



Controlling the Phase of Titanium Dioxide for Nanophotonic Devices

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Controlling the Phase of Titanium Dioxide for Nanophotonic Devices

A thesis presented

by

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to

The School of Engineering and Applied Sciences

in partial fulfillment of the requirements

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Abstract

In this thesis we investigate using different phases of titanium dioxide (TiO_2) for nanophotonic devices. We build on our previous work with amorphous and polycrystalline anatase TiO_2 thin films and nanophotonic devices to growth and develop rutile TiO_2 for nanophotonics. Rutile TiO_2 has a higher index of refraction than anatase or amorphous films, a property that is beneficial for photonic applications requiring high index contrast, such as waveguiding. We optimize the growth of rutile TiO_2 on an m-sapphire substrate by systematically varying deposition parameters such as temperature, pressure and oxygen concentration. We observe epitaxial growth of rutile TiO_2 , verified by x-ray diffraction rocking curve and ϕ -scans of multiple crystalline planes. We characterize rutile films in terms of material and optical properties. We select deposition conditions that maximize the epitaxial quality of our film to fabricate nanostructures.

We design and fabricate photonic devices using different phases of TiO_2 . We fabricate nanopillars of different diameters and measure their reflection using hyperspectral dark-field imaging. We observe that pillars of different diameters reflect different wavelengths. We also observe that the numerical aperture used to collect

reflected light affects the wavelength of light. We conclude that anatase TiO_2 is well suited for engineering wavelength-selective reflective metasurfaces.

We investigate using amorphous TiO_2 for a multi-layer metal/dielectric stack broadband absorber. We simplify previous designs that use multi-layer metal dielectric stacks to obtain near-perfect broadband absorption. We investigate configurations with $N = 1, 2$ and 3 layers of Cr/TiO_2 . We optimize the dimensions using a genetic algorithm and obtain absorption values of 84.6%, 97.5% and 98.9%, respectively for the 0.4 to $1.6 \mu\text{m}$ wavelength region. This approach improves the viability and scalability for fabrication. We demonstrate experimentally the absorptive properties of a one-layer device over the visible wavelength region and compare it to a gold substrate. We observe robustness against fabrication tolerances, achieving absorptive behavior for a range of dimensions.

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Citations to previously published work

Parts of this dissertation cover research reported in the following articles:

1. S. Griesse-Nascimento, O. Reshef, M. Moebius, C. Evans, E. Mazur, "Nonlinear Optics in TiO₂ Nanoscale Waveguides" *Nano-Optics: Principles Enabling Basic Research and Applications*, 449-449. Springer, Dordrecht, 2017.
2. C. C. Evans, K. Shtyrkova, O. Reshef, M. Moebius, J. D.B. Bradley, S. Griesse-Nascimento, E. Mazur, "Multimode phase-matched third-harmonic generation in sub-micrometer-wide anatase TiO₂ waveguides" *Optics Express* **23**, 6, 7832-7841, 2015.
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microring resonators with negative thermo-optic coefficient” *JOSA B* **32**, 11, 2288-2293, 2015.

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To José do Nascimento.

OVERVIEW

In this thesis we report on advances in developing thin films of rutile TiO_2 and the fabrication of nanophotonic devices using amorphous, anatase, and rutile TiO_2 .

Chapter 1 provides an overview of the field of nanophotonics, explores several applications of photonic materials that explore guiding, reflecting and absorbing properties of light-matter interactions, and the use of titanium dioxide for nanophotonics.

In Chapter 2 we describe the process of sputtering rutile TiO_2 thin films while systematically varying conditions. We characterize the material properties of samples via x-ray diffraction and photoelectron spectroscopy, as well as atomic force microscopy, to determine optimal deposition conditions for photonic-quality TiO_2 .

In Chapter 3 we further investigate our sputtered rutile films by characterizing the optical properties via prism coupling and ellipsometry. We investigate the lattice parameters for the source of birefringence via in-plane x-ray diffraction studies.

Chapter 4 describes the development of an optimized rutile TiO_2 film for fabricating nanophotonic devices. We characterize material and optical properties of this film, describe our nanofabrication process and demonstrate rutile TiO_2 pillar and waveguide nanophotonic structures.

In Chapter 5, we demonstrate the development of anatase TiO_2 nanopillar devices and characterize their reflection and scattering properties.

Chapter 6 focuses on the development of a perfect broadband absorber using amorphous TiO_2 nanostructure arrays. We discuss the theoretical approach of simplifying previous proposed multilayer device designs and demonstrate results toward one and two-layer absorbing devices.

CHAPTER 1: INTRODUCTION

Nanophotonic devices have revolutionized our lives with integrated cameras and night-vision photodetectors. They now promise to provide even further exciting developments in the future, with advances in sensors for self-driving cars[1], integrated photonic circuits for artificial intelligence computations, and quantum computing operations. Historically, silicon has been the material of choice for nanophotonic devices[1]–[5], given decades of material processing development that have addressed challenges from the growth of silicon to its nanoscale fabrication and characterization[6]. The development of this platform has led to an extensive infrastructure that facilitates working with silicon, but also fueled the growth of nanofabrication research and nanofabrication facilities that support novel materials.

As we better understand how to engineer materials to have specific properties and move toward specialized devices for specific functions, there is an opportunity to work with new materials that are tailored to provide superior performance for new devices. The challenge is three-fold and requires us to determine (1) which materials are of interest for (2) which applications and (3) how to develop this material to enable scalability and adoption of this platform.

We identified TiO_2 as a material with superior properties for a variety of applications, from waveguiding to sensing, to quantum information and information storage. We build on our work with amorphous and anatase TiO_2 to develop an optimized sputtering growth technique for rutile TiO_2 thin films with optical and material properties suitable for photonic applications. Furthermore, we develop novel devices with various phases of TiO_2

to further demonstrate the versatility of this material for real-world applications and discuss the design choices that can be made with knowledge of the material and optical properties of each phase of TiO_2 .

1.1 Nanophotonics

The field of nanophotonics has led to great advancements in the study of light-matter interactions[7]–[9] and the development of applications, ranging from optoelectronics[10]·[11]·[12], to quantum optics[13]–[15], solar cells[16], [17], and biosensors[18]·[19]. Materials with suitable optical properties (such as desired index of refraction, absence or presence of optical nonlinearity, and transparency or absorption in specific wavelength regions) and robust and cost-effective fabrication processes are required to enable nanophotonic applications. In this thesis, we use titanium dioxide (TiO_2) for various nanophotonic applications, including waveguiding, filters and absorbers. We discuss the requirements for each application and the benefits of using TiO_2 below.

Nanophotonic devices are structures with sub-micrometer dimensions that exploit material, optical and structural properties to manipulate light. Such interactions can involve the same physics of macroscale linear optical elements, such as lenses, mirrors and waveplates. In this case, nanoscale linear optical devices can be beneficial for decreasing the footprint of the device, which has the potential to decrease the amount of material and cost for the device, allows the devices to occupy a smaller space, opening up applications or allowing for more devices to be combined. Examples include cellphone cameras, photonic integrated circuit elements and complex free-space optical experiments that can be simplified on a

photonic chip with integrated photonics (such experiments often also make use of nonlinear optical components).

On the other hand, bringing structures to the same order of magnitude or smaller than the wavelength of light allows for the observation of optical phenomena that are too weak at the macroscale, including nonlinear optical interactions, Mie scattering, and plasmonic resonances. Each of these phenomena require specific material properties.

Integrated waveguides bring optical fibers to smaller scales on a platform that can be integrated with other devices. Fiber optics is essential for transmitting data over kilometer distances. Nanoscale waveguides, on the other hand, can be used in the linear or nonlinear optical regime for shorter distances, typically on the order of millimeters or centimeters.

1.2 Titanium Dioxide for nanophotonics

TiO₂ has garnered interest for both its electronic and optical properties[20]–[23]. TiO₂ nanofibers with diameters around 250 nm have been fabricated via electrospinning, and TiO₂ nanorods and inverse opal structures have been synthesized via a sol-gel template method[24]–[26]. These techniques and subsequent measurements show promise for the optical properties of the material, but do not readily allow for the design and high-precision fabrication of nanoscale photonic devices. We developed the first amorphous and anatase nanoscale waveguides by sputtering and standard lithographic nanofabrication processes[27]–[29]. We demonstrated many building blocks of linear and nonlinear integrated photonics, including waveguides, directional couplers, and ring resonators[27], [29].

Recently, atomic layer deposition (ALD) has been used to obtain amorphous TiO_2 nanostructures[30], [31] with smooth sidewalls. Although the amorphous phase has lower propagation losses compared to polycrystalline anatase (around 1.4 dB/mm vs. 3.5 dB/mm, respectively, at 780 nm)[27], photochromism limits its use to pulse durations above 6 ps[32]. This effect severely limits the viability of amorphous TiO_2 for applications that require high laser intensities or pulsed operation. In addition, high loss from grain boundaries and sidewall roughness in polycrystalline anatase limits the performance of nanophotonic devices based on this material.

1.3 Rutile TiO_2

Rutile TiO_2 , the more stable phase of TiO_2 , has an excellent combination of optical properties that make it an advantageous material for a number of photonic applications, including telecommunications[28], [29], [33], quantum optics[34]–[37], and photocatalysis[38]–[39]. It has a higher index of refraction ($n_o = 2.613$ and $n_e = 2.909$ at 589 nm) than anatase and amorphous TiO_2 , resulting in better confinement and waveguiding properties. Similar to anatase and amorphous TiO_2 , rutile also has a wide transparency window spanning the visible and telecom wavelengths (band-edge around 400 nm), a high nonlinear index of refraction ($30\times \text{SiO}_2$), low two-photon absorption and low fluorescence[40]. It is also cheap, which is a benefit over materials such as diamond, which also operates in the visible[41]. These properties are especially attractive for integrated nanophotonics, where waveguides serve as a crucial building block and rely on high index

contrast and low losses to confine and guide light. In addition, high optical nonlinearities are attractive for applications where wavelength conversion is desired[42].

Rutile TiO_2 in bulk crystal form is readily available[43]; however, rutile thin films are necessary for scalable development of integrated photonic devices using this material. Thin films allow for nanofabrication using standard lithographic processes for high-precision, scalable, low-footprint, CMOS compatible devices[44], [45]. Research in the area of rutile TiO_2 thin film growth has focused on electrical[46] and photocatalytic properties[47], with little attention paid to the guiding properties of these films. ALD of films consisting of a mixture of anatase and rutile were demonstrated by Aarik *et al.*[48]. Here, a higher index for TiO_2 was achieved on sapphire substrates compared to silica substrates. In addition, polycrystalline rutile with local epitaxial growth was achieved using a RuO_2 seed layer[46]. Pulsed laser deposition (PLD) yields epitaxial growth of rutile on sapphire[49] and MgF_2 [50]; however, optical characterization has been limited to UV absorption and did not investigate the visible and infrared regimes. A reliable technique for growing single-crystal rutile TiO_2 thin films with low loss and low concentration of defects and impurities remains elusive.

Epitaxially-grown thin films promise to lower propagation losses significantly and provide stronger and more controlled nonlinear optical phase accumulation compared to amorphous and polycrystalline films. Epitaxial growth can be achieved by growing TiO_2 on substrates with low lattice-mismatch and refractive index, and by optimizing growth parameters, such as pressure, temperature and oxygen concentration.

A reliable growth technique that delivers optical quality rutile TiO_2 thin films is needed to support scalable nanofabrication of TiO_2 photonic devices. The goal of the research

presented in this thesis was to develop optical-quality *rutile* TiO₂ thin film processing techniques that will enable transformative improvements in nanophotonic device performance by meeting the need for cost-effective materials, with high index-contrast and wide transparency range suitable for the visible spectrum. By systematically exploring the available parameter space and analyzing the crystalline phase, chemical composition and optical properties of grown films, we identified the optimal combination of parameters for obtaining epitaxial thin films with low defect and impurity concentration and low loss guiding. We also demonstrated a robust nanofabrication process for structuring rutile thin films of TiO₂ and fabricate and test novel nanophotonic devices.

Chapter 2: Deposition of rutile TiO₂ films and characterization of material properties

2.1 Deposition of Rutile TiO₂ Films by RF Magnetron Sputtering

Titanium Dioxide thin films have been grown by a variety of methods, including atomic layer deposition (ALD)[30], [31], [51], pulsed laser deposition (PLD)[50], [52], ultra-fast laser processing of Ti foil[53], sputtering[27], [54] and via sol-gel colloidal self-assembly techniques[25], [26]. High-quality TiO₂ films that are densely packed with few defects must be grown at low rates. In ALD, growth rates are known to be quite low given the time required to inject the precursors and empty the chamber for the next layer. We have previously deposited TiO₂ films for photonic applications via sputtering at deposition rates below 0.26 nm/min, approximating the rate of ALD. Although both processes are time-consuming, sputtering provides control over several growth parameters, enabling the optimization of TiO₂ growth by adjusting the pressure, temperature, oxygen concentration and target (e.g. Ti vs. TiO₂). We make use of this versatility to adjust the growth conditions of TiO₂ to obtain high-quality, epitaxial rutile TiO₂ films.

Rutile TiO₂ films have been developed via several techniques. Research in the area of rutile TiO₂ thin film growth has focused on electrical[46] and photocatalytic properties[47], with little attention paid to the guiding properties of these films. ALD of films consisting of a mixture of anatase and rutile were demonstrated by Aarik *et al.*[48]. Here, a higher index for TiO₂ was achieved on sapphire substrates compared to silica substrates. In addition, polycrystalline rutile with local epitaxial growth was achieved using a RuO₂ seed layer[46]. Pulsed laser deposition (PLD) has led to epitaxial growth of rutile on sapphire[49] and

MgF₂[50]; however, optical characterization was limited to UV absorption and did not investigate the visible and infrared regimes.

Sputtering allows for control of multiple growth parameters, which often translates to higher-quality epitaxial films[55]. For instance, the application of a substrate bias provides significant control over a wide range of film properties including resistivity, hardness, optical properties, etch rate, morphology, density, and adhesion[56]. Reactive sputtering of rutile TiO₂ has been performed by several groups [47][57], often resulting in films with a mixture of anatase and rutile phases, and often relying on post-annealing. For photonic applications, epitaxial films of a single crystalline phase are desired. Therefore, we build on our prior work with TiO₂ thin films and photonic devices[33], [58], [59] to optimize the material and optical properties for reliable use in nanophotonic applications.

2.1.1 Lattice matching of rutile TiO₂

Our previous work in depositing TiO₂ films makes use of a silicon substrate with thick oxide layer. This CMOS compatible platform is well suited for growing amorphous and polycrystalline anatase TiO₂. We adjust our process by selecting a crystalline substrate with lattice constants approaching those of TiO₂. This facilitates TiO₂ growth with a preferential orientation and structure[60]. In order to develop crystalline TiO₂ films and achieve rutile TiO₂ growth without the need for annealing, we select sapphire as the substrate of choice and optimize sputtering growth parameters, such as pressure, temperature and oxygen concentration.

The low index of sapphire (1.77 at 532 nm) allows for high index-contrast with TiO_2 . In addition, the wide transparency (with absorption edge around 260 nm) and relatively cheap price of sapphire over alternative substrates (such as MgO), provide additional benefits. Our initial tests of growing TiO_2 on a c-sapphire substrate leads to rutile TiO_2 growth with the extraordinary axis in the plane. This is undesirable for waveguiding applications, since this causes the field components of guided modes to experience different effective indices as they propagate around bends; as a result, the extraordinary axis in plane causes guided modes in waveguides to lose their characteristic mode profile. Because our platform is intended for photonic applications, including waveguiding, we require precise control of the effective index of the guiding mode and the mode profile, introducing birefringence effects in the plane of propagation is undesirable. The solution to this problem is to use m-sapphire as a substrate.

M-Sapphire has lattice parameters (0.2380 nm and 0.2166 nm) that allow rutile TiO_2 (with a-lattice parameter of 0.4594) to grow with the extraordinary axis out of plane (lattice mismatch of 3.4%). Rutile TiO_2 is birefringent ($n_o = 2.613$ and $n_e = 2.909$ at 589 nm). The birefringence out of plane allows for the use of well-known phase-matching protocols, while not interfering with the field components of the guided mode as it propagates through the device. We sputter TiO_2 thin films on m-sapphire, varying the deposition conditions one variable at a time and test the material and optical properties of the resulting films to determine the optimal deposition recipe for nanophotonic applications.

Table 2.1: Deposition conditions for sputtered TiO₂ films, summarizing samples names, power, temperature, oxygen concentration, power and thickness as measured by point-ellipsometry.

