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DEPARTMENT OF ENGINEERING SCIENCE AND MECHANICS

DEVELOPMENT OF OPTICAL LIMITER MULTILAYER COATING SYSTEM FOR DIRECTED ENERGY BEAM REFLECTION

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SPRING 2020

A thesis submitted in partial fulfillment of the requirements for a baccalaureate degree in Engineering Science with honors in Engineering Science

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ABSTRACT

The development of directed energy warfare has presented a new set of technological challenges for the Department of Defense. In the military, directed energy weapons are used to dazzle and disable sensors; a defensive measure is needed to protect components from high energy attacks without compromising sensor functionality. This study aims to develop and optimize an optical limiter coating system to reflect all light at high irradiances in a specific wavelength range, while still allowing for transmission of low irradiant signal at one target wavelength in order to maintain communication functionality.

An optical limiter coating is comprised of a multilayer sandwich structure: two distributed Bragg reflectors (DBRs) are mirrored about a non-linear optic (NLO). The DBRs reflect light at a range of wavelengths determined by the refractive indices and thicknesses of the individual layers. The NLO material exhibits two photon absorption resulting in transmission at low irradiances and absorption at high irradiances. For this study, silica (SiO₂) and titania (TiO₂) were chosen as the two DBR materials and tungsten disulfide (WS₂) was chosen as the NLO.

In this study, mirrored DBRs were fabricated using electron beam physical vapor deposition (EB-PVD) with the ultimate goal of creating optical limiter coating structures. A series of three trials fabricated monolayers, DBRs, and mirrored DBRs to test process feasibility, reproducibility, and optical response. Coatings were characterized using x-ray diffraction (XRD) for phase identification, field emission scanning electron microscopy (FE-SEM) for cross-sectional coating thickness, and UV-Vis-NIR spectroscopy for optical response. From these methods, EB-PVD proved to be a feasible fabrication process for the SiO₂/TiO₂ material system and produced coatings with the desired optical response. However, processing variability had a large impact between samples, which shifted the effective wavelength range for each coating.

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ACKNOWLEDGEMENTS

First and foremost, I would like to thank my advisor, Dr. Douglas Wolfe, for his support and guidance over the past two years. Your experience and insight were invaluable to this thesis work as well as to my professional development. I would also like to thank the OL project team of Patrick Albert, Justin Reiss, and Sergei Stepanoff for being the best group of people I have ever had the pleasure of working with. It's been an honor to work with all of you and I will miss our time together. I would also like to thank the staff members of the Applied Research Lab Advanced Coatings Department, in particular Mr. Ryan Romesberg, Mr. Scottie Showers, and Mr. Tom Medill for their instruction, troubleshooting help, and for always having the answers to my questions. Working at ARL has taught me so much about research and teamwork, and I am forever grateful for those experiences.

I would next like to acknowledge the staff members at the Penn State Materials Research Institute for their time and expertise in facilitating materials characterization and analysis. I would also like to extend gratitude to HAMR Industries, and in particular, to Dr. Michael Schmitt, for providing the funding for this work.

I would like to thank the Engineering Science and Mechanics department, and in particular my advisor Dr. Gary Gray, for his endless support, friendship, and countless office hours over the past four years. Your enthusiasm and passion for teaching is unparalleled and I am honored to have been your student.

Lastly, I'd like to thank my family and friends for always supporting me and challenging me to strive for excellence. I have them to thank for helping to shape me into the person I am today. Many thanks to you all.

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CHAPTER 1: INTRODUCTION

1.1 – Project Motivation

Lasers have become a ubiquitous technology in systems for industries like communications, medicine, and manufacturing, as well as for the Department of Defense. The United States military invests heavily in research and development to advance both offensive and defensive technologies to protect our nation, and there has been a large push in recent years to develop both offensive laser technologies as well as defensive measures to prevent against laser attacks. In the military, directed energy beam lasers are used in advanced sensing and communication applications to attack weapons and to dazzle sensors. With laser technology rapidly progressing, defensive coatings with novel optical properties are being developed to protect sensing equipment and other components from high energy laser attacks. For communication equipment, protective coatings must fulfill defensive requirements without compromising the component's ability to send and receive data.

The current technology used to protect components is absorptive optical limiter coatings, which act as a sacrificial layer to absorb high intensity laser irradiance and dissipate the energy as heat. Research in absorptive coatings has employed material systems with non-linear absorption properties, which can be tailored to function as transparent coatings at low irradiances, but utilize two photon absorption phenomenon to absorb light at high irradiances. While this is an effective approach, the absorbed energy destroys these coatings after a single high energy attack, leaving the underlying components vulnerable after a single use. Therefore, a more permanent solution is needed that can withstand repeated high intensity attacks.

This program proposes to develop a reflective optical limiter designed to reverse the direction of energy and reflect light away from the underlying component, much like a mirror,

instead of sacrificially absorbing the energy. Reflective optical limiters would implement the same non-linear optic (NLO) materials used in absorptive coatings, but sandwich the NLO structure between two distributed Bragg reflectors (DBRs) that act as mirrors to reflect high intensity light away from the component. The desired optical effect is two-fold: the coating system could have 100% reflection at high energies while still allowing for outward transmission at low energies. In application, the nonlinear absorption layer would be transparent to allow for outward communication to transmit from the component through the coating at low energies, and utilize two photon absorption to protect the component and absorb the incident high energies associated with directed energy weapons.

1.2 – Project Goals

The objective of this research project is to develop and optimize a reflective optical limiter coating system. A reflective optical limiter is a multilayer thin film coating structure that is intended to reflect 100% of incident light at a specific range of wavelengths. The coating system is comprised of two Distributed Bragg Reflectors (DBRs) sandwiched between a defect monolayer with nonlinear optical properties. The two DBRs are made up of two dielectric materials in alternating layers, which are optimized to reflect light at a range of wavelengths. The aggregate optical response is a wide stopband of reflected wavelengths centered about a single transmission peak at a targeted communication wavelength specific to the communication device. At high intensities, the transmission peak response would be suppressed to allow for 100% reflection of harmful directed energy.

For this study, optical limiters will be developed using electron beam physical vapor deposition (EB-PVD). This project plans to conduct a series of three deposition matrices, the goals of which are outlined below:

- Matrix 1: Develop processing parameters to deposit monolayers of the desired materials system using electron beam physical vapor deposition (EB-PVD).
- Matrix 2: Optimize the deposition process developed in Matrix 1 to create Distributed Bragg Reflectors to test reproducibility and optical performance.
- Matrix 3: Develop and optimize mirrored DBR structures and evaluate optical performance to determine the feasibility of creating optical limiter structures.

The completion of these three matrices will give insight to the feasibility in successfully depositing a reflective optical limiter with the desired optical response. Both the deposition process feasibility as well as the optical response of the coatings will be used as metrics to evaluate this material system as a contender for use as an optical limiter.

1.3 – Ethics and Design Considerations

This research is funded through the Applied Research Lab as a defense contract with the United States Army. As such, a unique set of design considerations must be put into place to address safety, ethical, economic, and environmental concerns.

First and foremost, design measures for this study were taken to ensure the safety and well-being of researchers and the general public. For each experiment, all safety protocols were followed in accordance with the safety handbook of the Advanced Coatings department, including wearing proper personal protective equipment at all times, never conducting experiments alone in the lab, and using lab equipment safely by following standard operating procedures. Because some lab equipment have high electrical inputs, safety measures to protect researchers were put into place including proper training sessions, grounding requirements, safety interlocks, and lock out tag out procedures.

Engineers have the ethical responsibility of ensuring that the technology they develop is both aligned with their own moral code and the interest of the general public. The technology developed in this program will serve to defend United States equipment and personnel against directed energy weapons. If successful, this research has the potential to increase the tactical advantage of the US military, saving money, time, and assets, and ultimately protecting military servicemen and women. Protecting the United States' military technology from adversarial threats is favorable to public health and domestic security, and can therefore be considered an ethical venture.

Economic considerations were largely important in designing the experiments completed in this study. Since project funding was derived from US tax revenue, the experiments were frugally designed to maximize the amount of research performed within the given budget. To conserve fiscal resources, measures were taken to conduct sample preparation and characterization in-house rather than paying a premium for external research. Additionally, collaborative measures were taken within the project team to maximize output for each labor hour spent on the project. In general, characterization was performed in batches by designated team members to minimize equipment and labor costs.

From an environmental standpoint, design measures were taken to minimize energy consumption, resource usage, and waste material. To account for these factors, experiments were thoughtfully planned out prior to execution, with measures to minimize the electricity and water consumed by lab equipment by powering off or putting equipment in rest mode. To minimize waste, all material purchased for this study was used in its entirety prior to disposal, and efforts were made to use existing lab stock materials prior to purchasing new ones. All

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waste was disposed of in accordance with the guidelines set by the Penn State Environmental Health and Safety department as well as the Penn State Applied Research Lab.

CHAPTER 2: LITERATURE REVIEW

To gain a full understanding of the optical limiter coating system and its novel reflective properties, this chapter will discuss a review of the materials system, deposition techniques, characterization methods, and engineering considerations. Section 2.1 discusses each component of the optical limiter coating system, including the Distributed Bragg Reflectors (DBR) and the non-linear optical defect layer, with special emphasis on the desired optical response and materials selection. Section 2.2 explores the deposition considerations for optical limiter structures, specifically for Electron Beam Physical Vapor Deposition (EV-PVD), the deposition method used to create samples for this study. Section 2.3 provides the necessary background information on the methods of characterization employed to understand optical limiter coatings, including scanning electron microscopy (SEM), x-ray diffraction (XRD), spectroscopy, and ellipsometry techniques. Section 2.6 discusses the applications of optical limiter coating structures, specifically for advanced applications in the military for communications and sensing applications.

2.1 – Optical Limiter Coating System

The goal of this study is to fabricate a coating with novel reflective properties to protect sensor components from high energy incident light. In industry, current optical limiter coatings are purely absorptive – they absorb high intensity light and dissipate the energy as heat. Due to high heat generation, absorptive coatings are destroyed after a single attack, leaving underlying components vulnerable to repeat attacks. However, experimental work with reflective coatings have been fabricated to work against repeated high energy attacks [1]. Reflective optical limiters have the potential to protect sensors and other components from damage and to mitigate thermal degradation in the coatings, becoming a more permanent solution than previous sacrificial coating solutions. Instead of absorbing the heat from high energy beams, reflective optical limiters are

designed to reverse the direction of energy and reflect laser beams away from the underlying component. Optical limiters are not a single coating material, but rather, a multilayer coating system composed of a defect layer comprised of a non-linear absorption material sandwiched between two distributed Bragg reflectors (DBRs), which are perfect reflections of each other about the defect layer. This structure is illustrated by the schematic in Figure 2.1. Note that in this example, the two DBR structures are comprised of SiO₂ and Si₃N₄ bilayers and are perfect reflections about the GaAs defect layer.



Figure 2.1. Diagram of a reflective optical limiter coating structure by Vela et al., with two Distributed Bragg Reflectors composed of SiO₂ and Si₃N₄, and a GaAs defect layer [1].

In this section, both the DBR and defect layer components are discussed individually, as well as how each component functions in the full system to produce the desired optical response. The justification of material system selection for each component of the coating system will also be discussed.

