021/am500458d.
- [7] M. D. Groner, F. H. Fabreguette, J. W. Elam, and S. M. George. Low-temperature Al₂O₃ atomic layer deposition. *Chemistry of Materials*, 16(4):639–645, 2004. doi: 10.1021/cm0304546.
- [8] Zhen Zhu et al. Influence of plasma parameters on ultrathin Al₂O₃ films for moisture barrier applications. *Japanese Journal of Applied Physics*, 57:125502, 2018.
- [9] Janne-Petteri Niemelä, Barbara Putz, Gustavo Mata-Osoro, et al. Mechanical properties of atomic-layer-deposited Al₂O₃/Y₂O₃ nanolaminate films on aluminum toward protective coatings. *ACS Applied Nano Materials*, 5:6285–6296, 2022. doi: 10.1021/acsanm.2c01000.
- [10] Lae Ho Kim, Yong Jin Jeong, Tae Kyu An, Seonuk Park, Jin Hyuk Jang, Sooji Nam, Jaeyoung Jang, Se Hyun Kim, and Chan Eon Park. Optimization of Al₂O₃/TiO₂ nanolaminate thin films prepared with different oxide ratios for OLED encapsulation via plasma-enhanced atomic layer deposition. *Physical Chemistry Chemical Physics*, 18(2):1042–1049, 2016. doi: 10.1039/C5CP06713H.

- [11] G. Wang, Z. Wang, J. Ren, et al. Innovative stress-release method for low-stress flexible Al₂O₃ encapsulation films in OLED applications. *npj Flexible Electronics*, 9:94, 2025. doi: 10.1038/s41528-025-00468-7.
- [12] Jae-Hyun Kim, Ameer Farithkhan, Myung-Jin Jung, and Se-Hun Kwon. Enhanced corrosion resistance of SUS304 stainless steel via atomic layer deposited Al₂O₃/ZrO₂ nanolaminates. *Coatings*, 16(1):55, 2026. doi: 10.3390/coatings16010055.
- [13] Max Born and Emil Wolf. *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*. Cambridge University Press, Cambridge, 7 edition, 1999. ISBN 9780521642224.
- [14] M. A. Ordal, R. J. Bell, R. W. Alexander, L. L. Long, and M. R. Querry. Optical properties of the metals Al, Co, Cu, Au, Fe, Pb, Ni, Pd, Pt, Ag, Ti, and W in the infrared and far infrared. *Applied Optics*, 24(24):4493–4499, 1985. doi: 10.1364/AO.24.004493.
- [15] P. B. Johnson and R. W. Christy. Optical constants of the noble metals. *Physical Review B*, 6(12):4370–4379, 1972. doi: 10.1103/PhysRevB.6.4370.
- [16] Steven M. George. Atomic layer deposition: An overview. *Chemical Reviews*, 110(1):111–131, 2010. doi: 10.1021/cr900056b.
- [17] J. Kruger. John Wiley & Sons, 2011. ISBN 9780470872864. doi: 10.1002/9780470872864.ch2.
- [18] Joseph R. Davis. *Corrosion of Aluminum and Aluminum Alloys*. ASM International, 2000. ISBN 9780871706492.
- [19] T. E. Graedel. Corrosion mechanisms for silver exposed to the atmosphere. *Journal of The Electrochemical Society*, 139(7):1963–1970, 1992. doi: 10.1149/1.2069527.
- [20] R. L. Puurunen. A short history of atomic layer deposition: Tuomo suntola’s atomic layer epitaxy. *Chemical Vapor Deposition*, 2014. doi: 10.1002/cvde.201402012.
- [21] A. C. Jones and M. L. Hitchman. Chemical vapour deposition and atomic layer deposition. In *Handbook of Thin Film Deposition*. 2012. doi: 10.1002/9781118892671.ch12.
- [22] K. Pfeiffer, S. Shestaeva, A. Bingel, P. Munzert, L. Ghazaryan, C. van Helvoirt, W. M. M. Kessels, U. T. Sanli, C. Grévent, G. Schütz, M. Mathis, V. Hinrichs, M. Lux-Steiner, M. Bader, M. Wuttig, and A. Szeghalmi. Atomic layer deposition for coating of complex 3D optics. *Advanced Optical Technologies*, 2017. doi: 10.1002/opph.201700013.
- [23] Oxford Instruments. *FlexAL® II ALD System Manual*. Oxford Instruments. System Operation Manual.

- [24] É. O'Connor. ALD system and process insights. White paper, RhySearch, 2024.
- [25] M. D. Groner, S. M. George, R. S. McLean, and P. F. Carcia. Gas diffusion barriers on polymers using Al_2O_3 atomic layer deposition. *Applied Physics Letters*, 88: 051907, 2006. doi: 10.1063/1.2168489.
- [26] Karyn L. Jarvis and Peter J. Evans. Growth of thin barrier films on flexible polymer substrates by atomic layer deposition. *Thin Solid Films*, 624:111–135, 2017. doi: 10.1016/j.tsf.2016.12.055.
- [27] Gregory N. Parsons, Steven M. George, and Mato Knez. Progress and future directions for atomic layer deposition and ALD-based chemistry. *MRS Bulletin*, 36(11): 865–871, 2011. doi: 10.1557/mrs.2011.238.
- [28] Enric Garcia-Caurel, Antonello De Martino, Jean-Paul Gaston, and Li Yan. Application of spectroscopic ellipsometry and mueller ellipsometry to optical characterization. *Applied Spectroscopy*, 67(1):1–21, 2013. doi: 10.1366/12-06883.
- [29] G. Binnig, C. F. Quate, and Ch. Gerber. Atomic force microscope. *Physical Review Letters*, 56(9):930–933, 1986. doi: 10.1103/PhysRevLett.56.930.
- [30] Allen J. Bard and Larry R. Faulkner. *Electrochemical Methods: Fundamentals and Applications*. John Wiley & Sons, 2 edition, 2001.
- [31] J. R. Macdonald. Impedance spectroscopy. *Annals of Biomedical Engineering*, 20: 289–305, 1992.
- [32] Mark E. Orazem and Bernard Tribollet. *Electrochemical Impedance Spectroscopy*. John Wiley & Sons, 2 edition, 2017.

DEPARTMENT OF MICRO- & NANOTECHNOLOGY
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden
www.chalmers.se



CHALMERS
UNIVERSITY OF TECHNOLOGY