Sample name	Power [W]	Temperature [°C]	O ₂ [%]	P [mTorr]	Thickness [nm]
TiO2_1	180	450	33	3	70
TiO2_3	180	350	33	3	48
TiO2_4	180	300	33	3	61
TiO2_5	180	250	33	3	66
TiO2_7	180	650	33	3	70
TiO2_9	180	450	43	3	66
TiO2_10	180	450	23	3	80
TiO2_12	180	450	43	4.5	67
TiO2_14	180	450	20	4.5	79
TiO2_15	180	450	15	4.5	75
TiO2_16	180	450	30	4.5	72
TiO2_30	180	150	33	3	70
TiO2_31	180	650	20	4.5	222
TiO2_32	180	68	33	3	70

2.1.2 Sputtering conditions for rutile TiO₂ films

We select the initial conditions for sputtering TiO₂ on m-sapphire. We use a Plassys Pulvé MP450S sputtering system at University of Franche-Comté in Besancon, France with a Ti target (99.99% pure) and add oxygen to the chamber environment. This allows for higher control over the oxygen content of sputtered samples than using a TiO₂ target. We vary each sputtering parameter at a time to study the effect of each parameter on the material and optical properties of TiO₂. A summary of sputtering conditions tested is shown in Table 2.1. Thickness of the films is determined by point-ellipsometry. We measure material

properties of the sputtered films using x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) to determine the benefits of each deposition variation on the composition and structural qualities of rutile TiO₂.

2.2 X-Ray Diffraction

X-Ray Diffraction (XRD) is a technique that measures properties related to the crystalline formation of a sample. We use $\theta/2\theta$ scans to confirm the composition and orientation of TiO₂ samples deposited on m-sapphire under varying temperature, pressure and oxygen atmospheric content. We also perform rocking curve measurements for rutile (002) that indicate the mosaicism of the sample (an indication of how much variability there is in the growth direction) and ϕ -scans that verify the in-plane crystalline growth and epitaxial nature of the samples.

2.2.1 Basic Theory

An incoming beam incident on a periodic grating with opening $d \leq \lambda$ will experience diffraction. Namely, the light will be reflected forming a periodic pattern determined by the periodicity of the grating, and the wavelength and angle of incidence of the beam. According to Bragg's Law, two parallel beams will reflect constructively when the path-length difference $2d\sin(\theta)$ is equal to an integer-multiple of the wavelength $n\lambda$:

$$n\lambda = 2d\sin(\theta)$$

or

$$\lambda = 2d\sin(\theta)$$

, where d has absorbed the integer n .

A crystalline structure with periodic features will exhibit a reflection pattern similar to a grating; however, other crystal planes will contribute to the diffraction pattern leading to reflected light that interacts constructively or destructively. In the case of crystalline diffraction, d corresponds to the lattice spacing of a crystal. The value of d can be readily calculated from the 2θ angles at which strong reflection occurs. X-ray diffraction (XRD) measurements take advantage of this phenomenon. As seen in the diagram below, the angles of a sample and the incoming and exiting beams can be described with angles ω , 2θ , ϕ and ψ . In the following sections, we describe how varying these angles allows us to perform various XRD measurements, that indicate information about the composition, mosaicity and in-plane structure of sputtered TiO₂ films.

2.2.2 Experimental Procedure

We perform X-ray diffraction measurements using a conventional Bragg-Brentano Bruker D8 Advance diffractometer with Cu K $_{\alpha}$ ($\lambda = 1.54056 \text{ \AA}$) radiation. $\theta/2\theta$ patterns are collected from 50 to 90 degrees to observe the composition and orientation of the films. Texture and epitaxial quality measurements (rocking curves and ϕ -scans) are performed using a four-circle Bruker D8 Discover diffractometer with Co K $_{\alpha}$ ($\lambda = 1.79026 \text{ \AA}$) radiation. Rocking curve measurements are performed at the rutile (002) 2θ peak and the

optimized full width at half maximum (FWHM) of the peak is extracted. ϕ -scans for rutile (111) are measured at $2\theta = 41.226^\circ$ and $\psi = 42.337^\circ$, and ϕ is rotated from 0 to 360 degrees. The instrument resolution for all measurements is 0.23° .

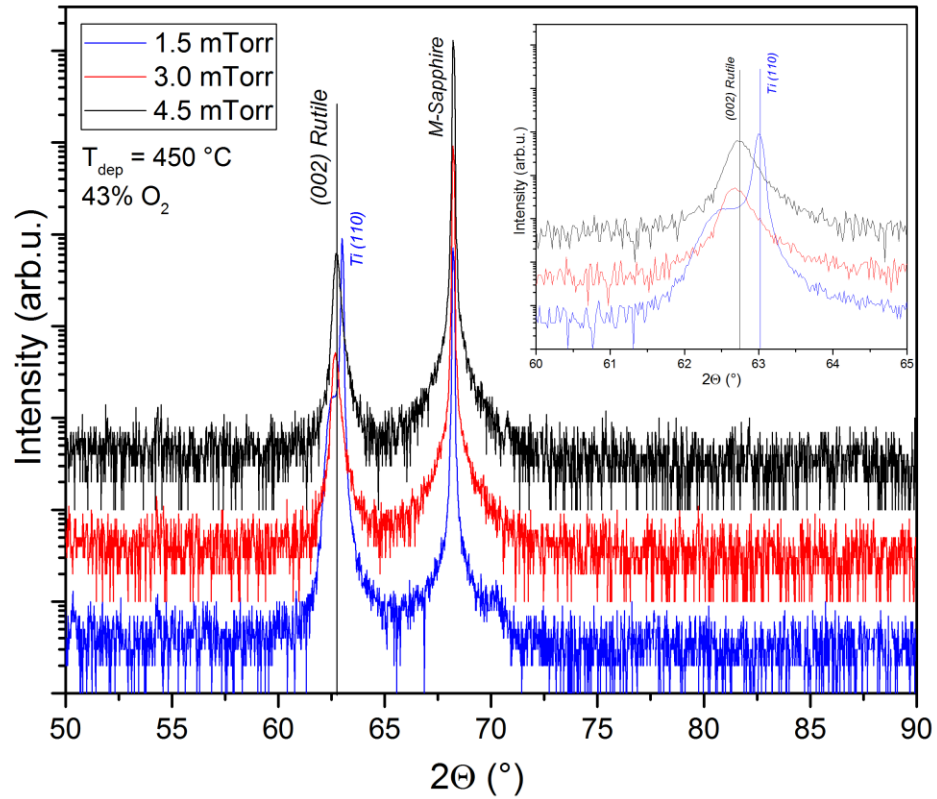


Figure 2.1: Pressure series 2θ measurement for samples deposited under 1.5 mTorr (blue), 3.0 mTorr (red) and 4.5 mTorr (black). All samples were deposited at 450°C and with 43% oxygen. Inset: close-up of rutile (002) curve, showing shift toward Ti (110) at low pressure. Courtesy of Sabina Kuprenaite.

2.2.3 2 θ Scans

We compare the 2 θ results for TiO₂ samples that can be grouped based on temperature, oxygen content or pressure used during depositions. Figure 2.1 shows 2 θ XRD patterns for samples deposited under different pressures, keeping the temperature and oxygen content constant at 450 °C and 43%, respectively. The shift in the blue curve indicates that TiO₂ at 1.5 mTorr (blue) is predominantly Ti (110), whereas the samples deposited at 3.0 mTorr (red curve) and 4.5 mTorr (black curve) consist of rutile (002).

Next, we investigate the effect of varying the oxygen content while maintaining the temperature and pressure constant. Figure 2.2 shows 2 θ XRD patterns for samples deposited under oxygen contents varying from 0 to 43 percent, keeping the temperature and pressure constant at 450 °C and 3 mTorr, respectively. The shift in the blue curve in the inset indicates that the film deposited with 0% oxygen results in Ti (110). This is expected, as the target used during sputtering deposition does not contain oxygen (is pure titanium) and therefore, the Ti atoms cannot combine with oxygen to form higher oxidation states of Ti. All other curves in Figure 2.2 correspond to the Rutile (002) peak. This indicates that oxygen content at or above 23% results in rutile TiO₂ at this constant temperature and pressure.

We again investigate the effect of varying the oxygen content, now at a higher pressure of 4.5 mTorr. Figure 2.3 shows 2 θ XRD patterns for samples deposited under oxygen contents varying from 15 to 43 percent, while keeping the temperature at 450 °C and pressure at 4.5 mTorr. All curves depicted correspond to the rutile (002) peak. This indicates that oxygen content at or above 15% will result in rutile TiO₂ at this constant temperature and pressure.

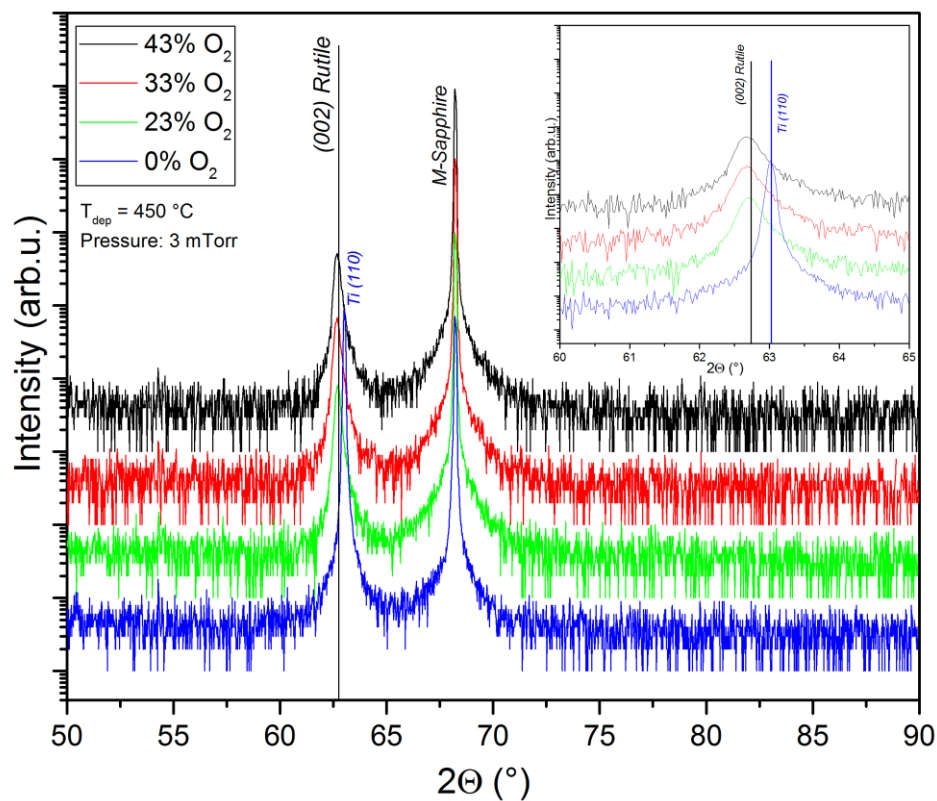


Figure 2.2: Oxygen content 2θ measurement for samples maintained at 3 mTorr and 450 °C. TiO₂ samples are sputtered with varying oxygen content: 0% (blue), 23% (green), 33% (red) and 43% (black). Inset: close-up of rutile (002) curve, demonstrating that all samples are rutile (002) except for 0% O₂, which is Ti (110). Courtesy of Sabina Kuprenaite.

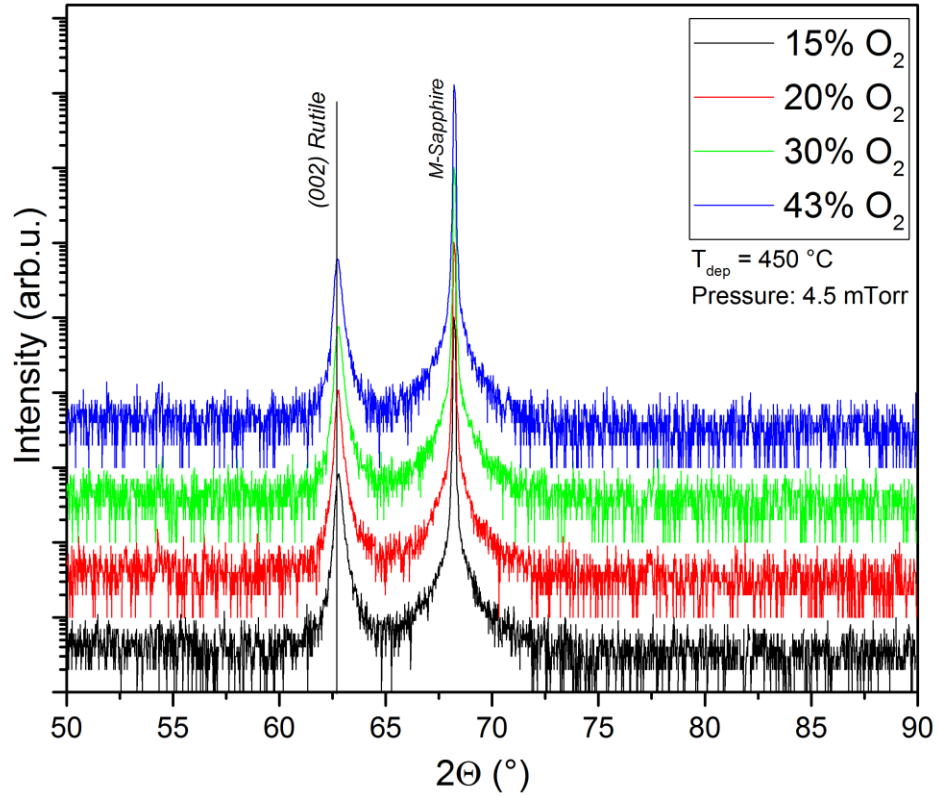


Figure 2.3: Oxygen content 2θ measurement for samples maintained at 4.5 mTorr and 450 °C. TiO_2 samples are sputtered with varying oxygen content: 43% (blue), 30% (green), 20% (red) and 15% (black). Courtesy of Sabina Kuprenaite.

Finally, we investigate the effect of varying the temperature, while maintaining the temperature and oxygen content constant. Figure 2.4 shows 2θ XRD patterns for samples deposited at different temperatures, keeping the pressure and oxygen content at 3 mTorr and 33%, respectively. All curves correspond to the rutile (002) peak.

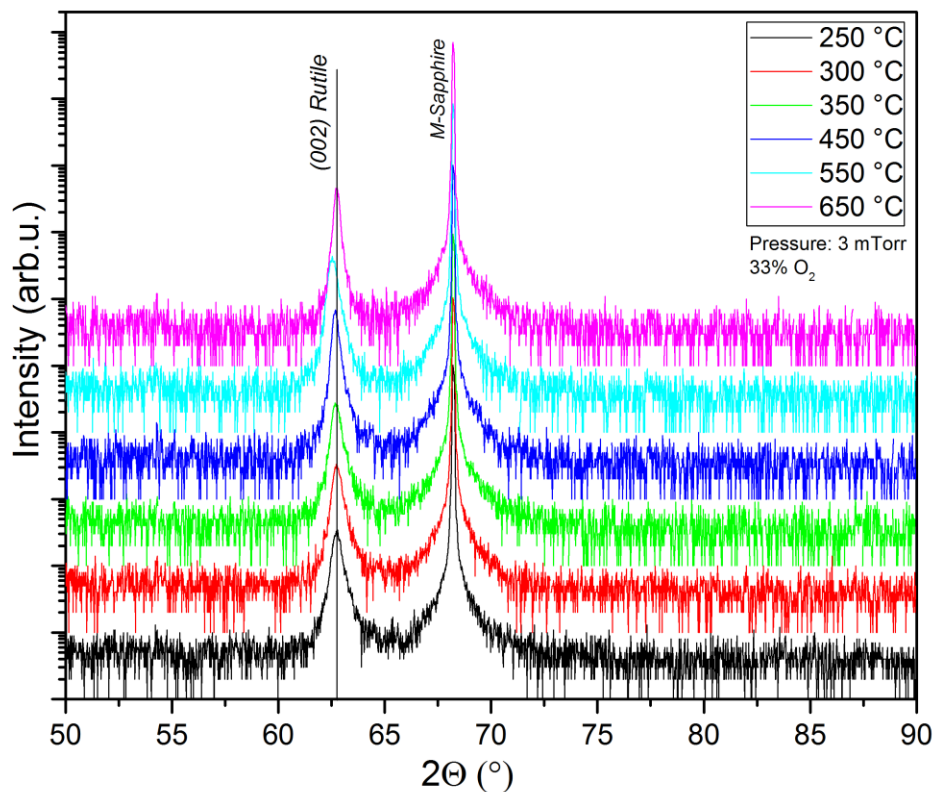


Figure 2.4: Temperature series 2θ measurements for TiO₂ samples maintained at 3.0 mTorr and 33% oxygen. TiO₂ samples are sputtered at different temperatures: 250 °C (black), 300 °C (red), 350 °C (green), 450 °C (blue), 550 °C (cyan) and 650 °C (magenta). All XRD patterns contain the rutile (002) and sapphire (300) peaks at 62.742 and 68.2601 degrees, respectively. Courtesy of Sabina Kuprenaite.