2.1.1 – Distributed Bragg Reflector (DBR)

The first component of an optical limiter coating system is a Distributed Bragg Reflector. The two Distributed Bragg Reflectors in the optical limiter coating structure are each made up of two dielectric materials (A and B) in a periodic multilayer stack as shown in Figure 2.2, a structure designed to optimize reflection of light at a range of wavelengths [18]. The dielectric materials are chosen based on their difference in refractive index, which controls how light will behave through the material.



Figure 2.2. Schematic of a Distributed Bragg Reflector and the incident and reflected light through alternating layers of material a and b. Note the disparity between refractive indices $\eta_a > \eta_b$ and layer thicknesses $t_a > t_b$ [2].

Because the optics in a Distributed Bragg Reflector is governed by the reflection and refraction at the interface between the high- and low- refractive index materials, it is important to understand the physics of an incident electromagnetic wave at the boundary between the two dielectric layers. In general, at a material discontinuity with change in refractive index $\Delta \eta$ an oblique incident wave vector **k** with incident angle θ_i will reflect at angle θ_r and refract at angle θ_t as shown in Figure 2.3. Wave vectors, **k**, **k'**, and **k''**, all lie in the same plane perpendicular to the boundary, called the plane of incidence. The result is that angle of incidence θ_i will equal angle of reflection θ_r , or $\theta_i = \theta_r$ and the angle of refraction θ_t is related to the angle of incidence θ_i by Snell's law [19]:

$$\eta \sin \theta_i = \eta' \sin \theta_t \tag{2.1}$$



Figure 2.3. Reflection and refraction of wave vector k at oblique incidence of a material discontinuity [2]. From Equation 2.1 it is shown that as refractive index η increases at a material discontinuity with $\eta' > \eta$ the angle of refraction θ_t will be less than the angle of incidence θ_i and the transmitted wave k' will bend toward the normal vector n as shown in Figure 2.3. Conversely, when refractive index η decreases at a material discontinuity with $\eta' < \eta$ the angle of refraction θ_t will be greater than the angle of incidence θ_i and the transmitted wave k' will bend away from the normal vector n.

Suppose the same principle is applied to a material discontinuity with two boundaries, where a wave propagates through three domains with refractive indices η_1 , η_2 , η_3 where layer 1 and 3 are identical such that $\eta_2 > \eta_1 = \eta_3$ as shown in Figure 2.4.



Figure 2.4. Wave propagation through three domains with refractive indices η_1 , η_2 , η_3 [3].

In this case, at each boundary, the wave will reflect and refract through the medium, and the intensity of the transmitted wave will increase or decrease based on the phase causing constructive or destructive interference between rays. Because of this interference, the free-space wavelength λ_0 and the film thickness *d* will affect the phase and intensity of transmitted and reflected light, as discussed in Equations 2.2 – 2.4 [20].

Because the thickness and refractive index of the DBR layers determine the wavelength range of light that will be reflected, each thickness of the high- and low-refractive index materials in the DBR must be both accurate and precise. Deviation from intended layer thicknesses can result in reduction in reflectivity and shifting of the wavelength range over which the coating is reflective. With the optimization of layer thickness, the reflected light will have constructive interference, helping to achieve near 100% reflectance. Additionally, adding more layers to the DBR will increase interference and amplify the optical effect, as modeled in Figure 2.5.



Figure 2.5. Reflectance of a Distributed Bragg Reflector as a function of wavelength, at a range of layers in the DBR [3].

Another consequence of incident waves on the optical effect of a DBR is the incident angle. As shown in Figure 2.6, increasing the incident angle at which light hits the surface of the DBR shifts the wavelength range. Not only does the critical wavelength (λ_c) decrease, but the range of wavelengths that are reflected, called the photonic stopband ($\Delta\lambda_0$), also decreases. Figure 2.6 shows this trend from $\theta_i = 0^\circ$ (red) to $\theta_i = 60^\circ$ (blue) stepping by 10° for each plot.



Figure 2.6. Reflectance spectra of a DBR at different angles of incidence from 0° (red) to 60° (blue) in steps of 10° [4].

The overall structure of a DBR, constructed as shown in Figure 2.2, can be optimized to create mirrors out of multilayer thin dielectric films that target light at a specific range of wavelengths based on the refractive index and thickness of the layers. Layer thickness (l) is governed by the equation:

$$\eta_a l_a = \eta_b l_b = \frac{\lambda_0}{4} \tag{2.2}$$

meaning that each layers optical thickness is equal to $\frac{\lambda_0}{4}$, or a quarter wavelength of the incident light. The DBR exhibits near 100% reflectance at a specific range of wavelengths, as shown in Figure 2.7(a), called the photonic stopband $\Delta\lambda_0$ calculated using:

$$\Delta\lambda_0 = \lambda_c \sin^{-1} \frac{\eta_a - \eta_b}{\eta_a + \eta_b}$$
(2.3)

where λ_c is the critical wavelength at the center of the stopband:

$$\lambda_c = \frac{2}{m} (\eta_a l_a + \eta_b l_b) \tag{2.4}$$

 η_a and η_b are the refractive indices of each material, l_a and l_b are the layer thickness of each material, and *m* is the integer shift of the incident wave.

As discussed, the model for DBRs compute each optical layer thickness to be $\frac{\lambda_0}{4}$, or a quarter wavelength. However, if a layer of optical thickness $\frac{\lambda_0}{2}$ is to be inserted within the DBR, it is possible to transmit radiation at a targeted wavelength within the stopband, as shown in Figure 2.7(b). To simulate a layer with thickness $\frac{\lambda_0}{2}$, two $\frac{\lambda_0}{4}$ thick layers of the same material sandwich a very thin defect layer. This phenomenon is the reason that the two DBRs must be reflections of each other about the non-linear optical defect layer and the defect layer must be very thin, which will be discussed further in Section 2.1.3.



Figure 2.7. Model of % Reflectance as a function of wavelength for a Distributed Bragg Reflector (a) without and (b) with a cavity layer with optical thickness $\frac{\lambda_0}{2}$ [3].

2.1.2 – Non-linear Optical Defect Layer

In a Reflective Optical Limiter, the non-linear optical defect layer is centered about two DBRs. The characteristic property of the defect layer is its non-linear absorption under high irradiance. At low irradiance, the defect layer is dormant and can be modeled as a vacuum. However, at high irradiance, the defect layer becomes reflective. In an optical limiter structure, the defect layer determines the light intensity threshold above which light will absorb rather than transmit through the layer, caused by the novel optical property of two-photon absorption (TPA) during high power incident light. The TPA phenomenon occurs when two photons, rather than one, are absorbed due to the incident light reaching a threshold of irradiance [21]. Visually, at low incident power the defect layer appears transparent (transmission); as power increases the film appears opaque (absorption). Recall that in order to transmit a signal at a specific wavelength through a DBR as shown in Figure 2.7(b), there must be a centered layer with optical thickness $\frac{\lambda_0}{2}$ rather than $\frac{\lambda_0}{4}$. To accomplish this, the second DBR is flipped such that material B sandwiches each side of the defect layer. Additionally, the defect layer must be very thin, as to not change the direction of the low irradiance waves passing through. As such, the defect layer is modeled as a 2D monolayer made from a Transition Metal Dichalcogenide (TMD) material.

Transition Metal Dichalcogenides are semiconductors of the form MX₂ where M is a transition metal atom like Mo or W, and X is a chalcogen atom like S, Se, or Te [22]. TMDs have unique optoelectronic properties, and are widely used as 2D layers in electronic devices. Specifically, TMDs are known for their unique nonlinear optics such as higher harmonic generation, saturable absorption, and two-photon absorption [23]. In particular, the two-photon absorption is what allows TMDs to act as a 2D defect layer in optical limiters. TPA is attributed to 2D confinement of light, band edge resonance, and a strong excitonic effect. The thinner the

material layer, the higher the TPA coefficient. Characterized using a Z-scan technique, MoS₂ had a TPA coefficient of $7.62 \times 10^3 cm/GW$, and 1 to 3 layers of WS₂ had a TPA coefficient of $1 \times 10^4 cm/GW$, which is $10^3 - 10^4$ order higher than conventional bulk semiconductors [23].

2.1.3 – Optical Response of a Reflective Optical Limiter

In a reflective optical limiter, two DBR structures sandwich the non-linear defect layer. The desired optical response is that the optical limiter behaves as a Bragg mirror at low irradiance, and at high irradiance the TPA effects from the defect layer allow for outward transmission at a targeted wavelength [20]. In application, the nonlinear absorption layer would allow for outward communication to transmit through the coating at low incident power, and absorb incident high energy wavelengths when the coating is attacked with high power, as shown by the transmission graph in Figure 2.8.



Figure 2.8. Theoretical transmission of a reflective optical limiter coating system at a range of wavelengths [1].

2.1.4 – System Considerations

To successfully deposit a reflective optical limiter at a target wavelength, specific parameters need to be optimized for coating performance and stability. In particular, the materials used for each component of the coating, the number of layers in the two DBRs, the coating thickness, the phase stability, and the mismatch in coefficient of thermal expansion should all be considered.

2.1.4.1 Material Selection

DBR materials have been heavily researched, and there are many materials systems that can be used as building blocks for a DBR structure, including SiO₂, Si₃N₄, TiO₂, and Al₂O₃ [1]. When selecting materials for a DBR, the main concern is to select similar materials that will adhere well to both the substrate and to each other, but that still have large differences in refractive index to achieve the desired optical properties. From an initial review of materials systems used in optical limiter coating systems, the following table of material properties was created based on 4 material systems: SiO₂ and TiO₂, Si and Si₃N₄, TiO₂ and ITO, and Al₂O₃ and TiO₂ (Table 2.1). For the scope of this paper, only the SiO₂ and TiO₂ system will be discussed.