These results indicate that rutile (002) can be obtained at any temperature above 250 °C at this pressure and oxygen content. Most approaches to growing rutile TiO₂ make use of high

temperatures, in order to obtain enough free energy for the TiO_2 lattice to form rutile TiO_2 . Our result in Figure 2.4 indicates that growing TiO_2 with a lattice matched substrate allows for lower temperature deposition of rutile TiO_2 . This opens the door for incorporating TiO_2 in devices and applications that use materials and fabrication processes that require low-temperatures. For instance, polymers can be used to structure TiO_2 walls for etch-free nanostructure fabrication[31]. However, many polymers have glass transition temperatures below 250 °C. Therefore, we investigate depositing samples at even lower temperatures to determine the threshold temperature for achieving rutile TiO_2 growth when using a sapphire substrate. We deposit samples at 150 and 68 °C and determine that even at these low temperatures, TiO_2 grows in the rutile phase. This indicates that the combination of lattice matching and the oxygen concentration of 33% and 3 mTorr optimize the growth of this phase.

2.2.4 Rocking Curve Scans

We perform rocking curve measurements at the rutile (002) peak for all rutile TiO_2 samples to gain a sense of the mosaicity of each sample to determine the quality of the out-of-plane growth.

Figure 2.5 depicts results from calculating the FWHM of the rocking curve rutile (002) peak for samples deposited at different temperatures, keeping the pressure and Oxygen content at 3 mTorr and 33%, respectively. We observe that the rocking curve FWHM values are near 1.1 degrees for the samples deposited at a temperature between 250 to 350 °C. However, as the temperature increases, the FWHM becomes narrower, indicating a

higher quality film with less deviation in the out-of-plane growth. The best rocking curve result is for the sample deposited at 650 °C, with a FWHM of 0.513°.

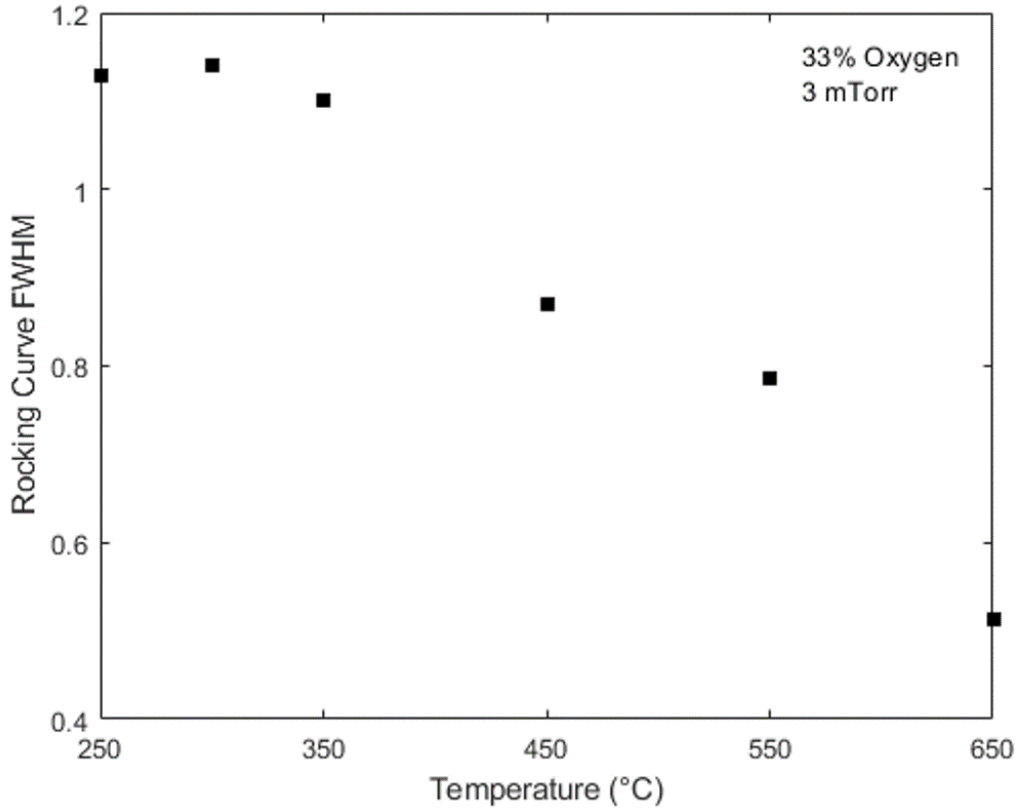


Fig. 2.5 Rocking curve FWHM for rutile (002) samples deposited at constant pressure and Oxygen content of 3mTorr and 33%, respectively, with temperature varying between 250 and 650 °C.

We also compare the rocking curve results for samples grown at different oxygen concentrations for two pressure settings. Figure 2.6 shows the oxygen series curve for 3 mTorr samples (blue, dashed curve) and 4.5 mTorr samples (black, solid curve).

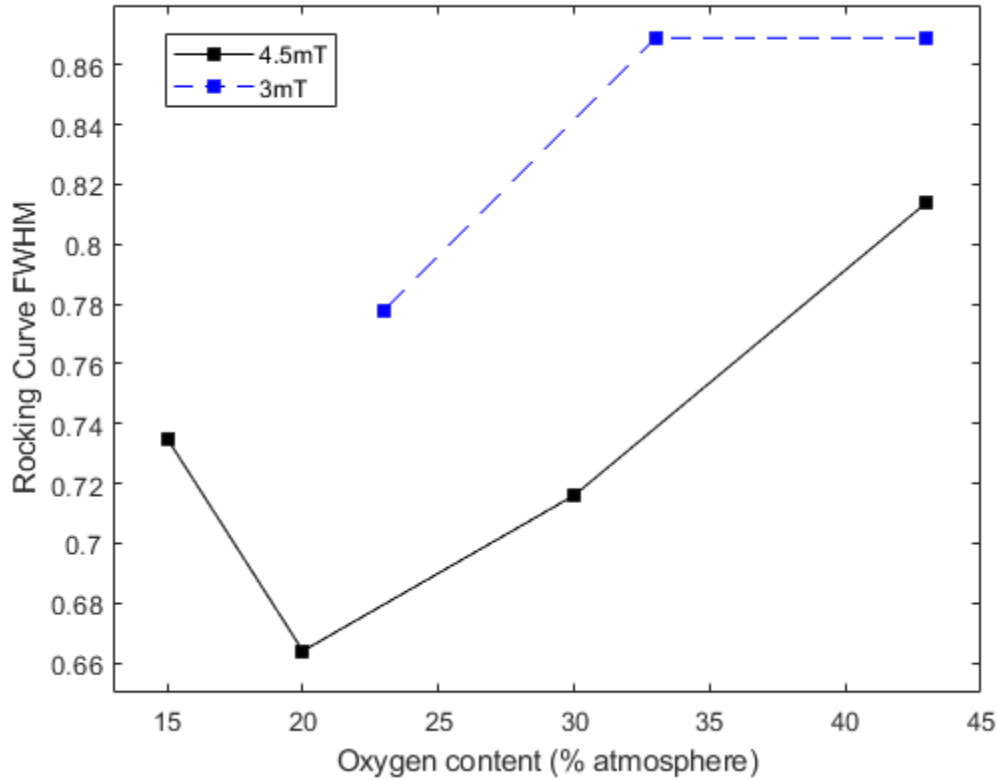


Figure 2.6: Rocking curve FWHM data for rutile samples grown with varying oxygen content at 3 mTorr (blue, dashed curve) and 4.5 mTorr (black, solid curve).

All samples were deposited at a temperature of 450 °C. We observe that the 4.5 mTorr data has lower FWHM values, indicating that this higher pressure leads to higher quality samples. In addition, we observe that both curves show a trend of higher FWHM at higher oxygen concentrations (e.g. above 35%). The best rocking curve result for 3 mTorr samples is achieved at 23% O₂; however, lower oxygen could lead to further improvement in mosaicity at this pressure. Although the sample with 0% O₂ resulted in titanium growth, further studies requiring a pressure of 3 mTorr could investigate oxygen concentrations

between 0 – 23%. In these experiments, the sputtering chamber was unable to accurately sense the oxygen concentration below 23% at a low pressure of 3 mTorr, limiting the range of this study. However, our data indicates that it is advantageous to increase the pressure to 4.5 mTorr to obtain higher texture quality, and the optimal oxygen concentration lies clearly near 20% at this pressure.

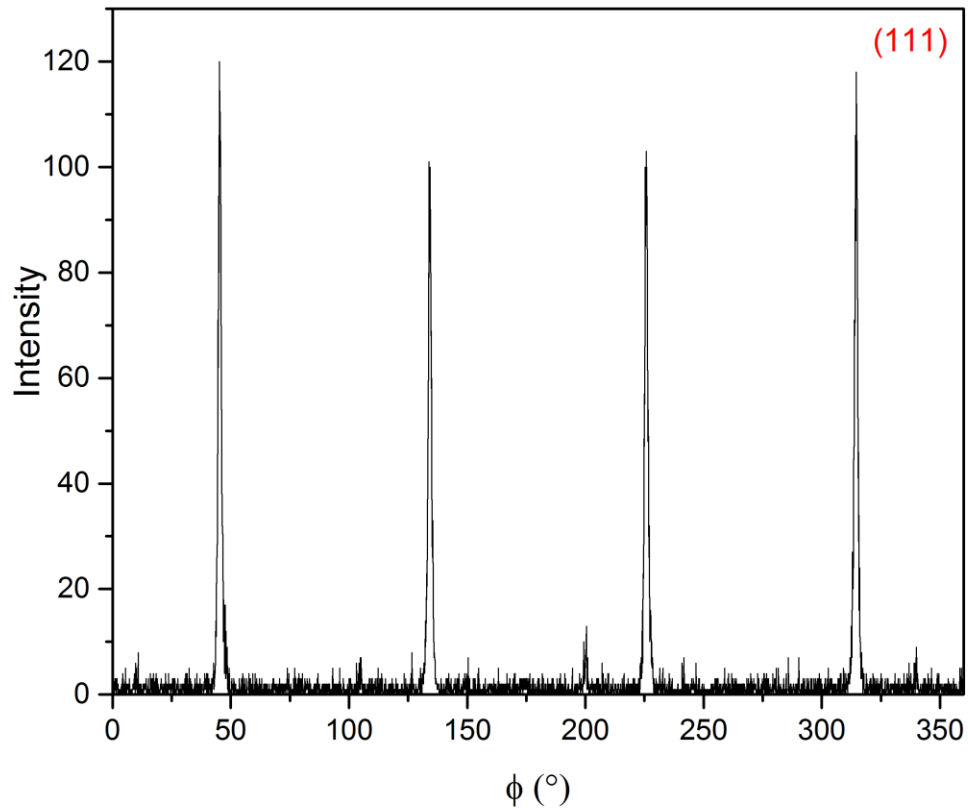


Figure 2.7: Phi scan of rutile (111) for a rutile TiO_2 sample. Periodic peaks with 90 degree-intervals indicate the epitaxial nature of the sample. Courtesy of Sabina Kuprenaite.

2.2.5 ϕ -scans

We investigate the epitaxial quality of our films using ϕ -scans of the rutile (111) plane. This plane is chosen for our study, given its high intensity diffraction. We plot the rutile (111) ϕ -scan data for one of the rutile TiO₂ samples. The periodicity of 90 degrees matches the expected result for rutile (111) crystallographic symmetry. We observe the same result for all rutile TiO₂ samples, confirming that all samples with rutile (002) growth were grown epitaxially, based on lattice matching with m-sapphire.

2.2.6 Conclusions from XRD studies

The investigation of material properties of TiO₂ samples by x-ray diffraction indicate that lattice matching with the m-sapphire substrate is achieved, resulting in epitaxial rutile (002) growth for most of the samples. Exceptions include the case where no oxygen is introduced to the sputtering chamber during deposition, resulting in metallic Ti (110), and the case where low pressure of 1.5 mTorr is used at 450 C and 43% oxygen. These exceptions indicate that the presence of oxygen and a pressure above 1.5 mTorr are necessary to grow rutile TiO₂ on an m-sapphire substrate. Rocking curve data demonstrates that the highest quality texture is obtained for a high temperature of 650 °C (using 3 mTorr and 450 C). Additionally, we determine that a higher pressure of 4.5 mTorr leads to an improvement of about 0.12 degrees in the rocking curve FWHM and that 20% O₂ is the optimal oxygen atmospheric percentage at this pressure. Given these results, we hypothesize that the

optimal rutile TiO₂ growth conditions on m-sapphire require a pressure of 4.5 mTorr, a temperature of 650 °C and 20% oxygen in the sputtering chamber.

2.3 Surface and texture quality of rutile films

Surface roughness is an important factor in determining the optical quality of photonic materials. Surface roughness causes light to scatter as a function of the wavelength of light and size of the grains. We investigate the surface roughness of TiO₂ samples deposited under different sputtering conditions using Atomic Force Microscopy (AFM).

2.3.1 Experimental Methods

An Asylum AFM is used to measurement the surface roughness of TiO₂ samples. A 7 nm-radius cantilever tip is used in non-contact alternating current mode. Root mean square roughness is extracted and averaged over multiple 1 µm x 1 µm regions for each sample.

2.3.2 Experimental Results

The AFM scans for six rutile TiO₂ samples are shown in Fig. 2.8. The top row of AFM scans depicts samples with low root mean square (RMS) surface roughness (from 0.38 to 0.52 nm). The samples on the bottom row have higher roughness. Although TiO₂_5 and TiO₂_14 had higher roughness values (around 0.80 to 0.95 nm) than the top 3 scans, the

most significant difference is visible for sample TiO₂_7, which had an RMS roughness of over 3 nm. While this sample has the appearance of a porous structure, the other samples have a granular surface with smaller grains.

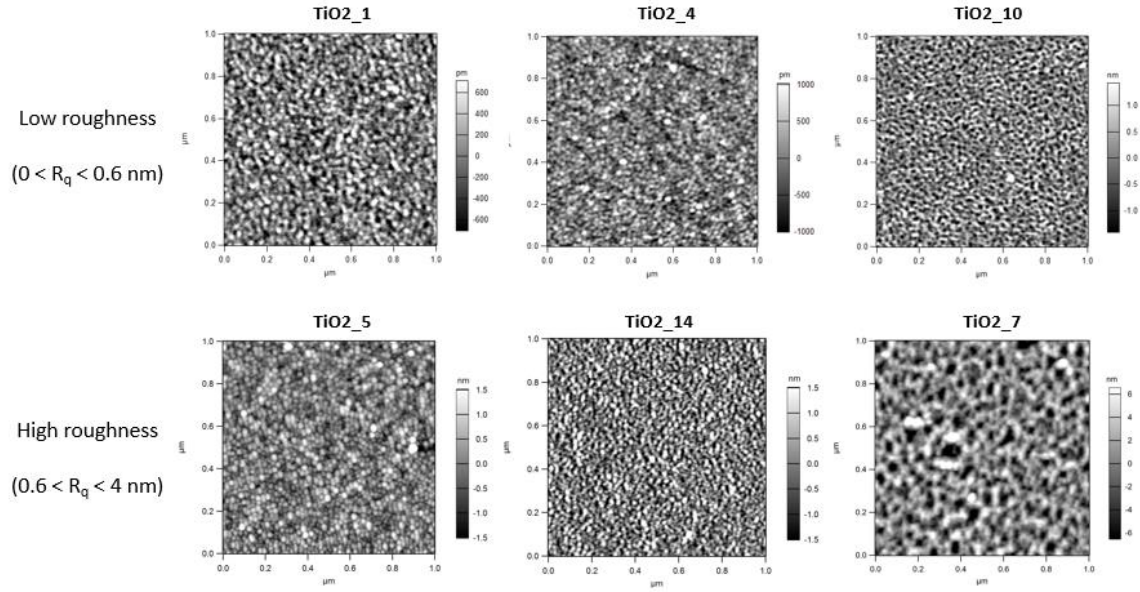


Figure 2.8: AFM scans for 6 rutile TiO₂ samples, showing samples with low roughness on the top row and samples with higher roughness in the bottom row. The sample with the highest roughness is TiO₂_7, which has a significantly different surface morphology compared to the other samples.

The RMS roughness values obtained for all measured samples are summarized in Table 2.3.1, along with the standard deviation from averaging over multiple 1 μm x 1 μm regions, and the deposition conditions for each sample. The power was kept constant at 180 W for all samples and is omitted from the table. Most samples show an RMS roughness in the

range of 0.38 to 0.60 nm. A few exceptions (samples number 5, 7 and 14) compute roughness above 0.60 nm but below 1.00 nm. The AFM scans for these samples are shown in the bottom row of Fig. 2.8. Samples 5 and 7 can be compared as part of a temperature series, where samples were deposited at the same pressure and O₂ content of 3 mTorr and 33%, respectively, but the temperature was varied.

Table 2.2: Summary of RMS roughness values obtained for rutile TiO₂ samples, along with standard deviation from averaging multiple measurements of the roughness, and deposition parameters for each sample. All samples were deposited at 180 W.