	Phase Transition	L	CTE		Vapor Pressure		Absoption Coefficent (cm^-1)			Refractive Indices		
Material	Phase	Temp. Range (°C) (1 atm)	(linear)	Toxicity	(Torr)	(°C)	$\lambda = 0.532 \mu m$	$\lambda = 1 \mu m$	$\lambda = 10 \mu m$	λ = 0.532µm	$\lambda = 1 \mu m$	$\lambda = 10 \mu m$
	Fused Silica	Metastable T<900°C	6.40E-07									
	α-Quartz	<573	5.00E-07	1							1.46	2.81
SiO2	β-Quartz	573-870		Nontoxic	1.00E-03	1050	4.74E+02	1.31E+02	6.69E+03	1.47		
	β-Tridymite	870-1470		1	1							
	β-Cristobalite	1470-1713										
	rutile (tetragonal P42/mnm)	0-1869										1.19
TiO2	Anatase (tetragonal I41/amd)	metastable < 600	9E10-6	Nontoxic	1.00E-03	1300	3.27E-02	0	1.88E+03	2.48	2.31	
	Brookite (orthorhombic Pbca)	metastable < 600										
	α-Si3N4 (hexagonal)	metastable over all T		Nontoxic								
Si3N4	β-Si3N4 (hexgaonal)	stable	3.30E-06	Nontoxic			0	0	1.45E+04	2.06	2.01	1.63
	γ-Si3N4 (cubic)	Only high pressure		Nontoxic	N/A							
TiN	c-TiN	All T	9.40E-06	Nontoxic				5.44E+05	No Data	1.23	2.19	No Data
Si	amorphous	-	2.60E-06	Nontoxic			2.07E+05	0	No Data	4.43	3.6	No Data
	rutile (tetragonal P42/mnm)	0-1869		Nontoxic	1.00E-03	1.00E-03 1300	3.27E-02		1			
TiO2	Anatase (tetragonal I41/amd)	metastable < 600	9E10-6					0	1.88E+03	2.48	2.31	1.19
	Brookite (orthorhombic Pbca)	metastable < 600										
	Amorphous to											
ITO	Cubic ITO + Rutile SnO2	< 1000	8.50E-06	Nontoxic	Subl	limes	9.97E+02	1.63E+03	No Data	1.91	1.3	N/A
	(Needs Annelaed after PVD)											
	Amorph.	Metastable <440°C										
	γ-A12O3 (cubic)	Metastable <700°C			1.007.02							0.79
41202	δ-A12O3 (hexagonal)			Nontorio		1550	No Doto	No Data	2.668-02	1.69	1.67	
AI205	κ-A12O3 (orthorhombic)	Metastable <730°C		Nontoxic	1.00E-05	1550	No Data	No Data	2.002+03	1.06	1.07	
	θ-A12O3 (monoclinic)	Metastable <1050°C	1.27E-05	1								
	α-A12O3 (trigonal)	<2051	7.20E-06									
	rutile (tetragonal P42/mnm)	0-1869				1300						1.19
TiO2	Anatase (tetragonal I41/amd)	metastable < 600	9E10-6	Nontoxic	1.00E-03		3.27E-02	0	1.88E+03	2.48	2.31	
	Brookite (orthorhombic Pbca)	metastable < 600										
	Fused Silica	Metastable <900°C	6.40E-07									
	α-quartz	<573	5.00E-07									
SiO2	β-quartz	573-870		Nontoxic	1.00E-03	1050	4.74E+02	1.31E+02	6.69E+03	1.47	1.46	2.81
	β-Tridymite	870-1470								1		
	β-Cristobalite	1470-1713										
AlSb	Cubic, ZnS strucutre	625.1	4.2E10-6	4	-	-	1.56E+05	7.76E+03	1.62E+02	4.7	3.4	3.1

Table 2.1. Material system properties for distributed Bragg reflectors at $\lambda = 0.532$, 1, and 10 μm .

Given the material systems of interest, lasing medium Nd: YAG is a standardized test for optical performance, based on a wavelength of 1.064 μm . Table 2.2 is a comparison of each material system at the wavelength of interest based on a standard Nd: YAG laser.

Lasing Medium	target λ (λc) (μm)	Material	Refractive Index	Individual Layer Thickness (nm)	Stopband Width (nm)	Minimum Number of Bilayers	Total Thickness (µm)	Reflectivity of Particle	
NA VAC	1.064	ITO	1.3	205	420	7	2.18	0.9995	
Nu. TAG	1.004	TiO ₂	2.5	107	430	1			
NH VAC	1.064	Al ₂ O ₃	1.7	159	266	10	2 20	0.0007	
NU. TAU	1.004	TiO ₂	2.5	107	200	12	5.20	0.9997	
NH VAC	1.064	SiO ₂	1.5	182	250	0	2.01	0.0007	
Na: YAG	1.064	TiO ₂	2.5	108	352	9	2.61	0.9997	
NI VAC	1.064	Si3N4	2.0	132	200	0	1.65	0.0000	
Na: YAG	1.064	Si	3.6	74	389	8	1.65	0.9996	

Table 2.2. Comparison of material system physical and optical properties based on Nd: YAG solid state lasing medium.

For this study, only the SiO₂ and TiO₂ system will be studied. This material system can be tailored to optimize performance over several laser types, including solid state, gas-ion, gas, and semiconductor, as shown in Table 2.3.

Table 2.3. Comparison of SiO₂ and TiO₂DBR material system tailored for different lasing mediums: Nd: YAG, ND: Glass, and CO₂.

Lasing		target λ	Refractive Indices		Optical band gap	Bilayer thicknesses		
Laser Type	Laser Type Medium		η_ (SiO ₂)	η_+ (TiO ₂)	Δλ (μm)	l _a (SiO ₂) (μm)	l_{b} (TiO ₂) (µm)	
Solid state	Nd: YAG	532	1.475	2.671	198.263	90.169	49.787	
Solid state	Ti: Sapphire	700	1.474	2.549	240.992	118.686	68.647	
Gas-Ion	Krypton	775	1.473	2.527	263.164	131.526	76.660	
Semiconductor	InGaAs	980	1.471	2.488	324.246	166.573	98.471	
Solid state	Nd: Glass	1060	1.470	2.480	348.743	180.238	106.872	
Solid state	Nd: YAG	1064	1.470	2.479	349.793	180.921	107.321	
Gas	HeNe	1152	1.470	2.471	376.876	195.948	116.538	
Solid state	Er: Glass	1540	1.443	2.433	506.414	266.763	158.219	
Gas	CO ₂	10000	2.812	1.388	-4403.808	889.110	1801.166	

After a review of the materials systems and properties, the two materials selected for this particular study, SiO₂ and TiO₂ were chosen because of their compatible phase stability, coefficient of thermal expansion, vapor pressure, low absorption coefficient, and large difference in refractive indices at 1.064 μm . Figure 2.9 shows the difference in refractive index between thin films of SiO₂ and TiO₂ from different reference sources at wavelengths ranging from 0 to 14 μm . Note that refractive index through a medium is dependent on the wavelength of incident light. Refractive index is directly related to the speed of light through a medium; as the speed changes the light will bend, or refract, through a medium. Since speed is simply the product of frequency of the light and wavelength, and frequency is constant for a particular light source, the refractive index will change as a function of wavelength for each sample tested.



Figure 2.9. Refractive indices of thin film SiO₂ and TiO₂ as a function of wavelength from 0 to 14 microns [5]–[8].

Additionally, the material properties shown in Table 2.4 outline the SiO₂ and TiO₂ material system.

Material Property	SiO ₂	TiO ₂
Coefficient of Thermal Expansion	6.4 x 10-7 / °C (fused silica)	9.0 x 10-6 / °C
Density	2.65 g/cm ₃	4.23 g/cm ₃ (rutile) / 3.78 g/cm ₃ (anatase)
Melting Temperature	1710°C	1843⁰C
Crystal Structure	Tetrahedral (quartz)	Tetragonal (rutile and anatase)
Refractive Index ($\lambda = 1 \ \mu m$)	1.46	2.47

Table 2.4. SiO₂ and TiO₂ material properties including CTE (at room temperature), density, melting temperature, crystal structure, and refractive index [5].

2.1.4.2 Number of Bilayers

The number of bilayers in an optical limiter coating system will determine the optical performance, namely, percent reflectivity. Since the target reflectivity is 100%, the following model was created to determine the minimum number of layers needed to achieve 100% reflection. Minimizing the number of bilayers is an important factor to decrease the overall coating thickness, thus reducing residual stresses as well as the cost of producing the coating. Figure 2.10 shows that the % reflectivity reaches a theoretical maximum at 6 bilayers; however, the initial target for depositions in this study will remain at 10 bilayers in order to account for variability in layer thickness and processing parameters.



Figure 2.10. Percent reflectivity versus the number of bilayers in a SiO₂/TiO₂ DBR structure at 10 μm incident light.

2.1.4.3 Phase stability

Ensuring that the chosen material system is stable both during fabrication as well as during coating use is important in avoiding delamination and coating failure. Optical limiter coatings can experience high temperatures from heat generation during usage, and unwanted phase changes could negatively impact the coating's ability to function properly. Thus, when selecting a material system, it is important to understand the phase diagrams of the materials as shown in Figure 2.11 and Figure 2.12, and how they interact at different temperatures. Phases of interest for SiO₂ are amorphous (fused silica) and α -quartz, and phases of interest for TiO₂ are the three most well-known polymorphs anatase (tetragonal), rutile (tetragonal), and brookite (rhombohedral), as shown in the composite phase diagram of TiO₂ in Figure 2.12 [10].



Figure 2.11. (Left) binary phase diagram of the Si-O system and (right) unary phase diagram of SiO₂ [9].



Figure 2.12. (Left) binary phase diagram of the Ti-O system and (right) unary phase diagram of TiO₂ [10].

2.1.4.4 Structure Development

During thin film deposition, the rearrangement of atoms on the surface of the substrate impacts the structure of the coating. When vapor particles reach the surface of the substrate, they adsorb to the surface and can either diffuse along the surface or reevaporate in a process called desorption; this process is dependent on the relative amount of energy of the atoms and the substrate. Through the process of adsorption and surface diffusion, nucleation occurs in which clusters of atoms form at the surface. These clusters eventually form stable nuclei, which grow into grains as the basis of the morphology of the coating. Increasing the substrate temperature can increase the mobility of atoms at the substrate surface. This phenomenon is best visualized by the structure zone model, which relates coating morphology to homologous temperature (Th), defined as the ratio of substrate temperature to melting point of the film (Equation 2.5).

$$T_h = \frac{T_{substrate}}{T_{melt,film}}$$
(2.5)

A schematic of the structure zone model is shown in Figure 2.13. Note that as homologous temperature increases, grain growth increases from fine grain quenched growth due to low surface

diffusion, to granular/columnar epitaxy caused by surface diffusion, and finally large grain growth caused by bulk/surface diffusion.



Figure 2.13. Structure zone model of a thin film and its effect on surface roughness as diffusion occurs [11].

2.2 – Deposition of Optical Limiters

Choosing a viable deposition technique is equally as important as selecting a material system in order to fabricate a reflective optical limiter successfully. For this study, Electron-Beam Physical Vapor Deposition (EB-PVD) is used to deposit DBR structures as well as the tungsten defect layer. EB-PVD was chosen for its ability to control deposition rate and coating thickness while flowing oxygen to create multilayer oxide coatings. To create WS₂ while minimizing chamber gas contamination, the samples will be pulled from the EB-PVD vacuum chamber after the tungsten is deposited and sulfidized in a modified Dean's rig prior to depositing the second DBR.

2.2.1 – Electron Beam Physical Vapor Deposition (EB-PVD)

Electron-Beam Physical Vapor Deposition (EB-PVD) is a type of PVD process that uses a focused electron beam to thermally evaporate material in a high vacuum chamber. The electron

beam is produced via thermionic emission from a tungsten filament which bombards a target material with electrons, causing the source material to vaporize. The high vacuum within the chamber allows the locally pressurized material vapor to disperse within the chamber and deposit on all surfaces in a direct line-of-sight, namely the substrates. A schematic of the EB-PVD process is shown in Figure 2.14, highlighting the path of the electron beam as well as the direction of evaporated or sublimated material.



Figure 2.14. Schematic of the Electron Beam Physical Vapor Deposition process, showing material transport process from target material to substrate via electron beam bombardment [12].

2.2.1.1 – EB-PVD Process Overview

The goal of the Electron Beam Physical Vapor Deposition process is to evaporate a target material into a material vapor cloud within the chamber, then solidify the material on the substrate surface. As shown in Figure 2.14, the target material sits in an ingot which is thermally regulated with chilled water. To initiate the evaporation process, power is supplied to the tungsten filament at a specific voltage and current, which yields an electron beam. The electron beam is bent 270

degrees by a magnet, which directs the beam onto the target material. The incident electrons from the electron beam excite the target material and cause it to experience a phase change, which forms a vapor cloud of target material in the chamber and coats the substrate [24]. A schematic of this process is shown in Figure 2.15.



Figure 2.15. Components of an Electron Beam Physical Vapor Deposition Chamber [13].

2.3 – Characterization Methods

To evaluate the effectiveness of fabricated coatings, several characterization techniques are needed. In collaboration with the Penn State Materials Characterization Lab (MCL), instrumentation techniques including scanning electron microscopy (SEM), x-ray diffraction (XRD), UV-Vis-NIR spectroscopy, and ellipsometry could be used. The following briefly discusses the physical principles and use cases of each technique.

2.3.1 – Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a characterization technique that uses a focused beam of electrons to scan a solid sample and produce a contrast map of secondary electrons, or backscattered electrons for more defined Z elemental contrast. For this study, a Thermo Scientific Apreo scanning electron microscope was used to image sample surface morphology, calculate thickness of cross-section and fracture surfaces, and identify sample elemental composition using energy dispersive spectroscopy (EDS).

2.3.2 – X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is used to determine atomic structure of crystalline materials. For this study, a Philips X'Pert model MPD system was used to perform x-ray diffraction scans using $\theta - 2\theta$ Bragg-Brentano scan geometry. In XRD scans, incident x-rays collide with electrons on a test specimen and elastically scatter x-rays in a diffraction pattern. This pattern yields information about the electron distribution in the material, and therefore can be used to determine crystallographic order on the atomic scale. For a given set of lattice planes with inter-plane distance d, incident wavelength λ diffraction peaks occur at positive integers n = 1,2,3,...,i in accordance with Bragg's Law:

$$2d_{hkl}\sin\theta = n\,\lambda\tag{2.5}$$

2.3.3 – Ultraviolet-Visible (UV-Vis) Spectroscopy

The Perkin-Elmer Lambda 950 is a high performance UV/Vis/NIR spectrophotometer capable of collecting transmission, reflection, and absorption data from wavelengths ranging from 200 nm to 3000 nm. Specifically, variable angle transmission, diffuse transmission, specular reflectance, diffuse reflectance, and total reflectance spectra can all be measured [15]. Figure 2.16 shows a schematic of the spectrophotometer optical design, including the 150 mm integrating sphere.



Figure 2.16. Optical design of the 150 mm integrating sphere for the Perkin-Elmer Lambda 950 UV-Vis-NIR Spectrophotometer [14], [15].

2.3.4 – Ellipsometry

Ellipsometry is an optical technique used to measure properties of thin films like refractive index, composition, surface roughness, thickness, and conductivity [25]. The J.A. Woollam Ellipsometer is used in this study to measure refractive index of deposited films. The Woollam Ellipsometer is equipped with NanoMetrics 8000X SE software to model materials based on many different numerical methods. In particular, the Cauchy thin film model on the software can also be used to back-calculate film thickness, but is dependent on the quality of the model for each material and as such should be used with digression. If film thickness is known, it can be a fixed input to the model for increased accuracy. Figure 2.17 shows a schematic of an ellipsometer and the reflection and refraction patterns within each layer of material.



Figure 2.17. Schematic of an ellipsometer showing incident linearly polarized light and reflected elliptically polarized light [16].

2.4 – Engineering Considerations

It is important for engineers to consider product development through the entire life-cycle of their product to ensure that all design specifications and industry needs are met. The primary engineering considerations for optical limiters are material selection, material scarcity, deposition technique, coating lifespan, manufacturability, and cost of the coating system. Material selection for the system will dictate not only the optical properties but also the adhesion and performance of the coating system. Materials must also be selected that are cost effective and available, so material scarcity is an important consideration. The deposition conditions will ultimately determine phase stability of the coating system. A phase change during operation could lead to delamination and coating failure, so material selection, deposition processing parameters like temperature and deposition rate, and post-deposition annealing procedures are all important to achieve phase stability. Deposition technique and material selection are critical as deposition selection limits material selection, and vice versa. In particular, deposition technique for both the DBR and the defect layer, including defect layer sulfidation, is an important consideration as each changeover in vacuum process takes time and money during the fabrication process and can affect coating adhesion. Residual stresses from CTE mismatch could cause spalling and failure of the coating, so the number of layers and thickness of the coating must be examined. Additionally, the time and cost of coating fabrication and scalability to manufacturing should be considered. In order for reflective optical limiter coatings to be viable in industry, each of these factors must be carefully considered together as a system.

CHAPTER 3: EXPERIMENTAL PROCEDURE

This chapter discusses the experimental methods used in this study to fabricate and characterize optical limiter coatings. Section 3.1 discusses an overview of film deposition by electron beam physical vapor deposition, including the substrate preparation, chamber setup, and deposition parameters. Section 3.2 gives an overview of the analytical characterization methods used to test coating optical performance and determine its material structure and properties.

3.1 – Optical Limiter Deposition

Electron beam physical vapor deposition (EB-PVD) was chosen as the preferred deposition technique for fabricating DBRs. The primary advantages of EB-PVD include a high deposition rate, structural and morphological control of the film, and ability to evaporate a variety of different material systems. For oxide DBR material systems, particularly the TiO₂/SiO₂ DBRs developed in this study, EB-PVD provides unique processing flexibility to tailor composition, microstructure, and performance.

3.1.1 – Substrate Preparation

To standardize and correlate data collected across several months of depositions, a standard substrate preparation procedure was used for each EB-PVD deposition. For all depositions, three $2 \ cm \times 2 \ cm$ silicon wafer squares and three $2 \ cm \times 2 \ cm$ optically graded fused silica squares were used in a stainless steel substrate holder for a total of 6 samples per deposition. A stainless steel substrate mask was made to standardize the location of each sample (Figure 3.1).


Figure 3.1. Substrate mask with three 2 cm x 2 cm silicon and three 2 cm x 2 cm fused silica substrates.

For DBR trials, an additional 1"x1" 316 corrosion resistant stainless steel square substrate was tack-welded onto the substrate mask to test for coating adhesion on metallic surfaces. 316 steel was purchased from McMaster-Carr at 1" x 24"x 1/8" and cut using a diamond blade. To obtain a mirror finish, these stainless steel substrates were ground with water lubrication using 320, 600, 800, and 1200 grit silicon carbide paper, and polished using 1 μ m and 3 μ m polishing solution with diamond extender and 0.5 μ m colloidal silica solution.



Figure 3.2. Substrate mask with 1"x1" 316 stainless steel square tack-welded to surface.

To clean samples prior to deposition, substrates were ultra-sonicated in acetone at 40°C for 10 minutes, ultra-sonicated in methanol at 40°C for 10 minutes, rinsed with methanol, and dried with N₂. To mark the orientation of each sample within the substrate mask, a small V was etched into the lower right-hand corner of the back side of each sample in positions A-F (Figure 3.3).



Figure 3.3. Reverse side of substrate mask with sonicated (A-C) silicon and (D-F) fused silica substrates.

The resulting samples have standard surface preparation and size, helping to standardize characterization and test coating properties. An example of coated fused silica and silicon is shown in Figure 3.4. The color gradient on the outside edges of each sample are caused by thickness variations across the surface of the coating. Because the substrate mask is 0.2" thick, a boundary layer forms at the step edge of the mask/substrate interface, causing the coatings to thin on the edge boundaries as shown by the color gradient from red to green in Figure 3.4a. Additionally, because EB-PVD is a line of sight process, the sample location (A-F in Figure 3.3) within the substrate mask causes uneven coating thicknesses, as coatings near the edge of the substrate mask will experience an uneven thickness gradient as seen by the gradient at the top in Figure 3.4b.



Figure 3.4. Optical limiter coating deposited on (a) optically graded fused silica and (b) silicon substrates.

3.1.2 – Electron Beam Physical Vapor Deposition (EB-PVD)

For the deposition of OL coatings, the Denton Vacuum chamber (Denton Vacuum, Inc. (DV-SJ/26)) was used (Figure 3.5), located in the Applied Research Laboratory Advanced Coatings Department. A review of the operation procedures for this equipment can be found in Appendix A. The chamber is approximately $30'' \times 26'' \times 26''$ and with a volume of approximately $0.3 m^3$. Two glass window ports on the chamber door allow for viewing the deposition process in situ.



Figure 3.5: (Left) Denton vacuum chamber and (right) control panel [17].

The chamber interior, as pictured in Figure 3.6, is lined with aluminum and stainless steel foil to keep evaporated material from coating the chamber walls and to assist in chamber clean-up and preparation between depositions. Key components, like the heater and hearth shields, deposition shutter, and substrate mask, are grit-blasted prior to each deposition.



Figure 3.6. (Left) Denton EB-PVD chamber interior, lined with stainless steel and aluminum foil and (right) stainless steel heater and water-cooled copper hearth.

As shown in Figure 3.6, a stainless steel heater with a molybdenum element is used to increase the substrate temperature for depositions. The upper temperature limit of the heater is 650°C, and temperatures used for depositions in this study range from room temperature ~25°C to 600°C. A stainless steel heater shield lines the interior of the heater to protect the heater from evaporated material, and is grit-blasted during chamber cleaning to mitigate contamination and re-evaporation of adsorbed material on the liner. The chamber hearth contains four copper crucibles that are thermally regulated with chilled water. Only one crucible is exposed to the electron beam while the other three are protected by the copper housing, allowing for multilayer depositions with different source materials in each crucible. A schematic of the EB-PVD process is shown in Figure 3.7. The electron beam (Temescal model STIH-270-2MB) assembly consists of a beam former and an electron-emitting tungsten filament.



Figure 3.7. Schematic of EB-PVD process showing line-of-sight evaporation from source to substrate.

For this study, the ion beam source (IBS) was used to pre-clean the substrates for ~ 10 minutes prior to each deposition. Bombarding the substrates with ions removes any remaining particulates from the surface and is the final step in preparing the sample surface for deposition.

IBS parameters used for pre-clean in this study were 300 mA (fixed) and ~600 V (controlled by gas flow). Because the coating material system is comprised of oxides, a background gas of O_2 was chosen for IBS to create a oxygen rich environment on the sample surface and to increase coating adhesion.

3.1.2.1 – Deposition Parameters

When operating the Denton EB-PVD system, several processing parameters must work in conjunction to control coating properties, including chamber pressure, gas flow, temperature, electron beam current, voltage, and beam pattern. Typical PVD processes range from 10-5 – 10-9 Torr, but for the purpose of this study and given the standard pressure ranges of the Denton vacuum system, pressure was held at ~10-4 Torr. The Denton chamber uses a dual-pump system, first a rough mechanical pump brings the chamber to low vacuum, and then a cryogenic pump removes the remaining atmosphere to achieve high vacuum. During coating depositions, chamber pressure was controlled via gas flow. For this study, ~50-100 sccm of O2 gas was used to maintain a pressure of ~10-4 Torr. In addition to chamber pressure and gas flow, deposition temperature is an important factor in achieving the optimal coating properties. Initial trials were conducted to determine deposition rate and coating structure for single layer materials prior to fabricating multilayer stacks. For these trials, temperatures of 300°C, 400°C, 500°C, and 600°C were compared. Ultimately, DBR and optical limiter mirrors were fabricated at 500°C for reasons further discussed in the following chapter.