	RMS Roughness [nm]		Deposition Parameters		
	Average	Standard Deviation	T [°C]	O ₂ [%]	P [mT]
TiO ₂ _1	0.41	0.13	450	33	3
TiO ₂ _3	0.44	0.05	350	33	3
TiO ₂ _4	0.38	0.03	300	33	3
TiO ₂ _5	0.80	0.03	250	33	3
TiO ₂ _7	3.06	0.48	650	33	3
TiO ₂ _10	0.52	0.01	450	20	3
TiO ₂ _12	0.60	0.02	450	43	4.5
TiO ₂ _14	0.95	0.07	450	20	4.5
TiO ₂ _16	0.45	0.04	450	30	4.5

2.3.3 Discussion

The results for the rutile TiO₂ samples with low surface roughness is a significant improvement over previous work with anatase TiO₂ grown on a substrate of silicon with

thick silicon dioxide (RMS roughness around 2.7 nm) and comparable to amorphous TiO₂ grown on a similar substrate (RMS roughness around 0.4 nm)[27]. We attribute this in part to the epitaxial growth of our rutile TiO₂ samples, confirmed via XRD ϕ -scans and achieved by lattice matching with the sapphire substrate. This epitaxial growth ensures that, in the plane of the sample, TiO₂ growth islands, present the same growth rate have the same orientation and do not form defective grain boundaries. The surface roughness observed from AFM scans is due to island formation at the air boundary. We attribute higher roughness to the growth mechanism of TiO₂ within each sample. At higher temperatures, atom mobility is higher, whereas at higher pressures, mobility decreases due to high adatom concentration on the surface.

Among the sample with high surface roughness, samples 5 and 7 correspond to the lowest and highest temperatures tested (250 and 650 °C, respectively), demonstrating that both high and low temperature extremes lead to increased surface roughness. A comparison of the remaining samples in the temperature series (samples number 1, 3 and 4) indicate at first glance that sample 4 deposited at 300 °C has the lowest roughness, with a roughness RMS value of 0.38 nm. However, the sample deposited at 450 °C also resulted in a low roughness of 0.41 nm, and the sample at 350 °C had a slightly higher value of 0.44 nm. When including the standard deviation of these measurements in our analysis, we see that the roughness for these samples have some overlap. We can attribute this error to the variability of roughness over the sample and measurement error (e.g. from rounding of the AFM tip after multiple scans). This overlap in the results indicates that the full temperature range of 300 - 450 °C can be considered optimal for samples deposited at 3 mTorr and 33% O₂.

Among the samples at other pressure or O₂ %, we see the following trends: the O₂ % series at 4.5 mTorr shows an optimized surface roughness of 0.448 nm at 30 % O₂. At 3 mTorr, the O₂ % series results are mixed: The sample at 33 % O₂ has a slightly better RMS surface roughness of 0.41 ± 0.13 nm; however, the standard deviation is high and overlaps with the RMS surface roughness of the sample at 20% O₂ (0.52 ± 0.01 nm). Therefore, our data indicates that there is higher impact to the surface roughness when varying the oxygen concentration at higher pressure, in this case 4.5 mTorr as opposed to 3 mTorr.

Table 2.3: Summary of XRD rocking curve (abbreviated RC) and RMS surface roughness values for samples deposited at different pressure and oxygen contents. All samples are kept at a temperature of 450 °C.

		20%	30%	43%
3.0 mT	RC [°]	0.78	0.87	0.87
	RMS [nm]	0.52	0.41	
4.5mT	RC [°]	0.66	0.72	0.84
	RMS [nm]	0.95	0.45	0.60

We further analyze this data by combining these insights with the XRD rocking curve of rutile (002) reflection data. We summarize both datasets in Table 2.3. Although the surface roughness data indicates that 30% O₂ is best (especially at 4.5 mTorr), the rocking curve data suggests that 20% O₂ improves the mosaicity of the sample (level of misorientation in the out-of-plane direction). Similarly, although AFM data indicates that a pressure of 3 mTorr leads to lower surface roughness, the RC data indicates the opposite trend, with

lower variability for the higher 4.5 mTorr pressure. Therefore, we conclude that by optimizing the samples for lowest surface roughness, we have a higher mosaicity and vice-versa. We further see evidence of this trend in the example of sample 7 (deposited at 650 °C, 3mTorr and 33% O₂). This sample had the highest surface roughness, but the lowest rocking curve value of all the samples (0.513°).

2.3.4 Conclusion from AFM studies

For photonic applications, both the quality of the growth of the material, as well as the surface roughness are important. Mosaicity can be improved by increasing the deposition temperature and by reducing the growth rate. However, this can lead to an increase in surface roughness. On the other hand, post-growth techniques for reducing surface roughness include chemical mechanical polishing (CMP). In addition, guiding losses (from surface roughness and top-down fabrication etching roughness) were shown to improve in TiO₂ waveguides by depositing a thin amorphous layer of TiO₂ on the structured sample using Atomic Layer Deposition (ALD)[61]. The latter techniques can be employed to decrease the effect of surface roughness in order to maintain high-quality epitaxial growth.

2.4 X-ray Photoelectron Spectroscopy (XPS)

We investigate the composition of titanium dioxide samples deposited under different sputtering conditions using x-ray photoelectron spectroscopy (XPS). Survey scans provide qualitative and quantitative information on the composition of the sample. High resolution

scans at the binding energy of specific elements are performed to verify their chemical state and type of bonding.

2.4.1 Experimental Methods

A Thermo Scientific K-Alhpa+ system from the Harvard Center for Nanoscale Systems (CNS) is used to perform survey and high-resolution measurements of the composition of titanium dioxide samples. The system uses an Al K-alpha source with a micro-focused monochromator, providing x-rays with energy of 1486.6 eV, line width of 0.85 eV and variable spot-size between 30-400 μm . The system is equipped with monatomic and cluster ion guns for surface cleaning and etching of the samples using variable energy from 200-4000 eV and 2000-8000 eV, respectively. In addition, a dual beam, ultra-low energy flood gun provides charge compensation.

Survey scans of the titanium dioxide samples are performed for binding energies between -10 to 1350 eV using a 400 μm spot-size, a dwell time of 10 ms and a pass energy of 200 eV. High resolution scans are performed for Carbon 1s, Titanium 2p and Oxygen 1s spectra using a 50 eV pass energy and 25 ms dwell time. A flood gun is used to limit charging of the samples.

XPS Advantage software is used to fit all high-resolution peaks with the Powell fitting algorithm and Shirley background subtraction. The fit peak shapes are a convolution of Gaussian and Lorentzian functions, constrained in this work to the same Gaussian/Lorentzian ratio (L/G product) for the $\text{Ti}2\text{p}_{3/2}$ and $\text{Ti}2\text{p}_{1/2}$ curves of each

oxidation state. Fits are optimized based on minimizing the χ^2 and reaching an Abbe criterion value closest to 1.

The C 1s high-resolution spectrum fit is used for internal charge correction by setting the adventitious carbon peak (associated with C-C, C-H bonds) to 284.6 eV[62]. Three additional carbon peaks are included in the analysis to improve the accuracy of the calibration. A peak corresponding to C-OH, C-O-C bonds is constrained to 1.5 eV above the adventitious peak. Another peak, corresponding to C=O bonds is constrained to 3.0 eV above the adventitious peak. Finally, a peak corresponding to O-C=O bonds is constrained to 4.5 eV above the adventitious peak. Although care was taken in extracting the most accurate peak location for the adventitious carbon, this calibration technique still has an error of at least ± 0.1 eV[62].

The Ti 2p spectra are analyzed by fitting peaks corresponding to all four different oxidation states of titanium. The binding and splitting energy for the Ti 2p_{3/2} and Ti 2p_{1/2} peaks of each oxidation state is restricted according to available data from the NIST XPS database, as well as standard sample data for Ti and TiO₂[63]. The binding and splitting energy for each oxidation state are as follows: Ti(0) with Ti 2p_{3/2} binding energy between 453.60 and 454.20 and splitting energy $\Delta = 6.1 \pm 0.06$; Ti(II) with Ti 2p_{3/2} binding energy between 454.90 and 456.10 and splitting energy $\Delta = 5.6$; Ti(III) with Ti 2p_{3/2} binding energy between 456.60 and 458.00 and splitting energy $\Delta = 5.2$; and, Ti(IV) with Ti 2p_{3/2} binding energy between 458.37 and 458.90 and splitting energy $\Delta = 5.7 \pm 0.08$. The intensity, as measured by the number of counts, between the Ti 2p_{3/2} and Ti 2p_{1/2} peaks of each species is fixed to a 2:1 ratio. The FWHM Ti 2p_{3/2} and Ti 2p_{1/2} peaks used for fitting is constricted to a ratio of 1:1.68.

XPS measurements are very sensitive to contamination. The titanium samples discussed here were exposed to air and various characterization measurements prior to XPS investigation. Therefore, a rigorous cleaning procedure was necessary to prepare the sample for XPS measurements. The titanium samples are chemically cleaned using a pirana etch solution with 3:1 ratio of sulfuric acid to hydrogen peroxide for 5 minutes, followed by solvent clean with sonication and N₂ blow dry. In addition, a closed polystyrene multi-well container wrapped in aluminum foil is used to transport the samples to minimize contamination from other plastics, adhesives and the air. Samples are mounted using gold pins to minimize charging, since TiO₂ and the sapphire substrate are insulating. Charging effects shift the XPS spectra peaks and can contribute to sample damage. Although the gold pins likely contribute to contaminating the sample, the alternative mounting technique using carbon tape on the bottom of the samples leaves substantial residue, without addressing the surface charging problem. Within the XPS system, a Ar⁺ cluster ion beam source is used for light sputter-etch cleaning of each sample at an energy of 6000 eV for intervals of 5 minutes, until the carbon and other possible contaminants are identified as less than 2% of the atomic percent of elements on the sample surface. This ion beam energy is chosen to maximize cleaning efficiency while minimizing changes to the shape of the XPS peaks due to charging. Changes to the shape of the curves indicate damage to the sample and affect the results from the fitting the data, leading to inaccurate atomic percents.

2.4.2 Survey scan (Ti to O ratio):

Figure 2.9 is an example of a survey scan for a titanium dioxide sample. The elemental binding peaks are identified using Avantage software (Thermo Avantage v5). The total

counts under each peak are used to determine the atomic percent of Ti and O. Survey spectra are obtained for titanium dioxide samples grown under varying conditions and the atomic percent of Ti and O for each sample is summarized in Tables 2.4 and 2.5.

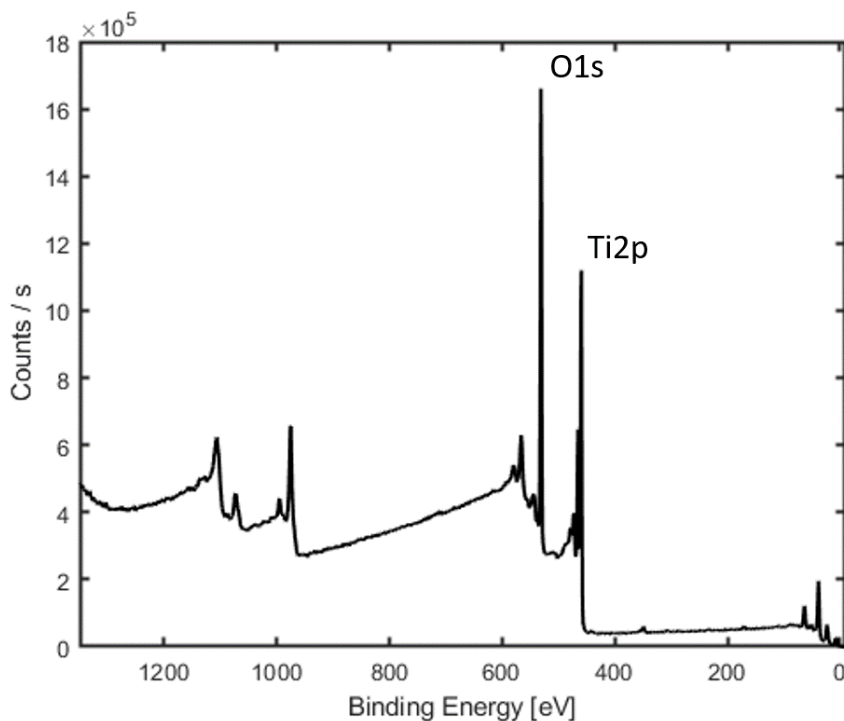


Figure 2.9: XPS survey spectrum for titanium dioxide sample. Ti2p and O1s peaks are identified with Advantage software.

The survey spectra results for the oxygen to titanium ratio fall consistently between 0.47 and 0.48. This is indicative of the presence of TiO_2 (Ti(IV) oxidation state). The slight deviation from a 0.50 ratio could be due to a small mixture of other Ti species or could be

due to a small presence of contaminants, such as carbon, which bind with the excess oxygen.

Table 2.4: Temperature series XPS survey results for samples deposited at 3 mTorr and 30 % oxygen atmospheric content.

Deposition Temperature [°C]	O1s [%]	Ti2p [%]	O : Ti ratio
250	32.42	67.58	0.480
350	32.04	67.96	0.471
450	32.22	67.78	0.475
650	32	68	0.471

Table 2.5: Oxygen series XPS survey results for samples deposited at 450 °C. First three rows are for samples deposited at 3 mTorr. Bottom two rows are deposited at 4.5 mTorr.

Deposition Pressure [mTorr]	Deposition O ₂ [%]	O1s [%]	Ti2p [%]	O : Ti ratio
3	23	32.82	67.18	0.489
	33	32.22	67.78	0.475
	43	32.43	67.57	0.480
4.5	20	32.73	67.27	0.487
	43	32.19	67.81	0.475

Analyzing the data for Table 2.4 and 2.5 separately, we observe that the survey spectra data does not indicate specific trends in the oxygen to titanium ratio. We can conclude that our samples are once again confirmed to consist of TiO_2 . We further investigate the composition of the samples using high-resolution scans of the Ti2p binding energy region.

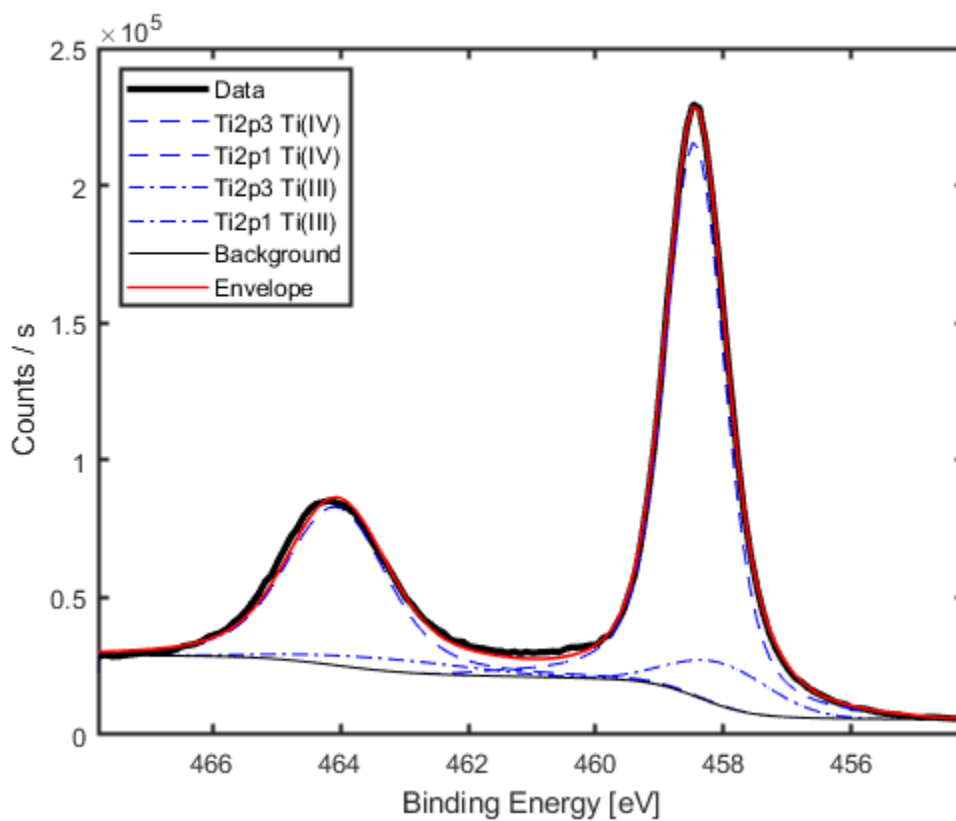


Figure 2.10: High-resolution Ti2p scan of sample 16. Raw data (thick black) is fit with Ti(IV) and Ti(III) peaks (dashed and dot-dashed blue curves, respectively), forming a fit envelope (red) that overlaps with the data. The background curve is shown in thin black.

Table 2.6 Summarized results from Ti2p high-resolution scans for temperature series samples. All samples are deposited at 30 % oxygen and 3 mTorr.

Sample	Oxidation state	Peak	Peak BE	Atomic %	
250 °C	Ti (IV)	2p 3/2	458.8	45.47	
		2p 1/2	464.42	49.16	94.63
	Ti (III)	2p 3/2	458	2.51	
		2p 1/2	463.2	2.73	5.24
350 °C	Ti (IV)	2p 3/2	458.89	45.99	
		2p 1/2	464.51	49.73	95.72
	Ti (III)	2p 3/2	458.00	1.99	
		2p 1/2	463.20	2.16	4.15
450 °C	Ti (IV)	2p 3/2	458.90	46.62	
		2p 1/2	464.55	50.43	97.05
	Ti (III)	2p 3/2	458.00	1.37	
		2p 1/2	463.20	1.49	2.86
650 °C	Ti (IV)	2p 3/2	458.84	43.37	
		2p 1/2	464.46	46.94	90.31
	Ti (III)	2p 3/2	458.00	4.61	
		2p 1/2	463.20	4.99	9.6

2.4.3 High resolution Ti 2p scan

We analyze Ti2p high-resolution spectra to obtain quantitative information regarding the oxidation state of Ti present in our samples. Figure 2.10 shows an example of Ti2p data and the oxidation state fit performed for our titanium dioxide samples. The data is plotted in black.

Dashed and dot-dashed blue lines show the curves for the Ti(IV) and Ti(III) species, respectively. The envelop of the combined fit curves is shown in solid red, overlapping the black data curve. The atomic percent for each Ti species curve in the fit can be extracted with Advantage software and is presented in Table 2.6 for samples in the temperature series.

In addition, samples with varying pressure and oxygen concentration are shown in Table 2.7. The curves for Ti^{4+} , corresponding to the presence of TiO_2 is consistently higher than Ti^{3+} . The percentage of Ti with oxidation state 0 and +2 is below 0.2 atomic percent for all samples and is therefore omitted.

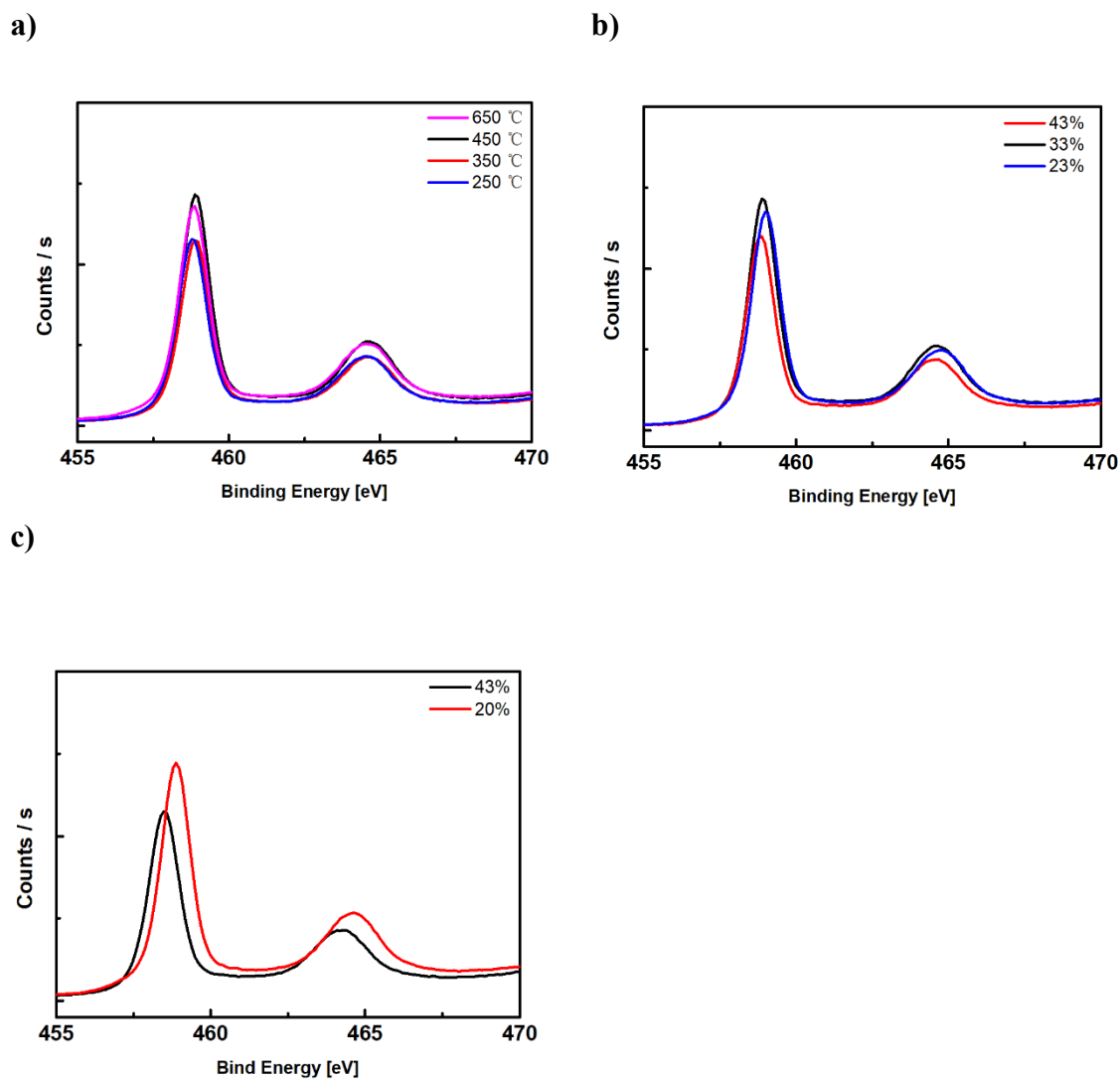


Figure 2.4.3: Stacked Ti2p scans for (a) temperature series data, and oxygen content series at (b) 3 mTorr and (c) 4.5 mTorr.

Table 2.7 Summarized results from Ti2p high-resolution scans for oxygen series samples at 3 and 4.5 mTorr. All samples are deposited at 450 °C.

Sample	Oxidation state	Peak	Peak BE	Atomic %	
23 % O ₂ 3 mTorr	Ti (IV)	2p 3/2	458.9	47.96	
		2p 1/2	464.52	51.92	99.88
	Ti (III)	2p 3/2	458	0.02	
		2p 1/2	463.2	0.02	0.04
33 % O ₂ 3 mTorr	Ti (IV)	2p 3/2	458.9	46.62	
		2p 1/2	464.55	50.43	97.05
	Ti (III)	2p 3/2	458	1.37	
		2p 1/2	463.2	1.49	2.86
43 % O ₂ 3 mTorr	Ti (IV)	2p 3/2	458.83	46.09	
		2p 1/2	464.45	49.84	95.93
	Ti (III)	2p 3/2	458	1.91	
		2p 1/2	463.2	2.07	3.98
20 % O ₂ 4.5 mTorr	Ti (IV)	2p 3/2	458.87	43.73	
		2p 1/2	464.49	47.3	91.03
	Ti (III)	2p 3/2	458	4.24	
		2p 1/2	463.2	4.59	8.83
43 % O ₂ 4.5 mTorr	Ti (IV)	2p 3/2	458.55	40.39	
		2p 1/2	464.17	43.71	84.1
	Ti (III)	2p 3/2	458	7.63	
		2p 1/2	463.2	8.25	15.88

We observe from Table 2.6 that the temperature series samples have a high (>90%) percentage of Ti⁴⁺. We see a light trend of increasing Ti⁴⁺ for increasing temperature. However, this changes abruptly for the sample deposited at 650 °C, the highest temperature tested. This is similar to the AFM results, where we observed a slightly higher RMS surface roughness of 0.8 nm at the lowest temperature, followed by an improvement in the roughness for temperatures ranging from 300 – 450 °C (mostly around R_q = 0.4 nm), followed by a sharp increase in the roughness for the 650 °C sample. Similar to the reason

for increased surface roughness, the reason for a slight decrease in Ti^{4+} concentration could be the presence of adatoms at the surface of this sample.

The trends in the data for the oxygen series, shown in Table 2.4.4, are more pronounced than in the temperature series. The Ti^{4+} concentration for samples at 3 mTorr (95 – 99 %) is clearly higher than for the samples at 4.5 mTorr (84 – 91 %). In addition, between the samples deposited at 4.5 mTorr there is a clear increase in the TiO_2 concentration for the sample deposited at 20 % O_2 compared to the sample at 43 %. This trend, even though less pronounced, is also seen for the data at 3 mTorr.

2.4.4 Conclusions from compositional analysis of TiO_2 films

We perform survey and high-resolution Ti scans of our sputtered samples and confirm that all samples are predominantly Ti with oxidation state +4. We find that TiO2_12, the sample deposited at 4.5 mTorr, 43 % O_2 and 450 °C has the lowest concentration of Ti^{4+} around 84.1%, whereas all other samples result in over 90% percent of TiO_2 . Our data indicates that lower concentrations of O_2 of about 20 % during deposition improve the concentration of TiO_2 to 99.9% for the case of 3 mTorr and 450 °C. If the trend is the same at 4.5 mTorr, it is possible that a lower oxygen concentration during deposition could optimize this further.

We attribute the lower concentration of Ti^{4+} in the sample deposited at 650 °C to the presence of adatoms at the surface. Since we found surface roughness to be formed on this sample on the order of 3 nm, and our XPS cleaning procedure was performed gently with a cluster source to avoid etching and changing the surface chemistry, it is possible that the XPS spectra mostly sampled the rough surface layer where formation of Ti_2O_3 may have

occurred. XPS typically samples the first 10 nm or less of the surface; this explains that the result primarily pointed to Ti^{4+} with a small mixture of Ti^{3+} . Depths profile studies could indicate differences in the composition of our films when comparing the treated surface and a few nanometers into the film. Interestingly, the samples in the 4.5 mTorr oxygen concentration series do not follow this trend of higher Ti^{3+} for higher roughness. Samples TiO2_12 (43% O_2) and TiO2_14 (23% O_2) had RMS roughness on the order of 0.6 and 0.95 nm, respectively, but have Ti^{4+} concentrations of 84.1 and 91.0%, respectively. We compare AFM and XPS results for these samples with rocking data in Table 2.8. We observe that the FWHM of TiO2_12 is higher, at 0.84 vs. 0.66 for TiO2_14. Therefore, it is possible that the higher mosaicity of these samples is also an indication of Ti_2O_3 inclusions.

Table 2.8: Comparison of results from XRD rocking curve, AFM and XPS Ti2p scans for samples in oxygen concentration series for samples deposited at 3 and 4.5 mTorr.

		20%	30%	43%
3.0 mT	RC [°]	0.78	0.87	0.87
	RMS [nm]	0.52	0.41	-
	Ti(IV) [%]	99.88	97.05	95.93
4.5mT	RC [°]	0.66	0.72	0.84
	RMS [nm]	0.95	0.45	0.60
	Ti(IV) [%]	91.03	-	84.10

Overall, our data confirm that our sputtering recipes succeeded in producing >84 % TiO₂ for all samples. Ti⁴⁺ concentration of 99.9 % was achieved when sputtering at 3 mTorr, 23% O₂ and 450 °C. We expect that depth profile studies of samples with higher roughness could lead to recording higher concentrations of TiO₂ for these samples by avoiding the surface area where other Ti species can form.

CHAPTER 3: OPTICAL CHARACTERIZATION OF RUTILE TiO₂

Optical properties of materials determine their suitability for specific applications. An important property for designing photonic devices is the index of refraction of a material. We investigate the optical properties of rutile TiO₂ thin films grown on m-sapphire. We measure the refractive index using prism coupling and spectroscopic ellipsometry. In addition, we investigate birefringence in TiO₂ films.

3.1 Prism Coupling measurements of rutile films

Prism coupling is a technique for coupling light into thin films to determine their refractive index and thickness. We discuss the theory of prism coupling and measure the index of rutile TiO₂ samples. An example of a TiO₂ measurement yielding one mode at 633 nm is shown in Figure 3.1.

3.1.2 Basic Theory

A prism coupler system makes use of refraction in a prism to vary the angle of incidence of light for coupling into a thin film sample of interest. The angle at which light couples into the film is used to calculate the index of refraction of the film.

A sample of interest is held in contact with a prism using a coupling head that applies pressure to maintain the sample against the prism. A laser beam is incident on the angled

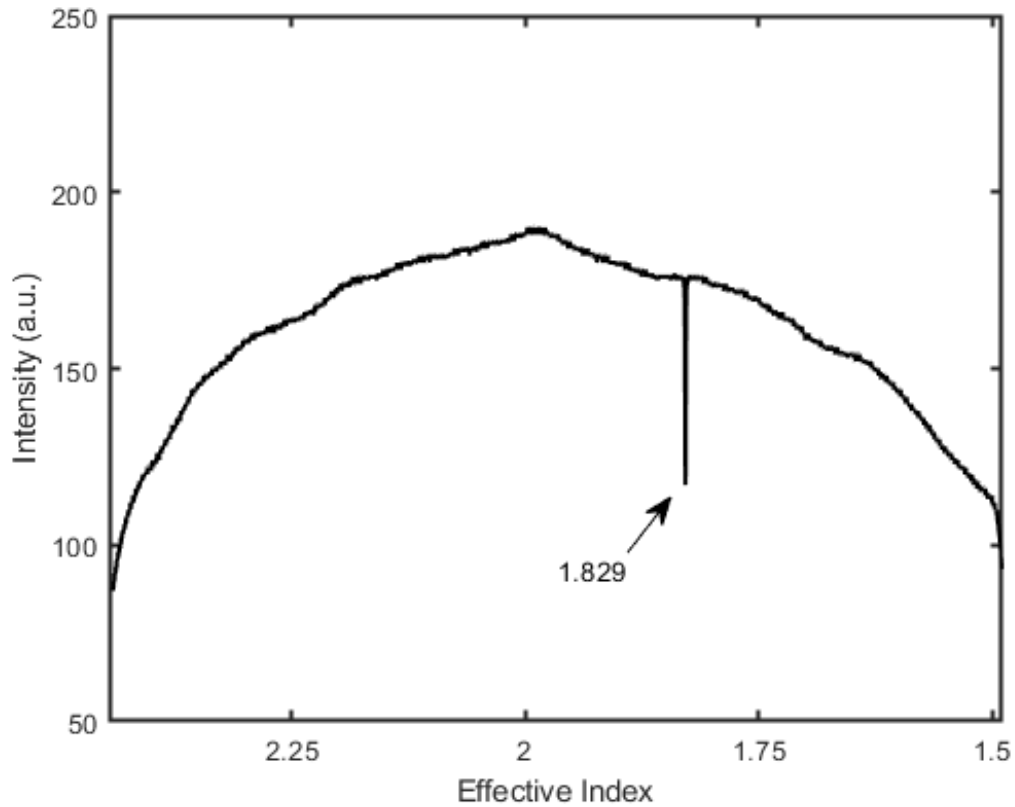


Figure 3.1: Example of a prism coupling measurement of a TiO_2 film with a sharp mode at effective index 1.829 at a wavelength of 633 nm.

prism facet while a rotation stage rotates the prism and sample in small steps. This rotation causes the angle between the direction of propagation of the beam and the facet of the prism to vary in small steps. As follows from Snell's law, laser light is transmitted from the air into the prism. The change in angle of incidence varies the angle at which the beam propagates within the prism to the next prism facet. The high index of the prism ensures that the beam typically experiences total internal reflection at this second facet and is reflected toward the third facet of the prism. After the third facet, light is transmitted to a

photodetector (which is also mounted on the rotary table that controls the angle of the prism and film). Maximum signal at the photodetector indicates that light did not couple into the sample.

At specific rotation angles, the angle of the beam at the second facet will violate the total internal reflection criteria and couple into the film. This causes a sharp decrease in the signal reaching the photodetector, resulting in the appearance of a transmission dip. The angle at which this dip occurs is dependent on the properties of the sample, including substrate index, film thickness and film index of refraction. If the substrate index is known, the two remaining variables (the thickness and index of the film) can be calculated with the angular information from two modes.

In order to obtain values for these variables when a number of modes m are detected, we use the mode equation below:

$$(2\pi/\lambda) \times n \times \cos(\theta_2) \times t + \Psi_{10} + \Psi_{12} = m\pi \quad (m = 0, 1, 2, \dots)$$

Here, λ is the wavelength of the laser beam, n is the film index, θ_2 is the angle of the beam within the film at each mode, t is the thickness of the film and Ψ_{10} and Ψ_{12} are correction terms for Fresnel phase shifts at the film-air and film-substrate interfaces. Solving these complex transcendental equations numerically yields the index and thickness of the film, as well as the mean and standard deviation of each calculation (when more than 2 modes are measured).