For initial trials, after temperature was determined, deposition rates were established to create repeatable processing parameters and to understand the effect of deposition rate on coating microstructure. Primary parameters controlling deposition rate via the electron beam source were e-beam voltage and current. For these trials, voltage was fixed at 5.3 kV, while current varied

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from 30-200 μ A, increasing with increasing desired deposition rate. Not only were e-beam current and voltage important factors for deposition rate, but also the electron beam pattern was standardized to create repeatable deposition rates. For the Denton chamber, latitudinal and longitudinal beam frequency can vary incrementally from 1 to 10. For this study, latitudinal frequency was set to 1 and longitudinal beam frequency was set to 5, as these values were found to create uniform coverage and beam velocity over the surface of the source material. Additionally, beam position and sweep were manually adjusted and recorded to standardize the area in which the beam was evaporating the source material, as a change in melt pool size would also impact deposition rate.

With regards to chamber setup, physical geometries within the Denton chamber were standardized to mitigate changes in processing parameters. These constants included a standard substrate height of 11.5" between evaporant source and substrate mask and a standard location near the top of the chamber for the quartz crystal monitor.

3.2 – Analytical Characterization Techniques

In conjunction with fabrication, characterization was performed during the development of optical limiter coatings to benchmark coating performance and tailor coating properties. Primary analytical characterization methods included scanning electron microscopy, x-ray diffraction, uvvisible spectroscopy, and ellipsometry.

3.2.1 – Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed to characterize coating surface morphology, fracture surfaces, and polished cross-sections. Instruments used included an Apreo SEM, Zeiss Merlin FESEM, and Zeiss Gemini (G500) SEM. SEM micrographs were used to determine coating thickness values and to analyze defects and coating uniformity. Fractured Si wafers were mounted on a 90 degree SEM mount. Because of the nonconductive nature of the samples, a 5 nm iridium coating was used on polished cross-sections to enable SEM data collection. For this study, secondary electron SEM micrographs were used to increase the contrast between disparities in atomic (Z) number, allowing for more distinguished material phases within the micrograph and to contrast alternating layers in the coating structure. Backscattered electrons are elastically scattered out of the test specimen, and materials with a higher atomic number phase have a larger probability of producing a backscattered electron, therefore producing areas of brighter contrast in the micrograph compared to lower atomic number materials.

3.2.2 – X-Ray Diffraction (XRD)

X-Ray diffraction (XRD) was used to determine atomic structure of crystalline materials. For this study, a Philips X'Pert model MPD system was used to perform X-Ray Diffraction scans using $\theta - 2\theta$ Bragg-Brentano scan geometry. These scans were performed at low angular sweep speeds and at small step sizes in order to increase counts and differentiate peaks from background noise. For the purposes of this study, scans were performed from 20 to 80 degrees.

3.2.3 – Ultraviolet-Visible Spectroscopy

For this study, a Perkin-Elmer Lambda 950 UV-Vis-NIR spectrophotometer was used to collect transmission, reflection, and absorption data from wavelengths $\lambda = 400 nm$ to $\lambda = 2000 nm$. A 150 mm integrating sphere was used to capture total reflection measurements. All data was collected from a ~5mm x 5mm area in the center of each sample, normal to the plane of the coating. Coatings deposited on fused silica were used for data collection via this technique, as this substrate is nearly 100% transparent in the UV-Vis-NIR range. Using an optically transparent substrate provides the assumption that all measured interference occurs through the coating.

3.2.4 – Ellipsometry

In this study, the J.A. Woollam Ellipsometer was used to measure refractive index of deposited films. The Woollam Ellipsometer is equipped with NanoMetrics 8000X SE software to model materials based on many different numerical methods. In particular, the Cauchy Thin Film model on the software was used to determine refractive index and to cross-reference film thickness.

CHAPTER 4: RESULTS AND DISCUSSION

This chapter outlines the results of a series of three matrices of trials performed to determine the material properties of monolayers and DBRs using SiO₂ and TiO₂. Several combinations of SiO₂ and TiO₂ coating structures were deposited via electron beam physical vapor deposition, starting with monolayers to establish deposition rates, followed by multilayer DBR structures and mirrored DBRs to create optical limiter coating structures. This progression from monolayer to DBR structure was designed to build the relationship between processing parameters, coating structure, material properties, and coating performance. Samples were characterized using x-ray diffraction for phase identification, FE-SEM to determine coating thickness and morphology, and UV-Vis spectroscopy to test optical response.

In this chapter, both qualitative and quantitative results from Matrices 1-3 (monolayers, DBRs, and mirrored DBRs) are presented alongside data discussion and analysis. Matrix 1 was used as a baseline to establish deposition rates and temperatures for each material (TiO₂ and SiO₂) independently through monolayer depositions. Next, Matrix 2 deposited DBR structures to test optical performance and reproducibility based on consistent deposition parameters. Finally, the goal of Matrix 3 was to optimize the fabrication of mirrored DBR coating structures. With the culmination of data from Matrices 1-3, the process-structure-property-performance relationships of optical limiter coatings can be established.

4.1 – Matrix 1: TiO₂ and SiO₂ Monolayers

Prior to depositing any multilayer structures, monolayers of TiO₂ and SiO₂ were deposited to establish deposition rates using the Denton vacuum EB-PVD system. The parameters used during this series of depositions is summarized in Table 4.1. From previous trials using the Denton system, a preliminary substrate temperature of 500°C and target QCM rates of 2 Å/s for TiO₂

and 5 Å/s for SiO₂ were used. The resulting coating cross-sections are shown in the FE-SEM images in Figure 4.1. Note that the average final thickness values were 154.9 nm and 287.8 nm for TiO₂ and SiO₂, respectively.

Run ID	Temp (°C)	QCM Target Rate (Å /s)	QCM Target Thickness (k Å)	QCM Average Rate (Å /s)	QCM Final Thickness (k Å)	Measured Thickness (nm)	Elapsed Time (min)	Calculated Rate (Å /s)
D190918-1 1 layer TiO2	500	2	1	1.9	1.00	154.9	11:00	2.35
D190919-1 1 laver SiO2	500	5	1	4.9	1.01	287.8	9:00	5.33

Table 4.1. Summary of Matrix 1 deposition parameters to deposit TiO2 and SiO2 monolayers.



Figure 4.1. FE-SEM of polished cross-sections of (a) TiO₂ and (b) SiO₂ monolayers deposited on silicon wafers.

From this matrix of monolayers, subsequent depositions used a simple proportion as shown in Equation 4.1 to calculate a new thickness baseline for the next deposition:

$$\frac{QCM \ thickness}{Measured \ thickness} = \frac{New \ QCM \ thickness}{Target \ thickness}$$
(4.1)

where QCM thickness is the final readout of the quartz crystal monitor, measured thickness is determined via cross-section FE-SEM image, and target thickness is calculated using Equations 2.2 - 2.4, as discussed in Chapter 2. This same proportion will be used to baseline multilayer depositions by first averaging the thickness values of each layer for each material, then solving for the new QCM thickness based on average values for *n* bilayers, as shown in Equation 4.2.

$$\frac{\sum_{i=1}^{n} (QCM \ thickness)_{i}}{\sum_{i=1}^{n} (Measured \ thickness)_{i}} = \frac{New \ QCM \ thickness}{Target \ thickness}$$
(4.2)

4.1.1 – TiO₂ Monolayers as a Function of Temperature

In addition to determining deposition rates, Matrix 1 was used to establish a stable deposition temperature for all subsequent SiO₂/TiO₂ depositions. After studying the phase stability of SiO₂ and TiO₂ in Chapter 2 (Figure 2.11-2.12) over the temperature range of the Denton system $(25^{\circ}\text{C} - 650^{\circ}\text{C})$, only TiO₂ was found to experience a phase change between anatase and rutile in this range, while SiO₂ remained α -quartz regardless of deposition temperature. To further investigate TiO₂ phase stability, TiO₂ monolayers were fabricated at varying deposition temperatures of 300°C, 400°C, 500°C, and 600°C. The purpose of this matrix was to evaluate the coating crystal structure and phase of TiO₂ as a function of temperature. The deposition parameters used in each of the four runs in this matrix are summarized in Table 4.2. Note that while O₂ flow rate changes from 67 sccm to ~100 sccm between runs 1 to 2, this was an intentional change to keep pressure constant at 7×10^{-4} Torr.

Table 4.2. Depositio	n parameters of Ti	O2 monolayers,	deposited at	300°C,	400°C,	500°C,	and 6	500°C
Electron beam voltag	e held constant at !	5.3 kV.						

Run #	Run ID	Deposition Time (min:sec)	Substrate Temp (°C)	O ₂ Flow Rate MFC1 (sccm)	QCM Rate (Å/s)	QCM Thickness (kÅ)	Average Coating Thickness (nm)	Dep. Rate (nm/s)	Evap. Rate (g/min)
1	D191022-1	4:18	300	67	5	0.614	141	0.546	0.0024
2	D191023-1	5:33	400	100.1	2	0.618	223	0.669	0.0012
3	D191023-2	4:52	500	99.4	2	0.617	169	0.8	0.0008
4	D191029-1	8:00	600	100	3.8	0.701	303	0.631	0.0006

Digital images of the four depositions of TiO₂ monolayers are shown in Figure 4.2. Note that color differences between samples are caused by differences in coating thicknesses interacting with the electromagnetic spectrum, as different thicknesses refract light at different angles.



Figure 4.2. Digital images of TiO₂ monolayers deposited on fractured Si wafers at (a) 300°C, (b) 400°C, (c) 500°C, and (d) 600°C.

GIXRD was performed on monolayers of TiO2 to determine the phase present in each



coating (Figure 4.3).

Figure 4.3. GI-XRD of TiO₂ monolayers on amorphous fused silica substrate deposited at 300°C, 400°C, 500°C, and 600°C.

All four scans were taken on amorphous fused quartz substrates, which explains the amorphous hump in the low 20 range. While a phase change from anatase to rutile was expected between 500°C and 600°C, the 600°C sample remained in the anatase phase, as shown in Figure 4.3. Some rutile phase was present in the sample deposited at 500°C but not in the 600°C sample, which could have been a result of variations in deposition processing or of the GI-XRD instrumentation.

In GI-XRD, the diffraction pattern is collected from planes parallel to the substrate surface, so it is sometimes difficult to correlate relative peak intensities as the plane changes with coating thickness. It is possible that there was a preferred orientation of phases within the coating that would affect the phase distribution observed by the diffraction pattern. Additionally, peak shifting can occur in GI-XRD patterns due to internal stress and strain within the coating. These factors impact the ability to identify different phases present within the material.

Because only small diffraction pattern variations were present over the temperature range, it was assumed that the TiO₂ phase was anatase and subsequent trials were performed at 500°C because previous deposition rate data was studied at this temperature for the Denton system using SiO₂ and TiO₂. While this set of depositions focused on the phase of TiO₂ monolayers, future work could be done to investigate the phases and stress states for multilayer coatings over this temperature range.

In addition to GIXRD, UV-Vis-NIR spectroscopy was performed to determine the percent transmission of the TiO₂ monolayers (Figure 4.4).



Figure 4.4. Percent transmission of four TiO₂ monolayers deposited at 300°C, 400°C, 500°C, and 600°C, collected using UV-Vis-NIR spectroscopy.