3.1.2 Experimental Methods

We perform prism coupling measurements with a Metricon Corporation Model 2010 prism coupler equipped with a He-Ne laser (632.8 nm wavelength) and 826 nm diode laser. Both lasers are >99% TE. We use a rutile TiO₂ prism cut at 43.8 degrees, capable of measuring modes with an effective index of refraction of 2.44 to 1.48. We measure thin TiO₂ films (typically around 60-70 nm thick) with only one transverse electric (TE) mode at each wavelength. To calculate the index of refraction with one mode, we enter the assumed thickness of the film, obtained from point-ellipsometry measurements.

We perform additional measurements of our samples by rotating them by 90 degrees to investigate the birefringence of our TiO₂ layer, computed as a difference in the result between measuring the samples oriented vertically vs. horizontally (0 and 90-degree rotation, respectively). For all measurements, we calculate the index of TiO₂ by using the extraordinary or ordinary index of sapphire in our model when measuring the samples at 0 and 90 degrees, respectively.

We confirm that the mode detected is the 0th order mode by using the mode-offset functionality of the Metricon software. This option calculates the index and thickness by varying the m-parameter of the mode in the mode equation. We find that the higher-order solutions lead to indices of refraction much higher than the known range of TiO₂ (e.g. 4 vs. 2.6), thus verifying that only the 0th-order result is feasible.

Table 3.1: Summary of indices of refraction obtained for sputtered rutile TiO₂ samples using prism coupling. Results for measurements at wavelengths of 633 and 826 nm are shown for both ordinary (n_o) and extraordinary (n_e) axes of sapphire. Deposition conditions for each sample are summarized on the right side of the table.

Sample	Index (633nm)		Index (826nm)		Thickness	Power (W)	Temp (°C)	O ₂ (%)	P (mTorr)
Substrate index	no	ne	no	ne					
TiO2_1	2.65	2.62	2.58	2.55	70 nm	180	450	33	3
TiO2_3	2.66	2.61	2.57	-	48 nm	180	350	33	3
TiO2_4	2.57	2.54	2.49	2.47	61 nm	180	300	33	3
TiO2_5	2.58	2.55	2.51	2.48	66 nm	180	250	33	3
TiO2_7	-	2.53	-	2.46	70 nm	180	650	33	3
TiO2_9	2.57	2.54	2.49	2.45	66 nm	180	450	43	3
TiO2_10	2.58	2.56	2.50	2.48	80 nm	180	450	23	3
TiO2_12	2.62	2.58	2.55	2.50	67 nm	180	450	43	4.5
TiO2_14	2.63	2.60	2.56	2.53	79 nm	180	450	20	4.5
TiO2_15	2.58	2.55	2.51	2.47	75 nm	180	450	15	4.5
TiO2_16	2.59	2.56	2.51	2.48	72 nm	180	450	30	4.5
TiO2_30	2.60	2.56	2.54	2.50	70 nm	180	150	33	3
TiO2_32	2.60	2.58	2.53	2.51	70 nm	180	68	33	3

3.1.3 Results

We summarize the values obtained for the index of refraction of rutile TiO₂ samples at wavelengths of 633 nm and 826 nm. We include results measurements performed along the ordinary and extraordinary axes of the m-sapphire substrate. Table 3.1 summarizes the results. Two samples have some omitted data: TiO2_7 has modes with effective indices of

refraction below the measurement range of the prism used during measurements; and, TiO₂_3 is too thin to measure at 826 nm along the extraordinary axis of m-sapphire.

We observe that the indices of refraction obtained at 633 nm vary from 2.66 to 2.57 along the ordinary axis of m-sapphire and present an average birefringence of 0.03, when compared to the indices obtained for the extraordinary axis of m-sapphire. Similarly, we obtain indices varying from 2.59 to 2.44 for measurements taken at 826 nm, with a similar birefringence of 0.03.

We further analyze these results by grouping and plotting the data according to the deposition temperature series. Figure 3.2 shows the data obtained for samples that were deposited under different temperatures while maintaining constant pressure and oxygen concentration at 3 mTorr and 33%, respectively. We observe that the highest indices are achieved for temperatures in the range of 350 – 450 °C. This indicates that the growth at these middle temperature ranges allowed for the highest density of TiO₂ to be grown.

Finally, we analyze the optical data by grouping the samples according to oxygen content series at 3 and 4.5 mTorr. Figure 3.3 shows the results. We observe that the variation in index of refraction is random. We conclude that varying the O₂ concentration did not have a significant impact on the index of refraction of our samples. Based on this analysis, we observe that the deposition temperature had the strongest impact on the index of refraction results.

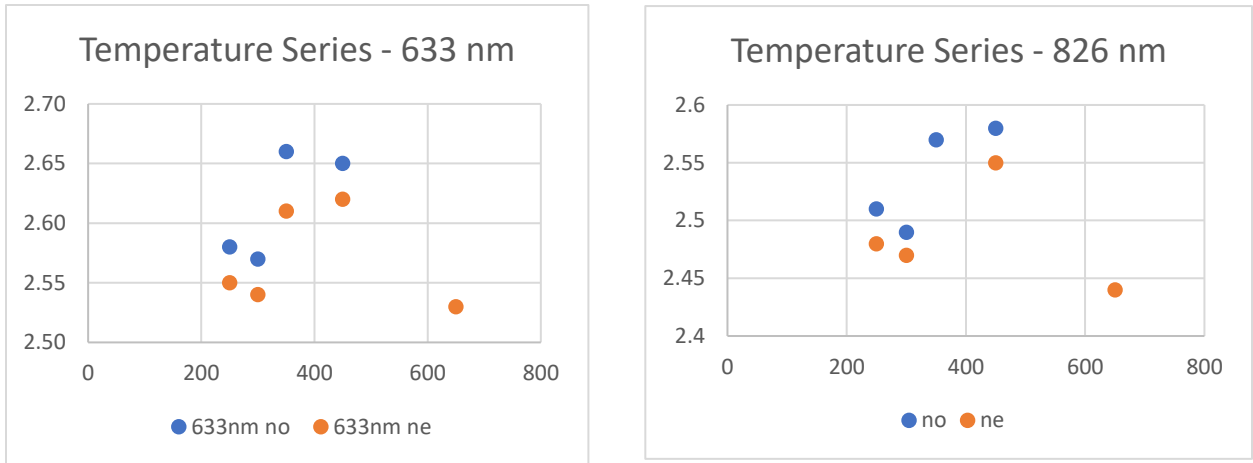


Figure 3.2: Plot of index of refraction of films vs. temperature of deposition measured at 633nm (left) and 826 nm (right). We observe that in both cases the highest index of refraction is computed at 350 and 450 °C.

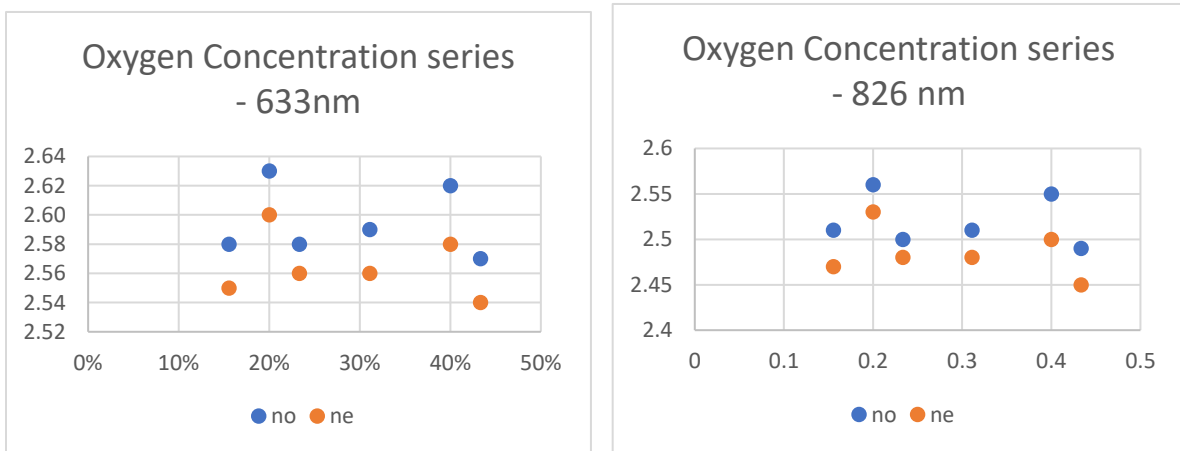


Figure 3.3: Plot of index of refraction of films vs. oxygen concentration measured at 633nm (left) and 826 nm (right).

3.2 Ellipsometry

Ellipsometry is a technique that characterizes the thickness and optical properties of films. We use two ellipsometric techniques to measure our samples. A point-ellipsometer at a wavelength of 633 nm to obtain a measure of the thickness of the sample. We confirm this thickness using prism coupling, which is discussed in detail in sections 3.1 and 4.1. We use spectroscopic ellipsometry to achieve a more accurate measurement of the dispersion in a rutile TiO₂ sample that we use to fabricate nanophotonic devices. This technique makes use of polarized light, varying the angle of incidence of the beam onto the sample and scanning a range of wavelengths to obtain a measurement of the dispersion of our sample.

We perform ellipsometry measurement of m-sapphire and rutile TiO₂ using a J.A. Woolam spectroscopic ellipsometer, for a wavelength range of 275 to 880 nm, at an angle of incidence of 70 degrees. The spectroscopic ellipsometry data is modeled using WVASE Software. We first measure the m-sapphire substrate separately and model the data using a Tauc-Lorentz fit. Since the substrate is transparent, the ellipsometry data presents multiple fringes from back reflections. This occurs because the sample does not absorb the ellipsometer beam and Fresnel reflections occur at the back of the sample, causing light to reflect back to the front facet, where more Fresnel reflections occur. This effect is typically avoided when using silicon as the substrate, since silicon is absorbing in the visible wavelength range. The Tauc-Lorentz model is capable of modeling the data accurately even with the presence of fringes. We measure the substrate at 0 and 90 degrees, to have accurate fits of the dispersion along the ordinary and extraordinary axes of sapphire, given possible birefringence in the film.

We model TiO_2 data using the appropriate m-sapphire fit (ordinary vs. extraordinary axis) as the substrate and a new Tauc-Lorentz layer on top, to represent the TiO_2 layer. We optimize both the substrate and TiO_2 fitting by monitoring the mean squared error of the fit and ensuring that it is as close to 0 as possible.

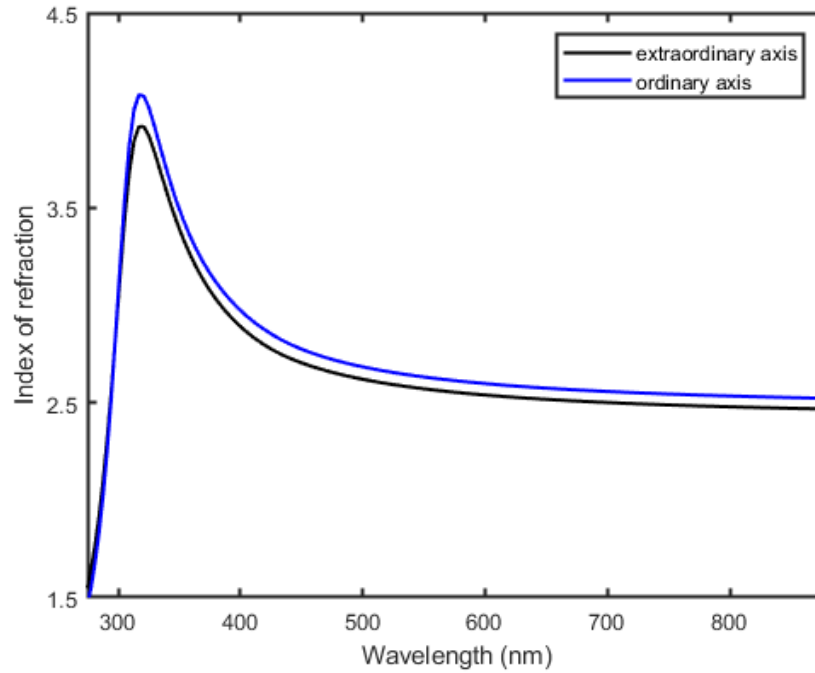


Figure 3.4: Ellipsometry result for TiO_2 measured along the extraordinary (black) and ordinary (blue) axes of sapphire. A slight birefringence is visible, showing that the index for the extraordinary axis curve has lower values than the ordinary axis curve.

The ellipsometric fit results for our rutile TiO_2 sample are plotted in Figure 3.4 in terms of index of refraction vs. wavelength. We find that the indices of refraction at 633 nm for the

ordinary and extraordinary axis orientations of sapphire are 2.524 and 2.582, respectively. Similarly, at 826 nm we find the ordinary and extraordinary axes index of refraction results to be 2.475 and 2.531, respectively. This is in agreement with the trend from prism coupling, where we generally find values near 2.6 and 2.5 at a wavelength of 633 nm for the extraordinary and ordinary axes orientations of sapphire, respectively. In addition, ellipsometry confirms the birefringence trend observed in prism coupling. Here, the birefringence is found to be around $\Delta n = 0.05$.

Our ellipsometry measurements confirm that we have obtained films with a higher index of refraction than anatase and amorphous films (~ 2.4 and 2.2 , respectively). Although we do not see a clear trend in the changes of the index of refraction based on deposition conditions (see section 3.1.3), we find that slight birefringence is found via multiple measurement techniques. Although we took care to model sapphire as accurately as possible, we investigate this birefringence further to verify that this is indeed a property of the film or if it is a possible source of error in the index of refraction models stemming from the birefringence of sapphire.

3.3 In-plane XRD measurements

Measurements from prism coupling and ellipsometry indicate the presence of birefringence. We investigate the source of birefringence in our TiO_2 films by performing in-plane XRD measurements and calculating the lattice parameters of TiO_2 . We analyze sample 7 and 1 to confirm the presence of birefringence in the TiO_2 layer, as opposed to only from the sapphire substrate.

3.3.1 Basic Theory

Rutile TiO_2 has a tetragonal unit cell with space group $P4_2/mnm$. Measurements of bulk rutile have characterized the lattice parameters of rutile TiO_2 to be $a = b = 4.59330 \text{ \AA}$ and $c = 2.95920 \text{ \AA}$ (PDF 21-1276). Given the birefringence detected via prism coupling and ellipsometry measurements, we examine if our rutile samples present stress or strain, leading to nonequal lattice parameters for a and b . In this case, we theorize that our samples could have a slightly modified lattice compared to standard rutile crystals, resembling an orthorhombic unit cell where the a and b lattice parameters have different values. Figure 3.3.1 depicts the (a) rutile TiO_2 , (b) tetragonal and (c) orthorhombic unit cells.

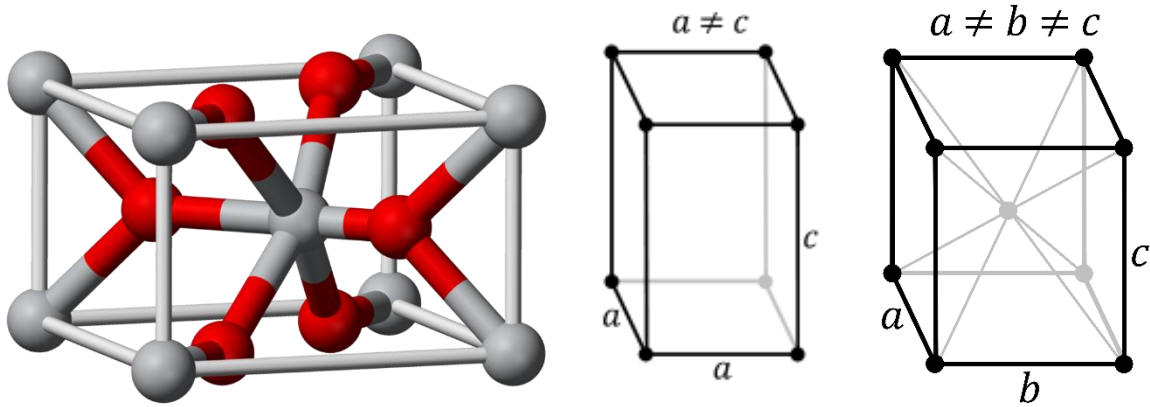


Figure 3.5: Unit cell for rutile TiO_2 (left), tetragonal (middle), and orthorhombic (right) crystals. The difference between the tetragonal and rhombohedral unit cells is that a and b have different values in the latter.

Reproduced from [64]–[66].

The crystal lattice parameters can be back-calculated from the 2θ angle measured in $\theta/2\theta$ XRD scans using the Bragg Law:

$$\lambda = 2d\sin(\theta)$$

To solve the equation above for d , one must input the x-ray wavelength λ used for measurements and divide in half the 2θ peak value observed, to input the value of θ . The equation below shows the Bragg Law solved for d :

$$d = \lambda / 2\sin(\theta)$$

The lattice spacing d relates to the Miller indices and lattice parameters of the unit cell by the following equation:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

The Miller indices for a given 2θ peak can be determined by cross referencing standardized tables (star quality PDF 21-1276 for rutile TiO_2). When measuring the rutile (002) peak, we can easily assign the indices as follows: $h = 0$, $k = 0$, $l = 2$. Subsequently, we can solve

for the lattice parameter c quite easily for this crystalline plane, since both denominators a and b have numerator equal to zero:

$$\frac{1}{d^2} = \frac{l^2}{c^2} \rightarrow c = d \times l$$

We probe other planes of rutile TiO_2 to solve for the lattice parameters a and b with the calculated value of c .

As seen in section 2.2.3, we have characterized the crystalline growth of our rutile films and determined that the out-of-plane orientation consists of rutile (002). We can further explore the crystalline planes of rutile TiO_2 oriented at angles (ψ) with respect to the out-of-plane direction. We visualize in Figures 3.6 and 3.7 the stereographic projection of the rutile TiO_2 crystalline planes for the case of rutile (002) out-of-plane orientation.

In figure 3.6 we observe that at the very center, we have a filled-in black circle indicating the rutile (002) plane location. In addition, we see four dark circles (red outline) located at equal distance $\psi = 62.643$ degrees from the center, indicating the location of the rutile (301) planes. In figure 3.7 we select the 8 circles located at $\psi = 55.233$ degrees, indicating the rutile (211) planes. The size of the circle is representative of the intensity of this signal compared to other peaks.

The crystallographic planes depicted in the stereographic projections in Figures 3.6 and 3.7 were chosen to have different Miller indices where h and k have different values.

Measuring these planes provides additional information about the lattice parameters of rutile TiO_2 by solving the Bragg Law.

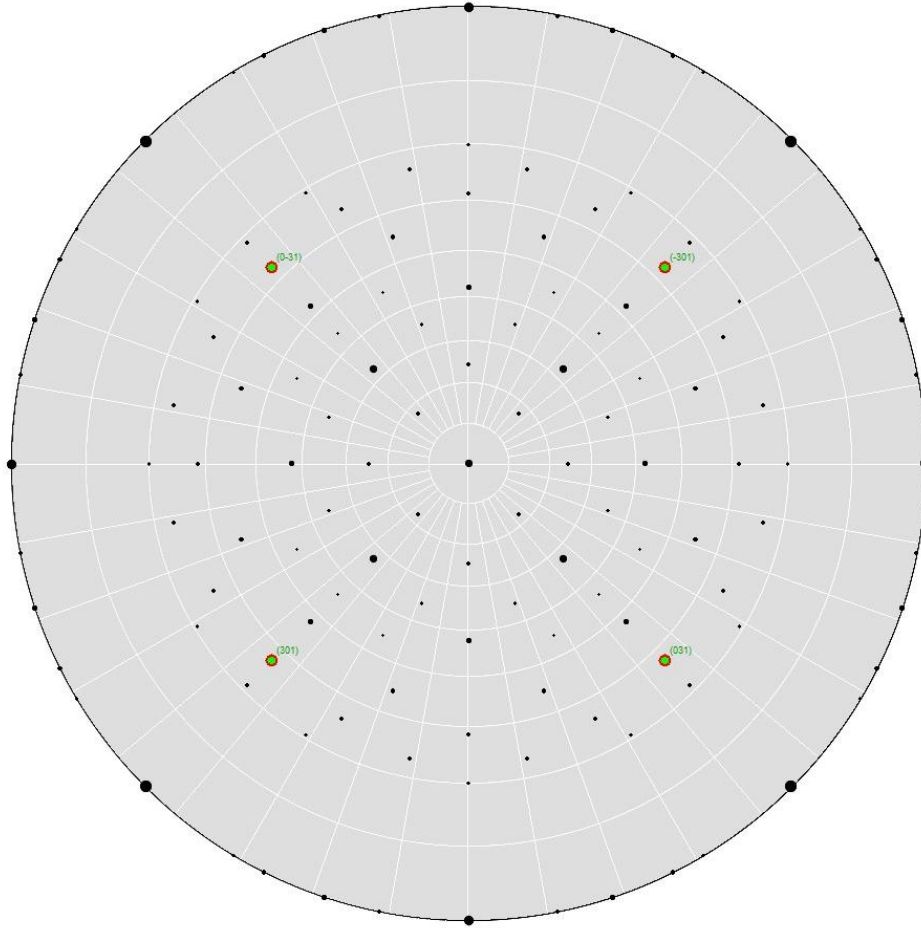


Figure 3.6: Stereographic projections highlighting the crystalline planes of rutile TiO_2 with (002) orientation at center shows the four rutile (301) peaks, located at $\psi = 62.643^\circ$ from the normal direction. Distance from the center can be measured by the 10-degree-step radial lines (white).

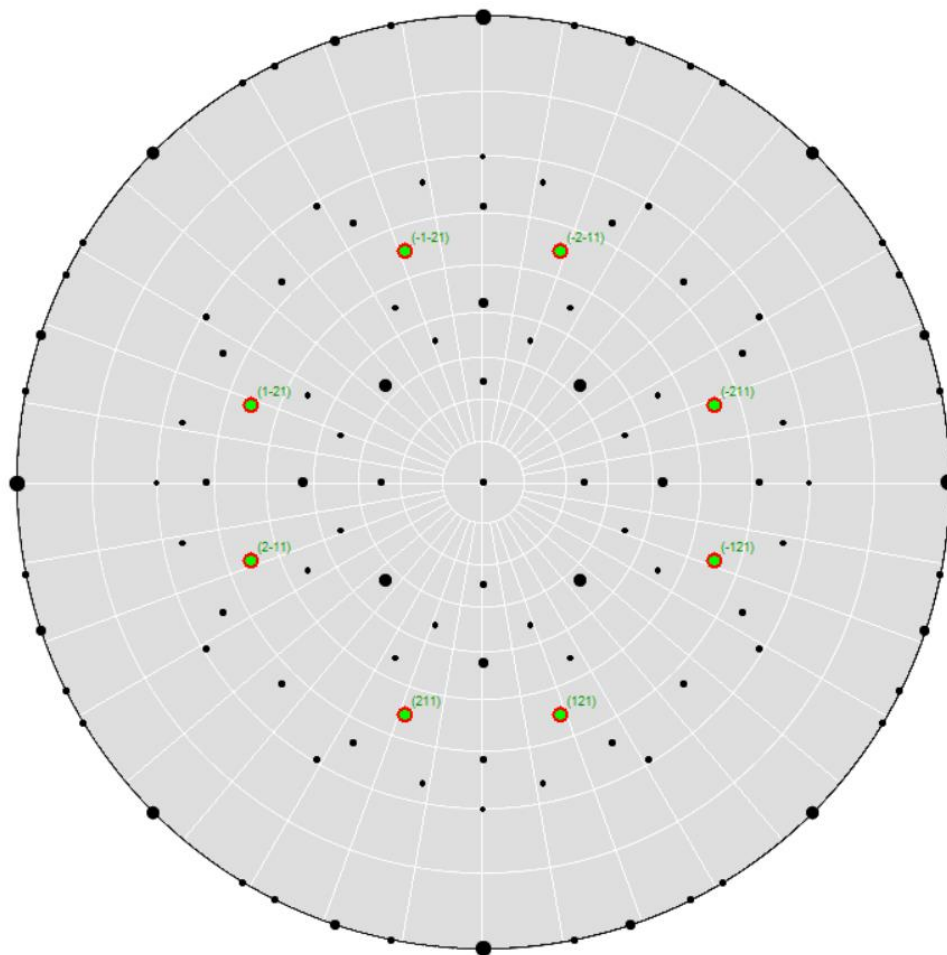


Figure 3.7: Stereographic projections highlighting the crystalline planes of rutile TiO_2 with (002) orientation at center (b) shows the eight rutile (211) peaks, located at $\psi = 55.233^\circ$ from the center.

We investigate the presence of these additional crystalline planes and calculate the resulting lattice parameters for our rutile TiO_2 films. In addition to solving for the lattice parameters, the presence of the peaks from the stereographic projections can provide additional confirmation of the epitaxial nature of our rutile TiO_2 films. The rocking curve results in section 2.2.3 and the phi-scan results of rutile (111) in section 2.2.4 confirmed that our samples are well oriented in the out of plane and in plane directions. The presence

of rutile (301) and (211) planes can provide additional demonstrations of this epitaxial growth.

3.3.2 Experimental Methods

A Bruker D8 Discover is used to measure the in-plane parameters of TiO₂. We perform a 2θ - ω scan at 0 degrees psi to confirm the presence of the rutile (002) and sapphire substrate peaks at 62.712° and 68.214° , respectively. We normalize measurements to the high-intensity sapphire peak. We tilt the sample to $\psi = 62.643$ degrees and $2\theta = 69.01$ degrees to measure the rutile (301) crystallographic planes. We perform a phi scan from 0 to 360 degrees to confirm the periodicity of the rutile (301) peaks. We compare our result to the expected symmetry from stereographic projections. We perform 2θ scans at the location of each phi peak by moving to the appropriate phi angle and scanning theta about the expected location of the 2θ peak for rutile (301). We fit the 2θ scans using a Gauss model in Origin software and enter each 2θ value into the Bragg equation to calculate lattice parameters. We repeat measurements for the rutile (211) crystallographic planes at the appropriate $\psi = 55.233^\circ$ and $2\theta = 54.323^\circ$ angles.

The data from rutile (002), (301) and (211) planes are chosen given their high intensity signal and because they each provide extra information for calculating the in-plane lattice parameters of our rutile TiO₂ sample. We use the value obtained for c in the rutile (002) measurement to calculate the a and b values based on two techniques: symmetry and system of two equations. In the first, we find the value for a or b from the rutile (301) measurements and assign the larger value to b . In the latter, we solve a system of equations

by comparing the results from rutile (211) and (121) planes. Both techniques are explained in my detail in section 3.3.4.

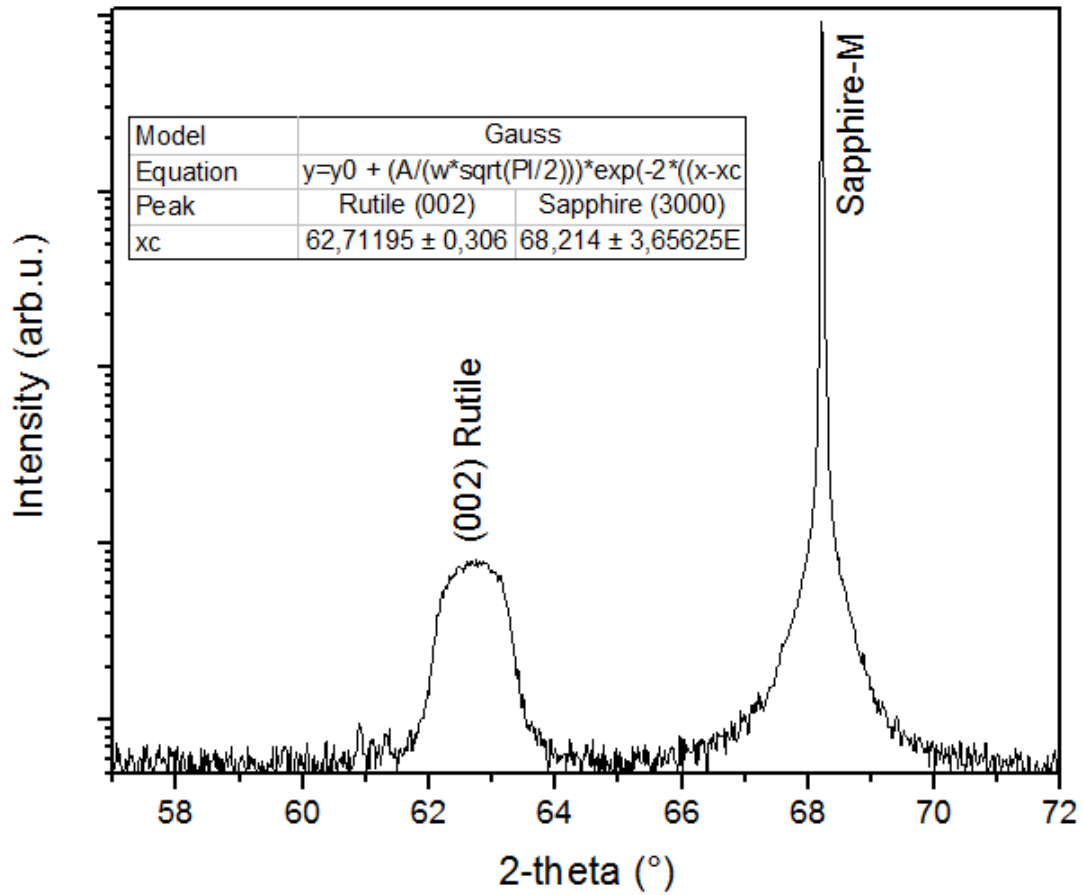


Figure 3.8: 2θ scan of TiO₂_7 with peaks for rutile (002) and the sapphire substrate at 62.712° and 68.214°, respectively.

We perform multiple measurements for each plane and calculate the standard deviation of each result. We also keep track of the placement of our sample during measurements and

use the same orientation when repeating measurements. Finally, we test measuring the sample rotated at 90 degrees to determine if the periodicity of the variation of the 2θ from a and b also changes by 90 degrees.

3.3.4 Results

We measure TiO2_7 and plot the results in Figure 3.8. We observe that the 2θ peak for rutile (002) is located at 62.712° . Using the Bragg law, we calculate that the c Miller index is equal to $2.961 \pm 0.013 \text{ \AA}$. The standard deviation is calculated based on the fit error.

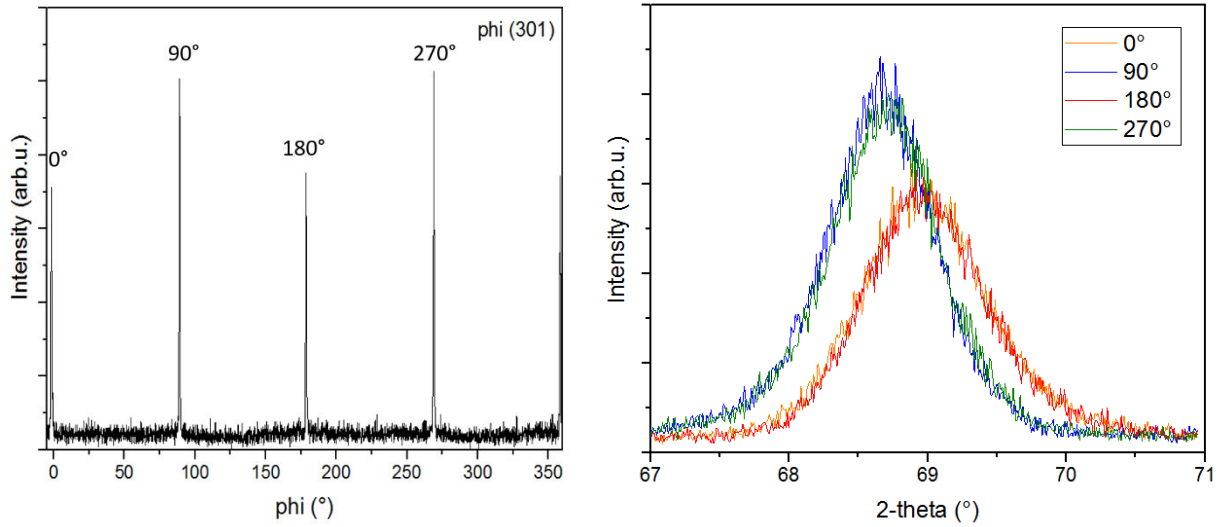


Figure 3.9: TiO2_7 rutile (301) phi scan (b) and 2theta rocking curve results for each phi scan peak (a).

Next, we measure the rutile (301) peak of TiO2_7. The results are displayed in Figure 3.9. We observe peaks at intervals of 90 degrees, as expected based on stereographic projections. $\theta/2\theta$ scans for each peak reveal that the peaks located at 0 and 180 degrees are

shifted by about 0.3 degrees from the peaks for the 90 and 270-degree peaks. This is indicative of the difference in the value of a and b , since the peaks are equivalent to measuring the (301), (031), (-301) and (0-31) planes, which alternate between the a and b directions.

We use the value for c obtained from the rutile (002) measurement to calculate the value of a and b . We find that the lattice parameter for the 0 and 180-degree peaks result is $4.59530 \pm 0.00026 \text{ \AA}$, whereas the result for the 90 and 270-degree peaks is $4.61712 \pm 0.0010942 \text{ \AA}$. This indicates a difference of about $0.022 \text{ \AA}$ between the a and b lattice parameters.