The transmission spectrum through TiO₂ monolayers is largely dictated by the optical band gap of TiO₂, reported to be ~3.0 eV for rutile, ~3.4 eV for anatase, and ~3.3 eV for brookite [26], [27]. For these largely anatase coatings, a ~3.4 eV optical band gap corresponds to a wavelength of ~376 nm. As discussed in Chapter 2, incident light at a lower energy (longer wavelength) than the band gap will transmit through the material and result in a more transparent film. Note the leftward shift in the transmission spectrum with increasing temperature, which could be a result of temperature or of variations in film thickness across the four samples.

Ellipsometry data was also collected to compare refractive indices over a range of wavelengths to reference values in the literature. As shown in Figure 4.5, refractive indices at 1000 nm varied from 2.2-2.3, while the literature value was reported at 2.5. The measured refractive indices found using ellipsometry were likely less than the literature value because the fabricated coatings were less than 100% dense. Porosity within the coating microstructure would decrease the coating density and lower the refractive index of the material. Experimental refractive index data is an important input for Equations 2.2-2.4 to model optical response of DBR structures in order to tailor coating systems to the desired critical wavelength (λ_c)and stopband ($\Delta\lambda$).



Figure 4.5. Refractive indices of TiO2 monolayers deposited at 300°C, 400°C, 500°C, and 600°C from 500-1000 nm, compared to reference refractive index data from Siefke, 2016 [8].

4.2 – Matrix 2: TiO₂/SiO₂ 9 Bilayer DBRs

Using the deposition rates determined in Matrix 1, TiO₂/SiO₂ multilayer DBR structures were fabricated. From preliminary modeling discussed in Chapter 2, the minimum number of bilayers needed to create an optical limiter with 99% reflection for the TiO₂/SiO₂ material system was 9 (Table 2.2), so 9 bilayer DBRs were chosen for this matrix. As per the calculations performed in Chapter 3, these DBRs were targeting SiO₂ layer thickness of 185 nm and TiO₂ layer thickness of 115 nm. In this matrix, SiO₂ fused starters were used as the evaporant source for each deposition. Figure 4.6 shows FE-SEM fracture surfaces of three DBR coating structures, with alternating layers of SiO₂ and TiO₂. For each FE-SEM image, note that the TiO₂ layers are brighter than the SiO₂ layers due to the different atomic contrast from each element, as discussed in Chapter





D191121-1B

D191219-1B

D200122-1B

Figure 4.6. FE-SEM of fracture surfaces of TiO₂/SiO₂ 9 bilayer DBRs deposited at 500°C from SiO₂ starters, sample ID: (a) D191121-1B, (b) D191219-1B, (c) D200122-1B.

While the TiO₂ rates and thicknesses are stable and consistent, large standard deviations and percent errors in SiO₂ layer thickness are apparent in the fracture surfaces in Figure 4.6 as well as in the summary of deposition thickness and rates in Table 4.3.

Run ID	Total Coating Thickness	Average SiO2 thickness	Average SiO2 deposition rate	Average TiO2 thickness	Average TiO2 deposition rate
D191121-1	5.93 µm	466.4 (±140) nm	$60.7 (\pm 33.9) \frac{nm}{min}$	118.8 (±4.1) nm	27.2 (±2.5) $\frac{nm}{min}$
D191219-1	3.98 µm	174.9 (±19.2) nm	45.1 (±26) $\frac{nm}{min}$	101.9 (±15) nm	22.8 (±3.2) $\frac{nm}{min}$
D200122-1	1.74 μm	76.84 (±41) nm	20.1 (±13) $\frac{nm}{min}$	102.6 (±26) nm	19.3 (±6.0) $\frac{nm}{min}$

Table 4.3. Summary of Matrix 2 depositions to produce 9 bilayer DBRs.

The resulting UV-Vis-IR transmission spectrum from these three depositions is shown in Figure 4.7. While the average layer thickness values are not aligned with the target values of 185 nm and 115 nm, measuring the percent transmission for each of these coatings was useful to verify the validity of the model by calculating the stopband values based on the experimental inputs. It is noteworthy that because these DBR structures do not have a center cavity layer, according to the model they should not have a transmission peak in the center of their stopband. However, 2 out of 3 do have a small transmission peak of 20% and 25%, as shown in Figure 4.7 (a) and (c). These small peaks could be explained by the large standard deviations in individual layer thickness, causing a pseudo-cavity layer within the DBR (a) and (c).



Figure 4.7. Percent transmission for 9 bilayer DBRs, sample ID (a) D191121-1E, (b) D191219-1E, and (c) D200122-1, collected using UV-Vis-IR spectroscopy.

The cause for the disparity in consistency between TiO₂ and SiO₂ is the evaporation mechanism of each source material. When bombarded with an electron beam, TiO₂ creates a circular melt pool that easily evaporates from a liquid to a gas phase, resulting in a constant flux and TiO₂ vapor cloud in EB-PVD processes. However, SiO₂ does not melt when bombarded with

an electron beam. Instead, the solid surface coalesces and sublimes directly into a gaseous phase, causing large variations in the flux of the vapor cloud depending on whether the electron beam energy is used to melt atoms on the surface or to sublime material into vapor. As a result, the SiO₂ is difficult to evaporate and reproduce consistent layers in multilayered coating structures. Additionally, once the surface of the SiO₂ starter fuses into a glassy phase, material in this area sublimes at a faster rate, creating "hot spots" throughout the electron beam sweep pattern. This phenomenon is shown in Figure 4.8 by the progression of a SiO₂ starter throughout 5 depositions. In these glassy areas, the material sublimes faster and deteriorates the starter, creating large divots, and eventually holes (Figure 4.8e) in the material. Deviations from planar geometry in the evaporant source negatively impacts the ability to establish repeatable deposition rates, and will be explored further in Matrix 3A.



Figure 4.8. Progression of a SiO₂ starter from (a) new, (b) heated for ~5 min at 5.3 kV and 60 μ A, (c) heated for ~1 hr at 5.3 kV and ~60 μ A (d) heated for ~2 hr at 5.3 kV and ~60 μ A, and (e) Post D191121-1, heated for ~3 hrs at 5.3 kV and ~60 μ A, with hole bore through to crucible liner.

4.3 – Matrix 3: TiO₂/SiO₂ Mirrored DBR structures

The goal of Matrix 3 was to optimize the fabrication of mirrored DBR structures while showing reproducibility and manufacturability of coatings. In Matrix 3, a total of 5 mirrored DBRs were fabricated, three 5x5 mirrors, one 7x7 mirror, and one 10x10 mirror. For the purpose of comparison, data analysis of Matrix 3 was broken into two sections: 3A and 3B. Matrix 3A directly compares the effect of varied SiO₂ evaporant sources on the reproducibility of three 5x5 bilayer DBR mirrors and the resulting changes in UV-Vis transmission spectra. Matrix 3B analyzes the effect of changing the number of bilayers in the DBR mirror between 5x5, 7x7, and 10x10 mirrors to observe residual stresses as a function of coating thickness and again compare the resulting UV-Vis transmission spectra.

4.3.1 - Matrix 3A: TiO₂/SiO₂ 5x5 Mirrored DBRs

After DBR fabrication was tested in Matrix 2, the next step was to fabricate mirrored DBRs, with a $\frac{\lambda_0}{2}$ thick layer in the center of the structure as discussed in Chapter 2. Given the challenges presented by the SiO₂ evaporant source in Matrix 2, three 5x5 mirrored DBRs were fabricated with three different SiO₂ evaporant sources: SiO₂ pieces, a SiO₂ sputtering target, and a SiO₂ starter. The goal of this matrix was to decrease both the percent error and standard deviation of SiO₂ layer thicknesses by changing the SiO₂ evaporant source material. Several processing variables were improved during Matrix 3 that successfully decreased layer-to-layer variability. Primarily, the electron beam pattern (position, sweep, and frequency) and the pre-heat time (~1 min with the deposition shutter closed prior to each layer) was standardized for each run. FE-SEM cross-sections and digital images of the 5x5 mirrored DBRs are shown in Figures 4.9 and 4.10.



D200219-1B

D200204-1B

D200221-1B

Figure 4.9. FE-SEM polished cross-sections of TiO₂ (lighter regions) and SiO₂ (darker regions) 5x5 mirrors deposited at 500°C with (a) SiO₂ pieces, sample ID D200219-1B (b) SiO₂ sputtering target, sample ID D200204-1B and (c) SiO₂ starter, sample ID D200221-1B.



Figure 4.10. Digital images of TiO₂/SiO₂ 5x5 mirrors deposited on Si wafers, sample ID (a) D200219-1B, (b) D200204-1B, and (c) D200221-1B.

A summary of the deposition thicknesses and rates are shown in Table 4.4. Note that the standard deviations of SiO₂ and TiO₂ layers are within the 10% tolerance values, but the target thickness values of 185 nm and 115 nm were still not met.

Sample ID	SiO2 evaporan t source	Total Coating Thicknes s	Average SiO2 thickness	Average SiO2 deposition rate	Average TiO2 thickness	Average TiO ₂ deposition rate
D200219 -1	pieces	3.31 µm	203.3 (±26) nm	$60.3 (\pm 10.7) \frac{nm}{min}$	122.5 (±14) nm	$34.6 (\pm 5.4) \frac{nm}{min}$
D200204 -1	sputter target	3.98 µm	203.6 (±27) nm	46.6 (±10) $\frac{nm}{min}$	162.5 (±19) nm	23.5 (±2.7) $\frac{nm}{min}$
D200221 -1	starter	5.71 μm	315.9 (±21) nm	39.5 (±3.6) $\frac{nm}{min}$	244.9 (±15) nm	37.3 (±3.2) $\frac{nm}{min}$

Table 4.4. Summary of Matrix 3 depositions to produce 5x5 mirrored SiO₂/TiO₂ DBRs.

Images of each SiO₂ starter source are shown in Figure 4.11. For each deposition in this matrix, the SiO₂ evaporant source presented challenges as expected. As previously discussed in Matrix 2, the root cause of the variability between depositions is likely nonlinear sublimation rates of the SiO₂ material. To mitigate this variability, three different SiO₂ evaporant sources were attempted: ~5mm SiO₂ pieces, a 1" SiO₂ sputtering target, and an SiO₂ starter.

Each source presents a unique set of both challenges and advantages. While SiO₂ pieces coalesce into a non-uniform, textured surface with variable heights and orientations based on the initial packing of the pieces, this source also seems to disperse energy well, likely because it has the highest surface area. SiO₂ pieces are also the least wasteful use of material as new pieces can be poured directly on top of the existing material at the start of each deposition. Meanwhile, both the SiO₂ sputtering target and starter provide flat sublimation surfaces, but must be pre-heated to coalesce the surface evenly before use to avoid hot spots. The sputtering target and starter sublime similarly, but because the sputtering target has a smaller surface area, it requires a more condensed beam pattern and must be changed out more frequently. Additionally, the SiO₂ sputtering target was tested resting on a bed of pieces to maintain a constant source to substrate height, so the effects of using the target as a standalone source are unknown. The SiO₂ starter has a greater surface area and thickness, but is more expensive. Qualitatively, the SiO₂ pieces ranked the highest as they are the most effective and least wasteful, followed by the SiO₂ sputtering target because it is cheaper and can be replenished at the start each deposition, and finally the SiO₂ starter as it is expensive and variable between depositions.

Based on the results of each 5x5 mirrored DBR produced in Matrix 3A, the SiO₂ pieces and sputter target were more precise and accurate compared to the SiO₂ starter. However, more repeated trials are needed to confirm these results. With SiO₂ pieces, there is a larger surface area for the electron beam to sweep over, so while the source surface is not flat like the surface of the sputter target or the starter, using SiO₂ pieces as an evaporant source is beneficial from an energy dispersion standpoint.



Figure 4.11. Digital images of SiO₂ evaporant sources (a-c) before and (d-f) after electron beam physical vapor deposition.

The resulting UV-Vis-IR transmission spectrum from these three depositions is shown in Figure 4.12. For these coating structures, a transmission peak caused by the center $\frac{\lambda_0}{2}$ thick layer exists in each stopband in accordance with the preliminary modelling in Chapter 2. Note that for D200221-1, the average layer thicknesses increased ~50% for SiO₂ and ~100% for TiO₂ compared to D200219-1, which accounts for the 800 nm rightward shift of the band gap from a transmission peak of 1190 nm to a transmission peak of 1990 nm. Figure 4.12 (b) exhibits asymmetric transmission peak tails, with a small increase in percent transmission to the left of each peak. This sample also has a much larger stopband, at ~700 nm compared to the ~400 nm stopband in Figure

4.12 (a). Further computational work is needed to compare and explain these spectra using the analytical model based on physical geometries of the deposited coatings.



Figure 4.12. Percent transmission of TiO₂/SiO₂ 5x5 mirrored DBRs, sample ID (a) D200219-1, (b) D200204-1, and (c) D200221-1, collected from UV-Vis-NIR spectroscopy.

4.3.2 - Matrix 3B: 5x5, 7x7, and 10x10 SiO₂/TiO₂ Mirrored DBRs

The results of Matrix 3A determined that SiO₂ pieces were the most advantageous evaporant source for the baseline experiments using 5x5 mirrored DBRs. In Matrix 3B, mirrored DBRs were fabricated to test optical performance by varying the number of bilayers in each mirror. A major concern in multilayer coating structures is residual stresses, which can lead to coating spallation and catastrophic failure. Within the desired material system, residual stress increases with coating thickness, so a thicker coating will result in higher stress and will be more prone to failure. Additionally, the number of layers in a DBR will change the optical performance of the coating, as modeled in Chapter 2. For Matrix 3B, the number of bilayers in each mirror varied from 5x5, 7x7, and 10x10 bilayers, not only to observe the resulting residual stresses, but also to test the optical performance and stopband of each mirrored DBR. Due to unforeseen circumstances, residual stress data was not able to be collected, but stress states can be observed on the coating by visually inspecting the the surface for cracks in the coating and monitoring the extent of cracking evolution over time. FE-SEM polished cross-sections and digital images of the resulting 5x5, 7x7, and 10x10 mirrors are shown in Figures 4.13 and 4.14.



Figure 4.13. FE-SEM polished cross-sections of mirrored SiO₂/TiO₂ DBRs with (a) 5x5, (b) 7x7, and (c) 10x10 bilayers.



Figure 4.14. Digital images of TiO₂/SiO₂ DBR mirrors with (a) 5x5, (b) 7x7, and (c) 10x10 bilayers, deposited on Si wafers.

As with Matrix 2 and Matrix 3A, these mirrors were fabricated to target a wavelength of ~1 μ m, or individual layer thicknesses of 185 nm for SiO₂ and 115 nm for TiO₂. While the standard deviations for this set of matrices is still within the acceptable 10% tolerance, the experimental coating thickness is higher than the target thickness values, which accounts for transmission peaks higher than 1000 nm for all three coatings, as shown in the UV-Vis spectra in Figure 4.15.

Sample ID	Total Coating Thickness	Average SiO2 thickness	Average SiO ₂ deposition rate	Average TiO2 thickness	Average TiO2 deposition rate
D200219-1 5x5 mirror	3.31 µm	203.3 (±26) nm	$60.3 (\pm 10.7) \frac{nm}{min}$	122.5 (±14) nm	34.6 (\pm 5.4) $\frac{nm}{min}$
D200220-1 7x7 mirror	5.31 µm	255.5 (±17) nm	78.3 (\pm 9.3) $\frac{nm}{min}$	118.4 (±13) nm	32.2 (±4.2) $\frac{nm}{min}$
D200205-1 10x10 mirror	10.7 μm	315.9 (±21) nm	39.5 (±3.6) $\frac{nm}{min}$	244.9 (±15) nm	37.3 (±3.2) $\frac{nm}{min}$



Figure 4.15. Percent transmission of three mirrored DBRs with (a) 5x5 bilayers, ID: D200219-1 (b) 7x7 bilayers, ID D200220-1, and (c) 10x10 bilayers, ID D200205-1, collected from UV-Vis-NIR spectroscopy.

From Figure 4.15, it is confirmed that the transmission peak shortens with increasing number of bilayers in mirrored DBRs, starting from a peak percent of \sim 50% in a 5x5 mirror, then decreasing to \sim 20% transmission in a 7x7 mirror, to an assumed \sim 0% in a 10x10 mirror. Because

the right limit of the stopband is not shown in the UV-Vis spectrum in (c), it is assumed that no transmission peak exists in this region. Similarly to the results from previous matrices, these results can be compared to the analytical model by inputting the physical geometries and optical constants of the deposited coatings to see the theoretical stopband wavelength range.

For optical limiter coatings, cracking is a large factor, as coating cracks will scatter light and could ultimately lead to coating failure. In all three matrices, surface cracks appeared on the optically graded fused silica substrates when analyzed using an optical microscope. More data is needed to understand the relationship of cracking evolution over time for these substrates.

4.4 – Metallic Substrate Adhesion

The substrates used throughout Matrix 1-3 were primarily silicon wafers and fused silica to facilitate physical and optical characterization techniques. However, in application, the optical limiter coatings will most likely be applied to metallic or even composite substrates. In order to test coating adhesion on metallic substrates, an additional 1"x1" 316 stainless steel substrate was tack-welded to the substrate mask as shown in Figure 4.16 for nxn mirrored DBR depositions.



Figure 4.16. Digital images of modified substrate planet with tack-welded 316 steel substrate on the surface.

The 316 stainless steel substrates were polished to a mirror-like surface as described in Chapter 3. The purpose of the 316 steel was to test the coating adhesion to a metallic substrate for each of the mirrored DBRs. The resulting coated metallic substrates are shown in Figure 4.17.



Figure 4.17. Digital images of coated metallic substrates from (a) 5x5 mirror, sample ID D200219-1G (b) 7x7 mirror, sample ID D200220-1G, and (c) 5x5 mirror, sample ID D200221-1G.

As shown in Figure 4.17, the coatings did not adhere to the metallic substrates in any of the three depositions, most likely due to the difference in coefficient of thermal expansion between the metallic substrate and the ceramic coating causing internal stress buildup during deposition. Another possibility is that the oxygen rich environment in the chamber (from flowing O₂) formed an oxide on the surface of the metallic substrates during IBAD pre-cleaning which could have limited adhesion. In the case of D200220-1G and D200221-1G (Figure 4.17 (b) and (c)), it appears as though the first layers of the coating completely spalled off during the deposition. In these two cases, only some of the layers are left attached to the metallic substrate, as evidenced by coating flakes present in the Denton chamber after venting. More characterization is needed to truly understand the adhesion properties between optical limiter coatings and metallic substrates. In the future, adhesion could be improved by applying a chromium bond coat to the metallic substrates prior to deposition and further studying the surface roughness of the substrates.

CHAPTER 5: CONCLUSIONS AND FUTURE WORK

5.1 - Conclusions

The goal of this study was to develop a reflective optical limiter with SiO₂/TiO₂ deposited using EB-PVD. In a series of three matrices, monolayers, DBRs, and mirrored DBRs were fabricated to investigate feasibility and reproducibility of the deposition process. The optical response of the coatings was measured using UV-Vis-IR to evaluate optical performance. As a result of the three matrices, mirrored DBRs were successfully fabricated to produce the desired optical response. In the case of run D200219-1, over 98% absorption was achieved over a 350 nm wavelength range with a centered transmission peak of 1190 nm (Figure 4.15a). However, large amounts of variability between depositions was found in average layer thicknesses, resulting in bandgaps and transmission peaks that were shifted either to the left or right of the target values.

5.2 – Future Work

The EB-PVD deposition process developed in this study, while able to successfully fabricate optical limiter coating structures, faced several processing challenges that hindered reproducibility. In the future, several EB-PVD processing changes can be made to resolve challenges with nonuniform SiO₂ sublimation, residual stresses, and coating adhesion.

5.2.1 – Establish Reproducibility

For the SiO₂/TiO₂ material system, one of the main challenges faced was the sublimation of silica. For depositions at an industrial scale, this challenge would be mitigated by using a more sophisticated EB-PVD chamber with a programmable beam sweep pattern, rod-fed source material, and in situ thickness measurements. In the future, the Denton vacuum system could be modified to implement these changes. A rod-fed system could be installed to the Denton chamber to use a silica rod as a continuous source material. A rod-fed evaporant source would allow for a

continuous surface area of SiO₂ to be evaporated which, with the conjunction of a sophisticated beam pattern, would lead to a more uniform silica sublimation rate. Another process improvement for the Denton system would be to install a laser interferometer to measure coating thickness insitu. A precise in-situ coating thickness measurement would greatly decrease variability between depositions in adjusting the thickness based on values from the quartz crystal monitor. These processing changes have the potential to improve the feasibility of the SiO₂/TiO₂ material system.

Additionally, based on current functionality of the Denton system, processing parameters for the SiO₂/TiO₂ material system could be improved by depositing silica via reactive deposition. With a reactive method, silicon source material could be evaporated and react with O₂ gas from the ion beam source (IBS) to form a SiO₂ coating. Because silicon is known to evaporate easily via EB-PVD, reactive Si evaporation would decrease some of the variability seen between SiO₂ depositions caused by SiO₂ sublimation.

5.2.2 – Mitigate Residual Stress

Another major issue for the SiO₂/TiO₂ material system is residual stress states. More characterization is needed to fully understand the tensile stress buildup both thermally and mechanically during EB-PVD as well as over time by water vapor adsorption in the coating, both of which are likely to cause cracking. Future work will be done to examine the extent of surface cracking over time for existing and future samples. To mitigate residual stresses, one approach is to implement an EB-PVD processing change with ion beam assisted deposition (IBAD). IBAD uses an ion beam source (IBS) to eject ions and flow gas directly at the substrate, thus increasing the flux and surface energy of the deposition. Although deposition rates will need to be re-established using this method, IBS assisted depositions would act to induce compressive residual stresses, which would decrease the overall stress state of the coating system.

Another approach to mitigate residual stress could be to stabilize the amorphous phases within the SiO₂/TiO₂ material system by depositing at lower temperatures. By decreasing the deposition temperature, not only would the thermal stresses be greatly reduced, but an amorphous titania structure could be stabilized using dopants and Nitrogen gas flow. However, this would likely require sub-room temperature deposition temperatures, which would add another set of processing challenges. Because only monolayers as a function of temperature were studied, temperature trials are needed to investigate the effects of changing temperature on the overall coating system.

5.2.3 – Improve Coating Adhesion

The third primary objective for future work on this program will be to improve coating adhesion properties, especially with respect to the metallic substrates. For all three depositions using stainless steel substrates, none of the coatings adhered to the surface of the steel, likely due to oxidation of the substrate during IBAD pre-cleaning. To increase the adhesion between the metallic substrates and the coating, further investigation into measuring the surface roughness of the polished metallic substrates via profilometry is needed. To improve adhesion directly, a chromium bond coat or electroplated surface on the metallic substrates would stop surface oxidation and improve adhesion. Finding a method to adhere coatings to metallic surfaces is crucial for industry applications of optical limiters.

For adhesion between individual coating layers, more data is needed to understand the coating surface topography and effect of defects on the DBR structures. Unfortunately, surface topography images were unable to be collected for this study, so future work is needed to relate the surface morphology to optical response. It is suspected that the titania deposition rate will need

to decrease in order to reduce the number of defects caused by spitting from the source material during depositions.

5.2.4 – Perform Additional Characterization

For this study, UV-Vis spectroscopy was used to measure the optical response of fabricated coatings. For all UV-Vis scans, data was collected in the center of the sample and normal to the plane of the coating. Further testing is needed to test the variability of the optical response across the length of the coating, as well as the optical response at different incident angles. In application, optical limiters would need to reflect incident light from all angles, so it is important to understand how changing the incident angle affects the transmission spectra of an optical limiter.

For the next steps in realizing a reflective optical limiter, more work needs to be done to characterize WS₂ as a non-linear optical material. Research outside the scope of this paper has been done to deposit thin films of tungsten via EB-PVD and sulfidize ex-situ in a furnace. While removing samples from the Denton system to sulfidize mid-deposition is not ideal from a processing standpoint, it is a feasible method to produce a full optical limiter coating with WS₂ as the NLO. Future work will primarily be focused on integrating a WS₂ cavity in the center layer of a mirrored SiO₂/TiO₂ DBR to create a full optical limiter coating structure.

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APPENDIX A: DENTON EB-PVD CHAMBER OPERATING PROCEDURE

Electron Beam Physical Vapor Deposition (EB-PVD) is a thin film physical vapor deposition process that is used to deposit coatings under vacuum with the assistance of an electron beam. EB-PVD is performed at the Penn State Applied Research Laboratory using a Denton vacuum chamber. The purpose of this document is to outline an instruction procedure for the operation of the Denton vacuum chamber from start to finish during a deposition. This instruction set is specifically tailored to the employees who will be operating the Denton system at the Advanced Coatings Department of the Penn State Applied Research Lab. The equipment setup, control board, and safety procedures are specific to the Denton chamber belonging to this facility.

The purpose of these instructions is for current trained users as well as new users to follow during training sessions and operation of the Denton vacuum chamber. This instruction set is to be used in conjunction with an in-person training session administered by a current trained user. Please consult trained users prior to operating equipment. The in-person training session explains more information behind each step in these instructions, so in-depth EB-PVD explanations have been from this particular document for sake of readability during operation. For more information about the Electron Beam Physical Vapor Deposition (EB-PVD) process, consult the attached EB-PVD definition document.

List of Materials Needed

- Denton Vacuum Chamber
- Control Panel
- Scientific Log Book
- Wire Brush
- Shop Vac
- Aluminum/stainless steel foil

Precautions



- The Denton EB-PVD vacuum chamber requires high power to operate. Do not operate the equipment without someone else in the lab.
- The chamber should be left pumped down (at high vacuum ~10-5 Torr) while idle.
- The Denton EB-PVD vacuum chamber operates at high temperatures up to 650°C. Use caution when opening the chamber and check temperature gauge before touching hot components.
- Record all operations in the Denton scientific log book. When recording operations, include the date, operator initials, and list all maintenance and/or usage.
- For all toggle switches, UP is the OPEN or ON position, while DOWN is the CLOSED or OFF position (shown below)



OPEN/ON position



CLOSED/OFF position

OPERATING PROCEDURE

Venting the Chamber

- 1. CLOSE **HI-VAC VALVE**
- 2. OPEN VENT VALVE

Pressure will read 470-500 Torr You will hear air rushing Wait until chamber door opens (should take ~5 min)



3. CLOSE VENT VALVE

Prepping the Chamber/Loading Samples

- 1. Clean chamber interior: brush with wire brush
- 2. Vacuum out debris with shop vac
- 3. Replace foil (if needed)

Foil liner should be replaced every week or every 5 system uses, record foil replacement in log book

- 4. Place samples in substrate planet
- 5. Mount sample holder in heater (twist in by hand)
- 6. Load evaporant pots

Record pot #, material, and initial mass in log book




7. Close chamber door after samples are loaded and chamber interior is cleaned

Pumping Down the Chamber

- 1. CLOSE VENT VALVE
- 2. OPEN ROUGH VALVE
- 3. Turn ON MECH PUMP

pump until pressure reaches 290 mtorr on pressure gauge takes 2-2.5 minutes

4. CLOSE ROUGH VALVE

observe leak up rate (< 2 mtorr/sec)

- 5. OPEN HI-VAC VALVE
- 6. Turn OFF MECH PUMP

Ramping Up for the Run

- 1. Turn ON SAMPLE ROTATION
- 2. CLOSE DEPOSITION SHUTTER
- 3. OPEN GAS FLOW VALVE
- 4. OPEN **O**₂
- 5. Turn ON breakers (Heater, E-Beam pwr supply)

Breaker box is located on wall behind chamber

- 6. Turn MFC-1 ON
- Turn MFC-1 to FLOW and rotate dial counterclockwise, increase gas flow to ~100 sccm

Gas flow value is the red value to the right of the MFC-1 label, do not exceed 200 sccm









66

Standard Long frequency: 1 Standard Lat frequency: 5 *Turn beam position and sweep* to desired values based on material

4. Turn up EMISSION CONTROL dial to desired E-beam power

- 2. Toggle to correct process number and
- 1. Press **MENU** to get to the main screen

 - press F2 to set active process
- 3. Adjust beam sweep and frequency

Set active process









8. Increase temperature to set point using ^ key,

Operate above this temperature

Wait until Temperature has reached desired set point Before starting the run

Starting the Run

- 1. Turn voltage key to ON
- 2. Turn EMISSION CONTROL dial to 0
- 3. Turn HV ON
- 4. Turn on Gun 1 Filament

Running the System







This will initialize the active process

7. Deposit until desired coating thickness is obtained

Montitor thickness on QCM screen Monitor inside of chamber through glass Window for coating or E-Beam abnormalities

8. CLOSE DEPOSITION SHUTTER

9. Press STOP on QCM

Record all run parameters and coating thickness in log book





10. Dial down EMISSION CONTROL to 0

Repeat steps 4-10 for multiple layer coatings



Ending the Run

- 1. Turn OFF GUN 1 FIL
- 2. Turn HV OFF
- 3. Turn KEY OFF



4. Set Temperature to 0

Decrease temperature to set point using down key, then press SEL to begin ramping down temperature



5. Flip E-Beam Breaker and Heater Breaker OFF

Let E-beam cool down for ~15 minutes before flipping breakers off

6. Turn water chamber supply off

Let system cool down for at least an hour before venting (safe to close chamber water supply valve when chamber temperature $<200^{\circ}C$)

Venting the Chamber After a Run

- 1. CLOSE GAS FLOW VALVE
- 2. CLOSE **O2**
- 3. CLOSE HI VAC VALVE
- 4. OPEN VENT VALVE

Wait 5 min, chamber door will open

5. CLOSE VENT VALVE

Remove samples, keep chamber closed and pumped down when not in use





APPENDIX B: NON TECHNICAL ABSTRACT

Lasers have become a ubiquitous technology in systems for communications, manufacturing, and the military. The development of directed energy warfare has presented a new set of technological challenges for the Department of Defense. In the military, directed energy weapons are used to attack weapons and to dazzle sensors. A defensive measure is needed to protect sensors from high energy laser attacks without compromising sensor functionality. The goal of this project is to develop a reflective coating called an optical limiter as a defense mechanism for sensor components to protect against directed energy. An optical limiter is a multilayer thin film coating structure that is intended to reflect 100% of high intensity incident light at a specific range of wavelengths while still allowing low intensity light to pass through at a specific wavelength. In this study, multilayered optical limiter coatings were made from silica (SiO₂), titania (TiO₂), and tungsten disulfide (WS₂). Three matrices were performed to test feasibility and reproducibility of coating fabrication. While coatings were successfully made with the desired optical response, processing variability impacted reproducibility between each matrix.

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EDUCATION

Bachelor of Science, Engineering Science and Mechanics The Pennsylvania State University Schreyer Honors College

- Minor: Engineering Mechanics
- Thesis: Development of Optical Limiter Multilayer Coating System for Directed Energy Beam Reflection
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WORK EXPERIENCE

Undergraduate Researcher, Applied Research Lab (ARL) - Advanced Coatings University Park, PA October 2018 – May 2020 Conduct thin films materials synthesis and processing research led by Dr. Douglas Wolfe Use scanning electron microscopy (SEM), x-ray diffraction (XRD), ellipsometry, UV-Vis-NIR spectroscopy, and profilometry techniques to characterize and analyze material structure and property relationships Fabricate thin films using electron beam physical vapor deposition (EB-PVD) and magnetron sputtering R&D Engineering Intern, 3M Maplewood, MN 3M, Corporate Research Systems Lab (CRSL) Summer 2018 and 2019 Summer internships in 2018 and 2019 on Agile Scrum product development teams Developed variable-friction haptic display surfaces using 3M materials to create integrated LCD display with cover glass mount Designed multilayer Dielectric Elastomer Actuator (DEA) system, built material actuation test to evaluate electromechanical material performance and degradation under cyclic loading Lead author of 3 technical reports, and writer on 2 invention submissions for 3M intellectual property Undergraduate Research Assistant, Department of Civil and Environmental Engineering University Park, PA Researcher at the Penn State SALTS Lab led by Dr. Nathaniel Warner and Dr. Alandra Kahl March – August 2017 Prototyped and programmed open source Mayfly conductivity probe for water quality analysis of Pennsylvania watersheds Phase-tested electronic/software designs, implemented electrode modifications to optimize resistivity measurements ENGINEERING PROJECT TEAMS 3M Curiosity Code Hackathon - AWS DeepRacer 1st Place Maplewood, MN Trained AI DeepRacer car in a simulation to race around a track, won first place out of over 50 participants July 2019 Study Abroad in Israel (Intel AI Challenge) - Ben-Gurion University of the Negev Be'er Sheva, Israel Competed in Intel AI challenge on a team with MBA students from Ben-Gurion University Spring 2019 Visited Israeli tech start-ups and spoke with entrepreneurs as part of an Entrepreneurial Leadership study abroad Amazon Alexa Skills Challenge Hackathon – 2nd Place Team Maplewood, MN July 2018 Learned Amazon Web Services (AWS) platform, designed and coded new Alexa skill "Safety Buddy" Placed 2nd out of 25 teams for Internet of Things (IoT) device that integrated audiovisual feedback with 3M hearing protection LEADERSHIP & INVOLVEMENT Backpacking Trip Instructor, Penn State AURORA Outdoor Orientation Program Spring 2017 – Fall 2019 Teaching Intern (TI), Dynamics Spring 2019 Cadet, Hospitality THON Committee Fall 2018 - Spring 2020 Math Study Group Facilitator, Women in Engineering Program Fall 2017 - Spring 2019 Vice President and Secretary, Society of Engineering Science Spring 2018 – Spring 2020

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