Next, we measure the rutile (211) peak of TiO₂_7 to obtain another measure of the difference between a and b . The (211) crystallographic planes intercalate assigning the 2 and 1 to h and k . Therefore, there is a difference in the contribution of the a and b parameter in the 2θ angle observed for each plane. Figure 3.10 Shows the phi scan and 2θ results. In the phi scan, we observe 8 peaks as expected from the plane symmetry. We can separate these peaks into two groups: The first group, has a peak located at 25 degrees and subsequent peaks at 90-degree intervals. The second group has a peak located at 63 degrees (a difference of about 37 degrees from the first peak of the other group) and has subsequent peaks also at a 90-degree-intervals. These two groups correspond to the variations where $h = 2$ and $k = 1$, or the opposite ($h = 1$, $k = 2$).

We use the value obtained for c in the rutile (002) measurement and calculate the a and b values by solving a system of 2 equations by comparing the results from rutile (211) and (121) planes. Our process for calculating a and b when their values are unequal is described in Table 3.2.

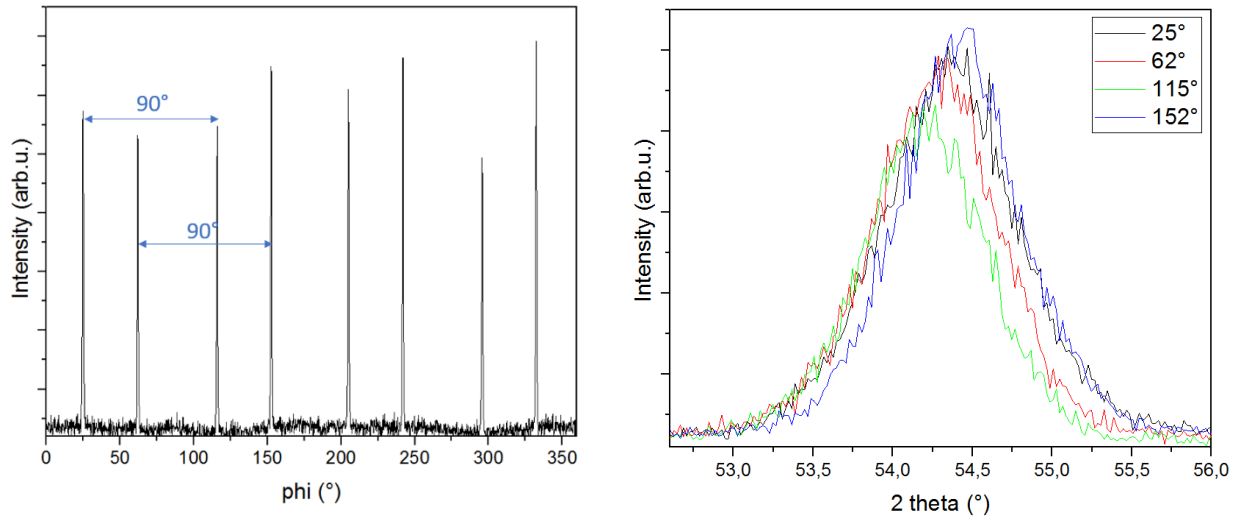


Figure 3.10: TiO₂_7 rutile (211) phi scan (b) and 2theta rocking curve results for each phi scan peak (a).

Table 3.2: Process for solving system of two equations. We separate a and b , and h and k from the rest of the Bragg equation and assign the solution for the (211) plane to variable z_1 and the solution to (121) to z_2 . We solve first for b by setting both equation in terms of a .

(211)	$z_1 = \frac{2^2}{a^2} + \frac{1^2}{b^2}$	$z_1 = \left(\frac{2 \sin(\theta)}{\lambda} \right)^2 - \frac{1^2}{c^2}$	$a^2 = \frac{2^2 b^2}{z_1 b^2 - 1}$	$\frac{2^2 b^2}{z_1 b^2 - 1}$
(121)	$z_2 = \frac{1^2}{a^2} + \frac{2^2}{b^2}$	$z_2 = \left(\frac{2 \sin(\theta)}{\lambda} \right)^2 - \frac{1^2}{c^2}$	$a^2 = \frac{1^2 b^2}{z_1 b^2 - 4}$	$= \frac{1^2 b^2}{z_2 b^2 - 4}$

We assign a variable z to each solution and solve for a . We can then equate the two equations and calculate b using numerical methods. The value of b allows us to solve for

a. We find that the result from solving for the lattice parameters in this way gives *a* and *b* equal to 4.57923 and 4.60994, respectively.

We average the result for *c* from 2 θ results from 5 measurements, obtaining $c = 2.962373 \pm 0.002262 \text{ \AA}$. This standard deviation is determined from averaging the value of *c* obtained from the 2 θ result for each measurement, as opposed to the fit error of rutile (002).

We summarize in Table 3.3 the results of *a* and *b* obtained for different measurements and calculation techniques. We find a clear difference in *a* and *b* of about 0.030 $\text{\AA}$. We also determine that the values of *a* and *b* are roughly 4.589 ± 0.010 and $4.619 \pm 0.013 \text{ \AA}$, respectively.

Table 3.3: Summary of results for *a* and *b* obtained over multiple measurements using symmetry and system of equation approaches.

Measurement	Calculation method	<i>a</i> ($\text{\AA}$)	<i>b</i> ($\text{\AA}$)	Difference (<i>b</i> - <i>a</i>)
Rutile (301)	Symmetry	4.59530	4.61712	0.02182
Rutile (211)	System of 2 equations	4.57923	4.60994	0.03071
Rutile (301)	Symmetry	4.58818	4.61305	0.02487
Rutile (211)	System of 2 equations	4.57436	4.59916	0.02480
Rutile (301)	Symmetry	4.59544	4.63548	0.04004
Rutile (301)	Symmetry	4.58269	4.61777	0.03508
Average		4.58866	4.61885	0.03019
Standard Deviation		0.01001	0.01312	0.00613

We find that there is a small, but measurable difference of $0.030 \pm 0.006 \text{ \AA}$ in the a and b lattice parameters of rutile TiO_2 . We confirm that this difference does not stem from possible differences in the sapphire birefringent indices of refraction – they are due to stresses in the rutile lattice. Furthermore, the obtained values, over multiple measurements further confirm that our samples are the rutile phase of TiO_2 . The values for anatase and Ti_2O_3 have significantly different lattice parameters ($a = b = 3.7852$ and $c = 9.5139$ for anatase from PDF 21-1272 and $a = b = 5.1390$ and $c = 13.6590$ from PDF 10-0063). As an additional test, we measure the (300) plane of Ti_2O_3 and do not observe the expected phi-scan peaks. Therefore, we confirm once again that we have succeeded in growing epitaxial rutile TiO_2 thin films.

CHAPTER 4: NANOFABRICATION OF PHOTONIC STRUCTURES USING OPTIMIZED RUTILE TiO₂

We sputter a rutile TiO₂ film using parameters from optimizing the epitaxial quality of deposited films. We use top-down nanofabrication techniques to structure the sample into waveguides and pillars with sub-micron dimensions. We measure the optical properties of rutile nanostructures.

4.1 Sputtering and Characterization of TiO₂_31

We deposit a new TiO₂ film on m-sapphire using RF magnetron sputtering. We use a 2” m-sapphire substrate (Roditi Int, epitaxially polished) to grow enough material for nanofabricating multiple devices. Sputtering is performed with the following deposition parameters: a power of 180 W, temperature of 650 °C, oxygen concentration of 20 %, and pressure of 4.5 mTorr. We choose these parameters based on optimizing the rocking curve results, indicating higher quality textured growth, as discussed in section 2.2. We characterize the material and optical properties of this rutile TiO₂ sample using Raman, AFM, ellipsometry and prism coupling.

We measure the Raman spectrum of our rutile TiO₂ sample and sapphire substrate using a 1-mW Helium-Neon laser, with excitation wavelength at 633 nm. A Renishaw inVia microscope focuses the laser light onto the sample using a 50X objective and collects the Raman spectra, which is diffracted by a 1200 groove/mm grating onto a charged coupled

device (CCD). Figure 4.1 shows Raman data for sapphire is collected for 20 seconds and 4 repetitions. The thinner TiO₂ film is averaged over 10 repetitions of 30 seconds.

The m-sapphire substrate data shows peaks at 378.9, 417.4, 429.5 and 644.5 cm⁻¹. Rotating the substrate by 90 degrees, we find three additional peaks at 449.7, 577.7 and 749 cm⁻¹ as well as the suppression of the peak at 644.5 cm⁻¹. These sapphire peaks correspond to E_g and A_{1g} symmetry[67].

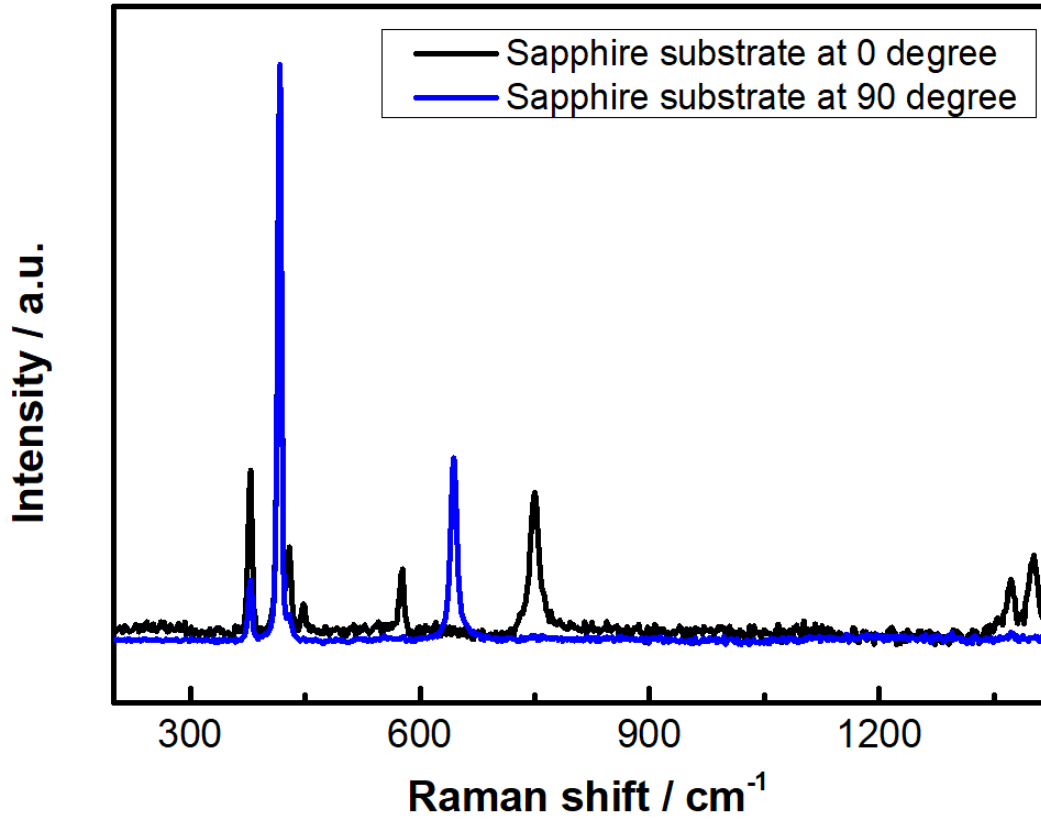


Figure 4.1: Raman spectrum for sapphire substrate oriented at 0 (black) and 90 (blue) degrees.

Our TiO₂_31 spectrum shown in Figure 4.2 confirms the presence of the rutile phase based on the rutile A_{g1} and E_g peaks located at 613 and 477 cm⁻¹, respectively. The main peak at 417.4 cm⁻¹ and subsequent smaller peaks at 374.8, 429, 577.5 and 749.7 cm⁻¹ correspond to the 90-degree orientation of m-sapphire. The slight broadening of the 613 cm⁻¹ peak can be attributed to damping of phonons due to small imperfections in the long-range order of the rutile TiO₂ layer. The absence of anatase peaks at 144, 197, 399, 515, and 639 cm⁻¹ [68], confirms that this phase is not present. Similarly, the Ti₂O₃ peaks at 269, 302, 347, and 452 cm⁻¹ are not observed[69].

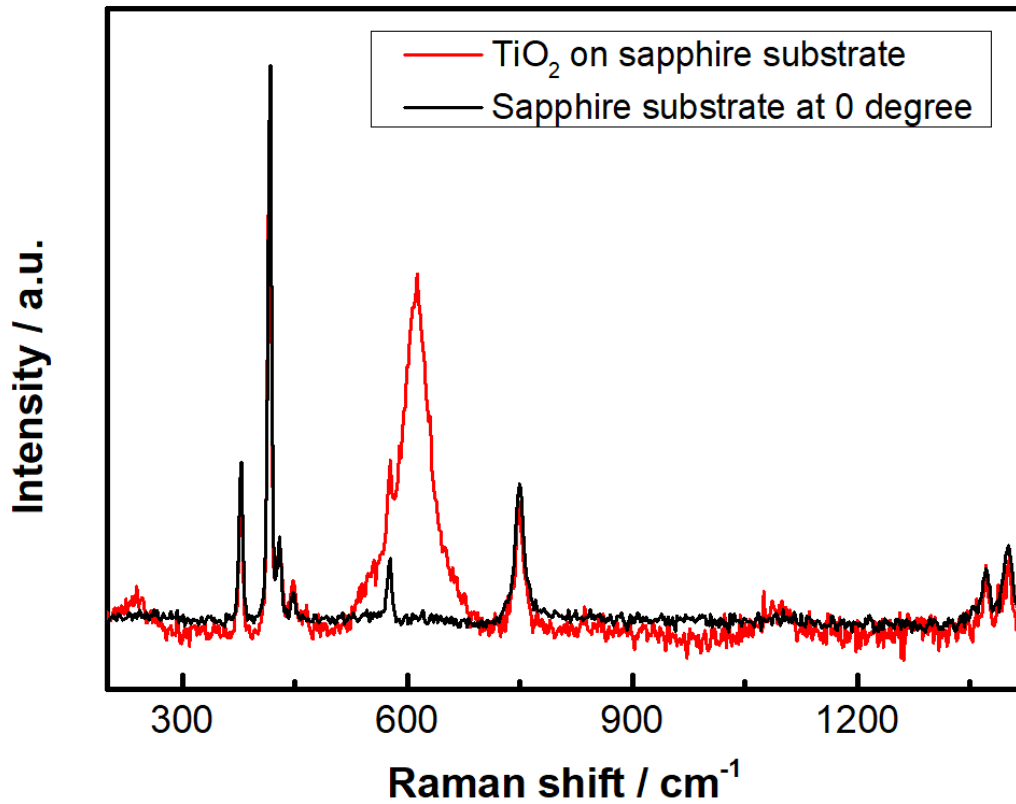


Figure 4.2: Raman spectrum for TiO₂_31, with rutile peaks at 447 and 613 cm⁻¹ and sapphire peaks.

We measure the surface roughness and structure of TiO₂_31 using Atomic Force Microscopy (AFM). A Veeco Dektak AFM is used with a 7 nm-radius tip in alternating current non-contact mode to scan a 0.8 x 0.8 μm region of TiO₂_31. The scan image is displayed in Figure 4.3. We find that the RMS roughness of the surface is on the order of 2.25 nm. We also take a slice of the AFM data and determine that domains at the surface are on the order of 50 nm. We find that the surface roughness is lower than but on the same order as TiO₂_7 (RMS = 3.06 nm). Both of these sample were deposited at the temperature of 650 °C, but TiO₂_7 was at a lower pressure (3 mTorr vs. 4.5 mTorr) and higher oxygen content (30% vs. 20%). Although the surface roughness of both of these samples is higher than other samples, TiO₂_7 had a better mosaicity. Therefore, in sample TiO₂_31 we make the choice to optimize our recipe based on mosaicity instead of surface roughness.

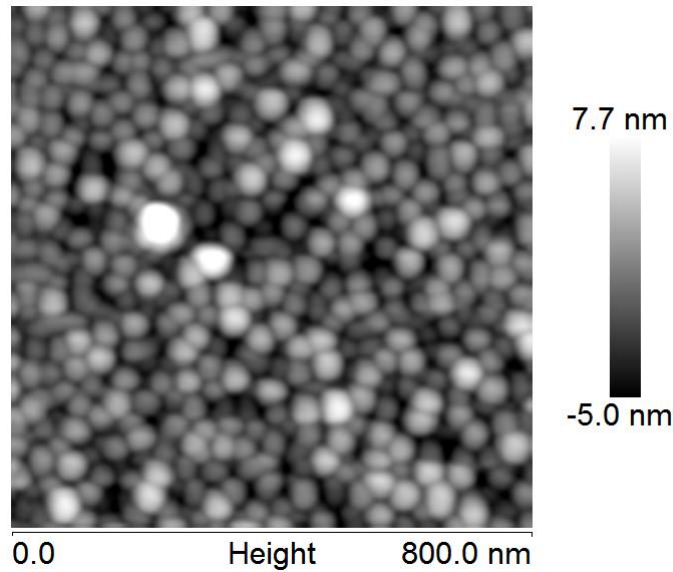


Figure 4.3: Atomic Force Microscopy scans of TiO₂_31, revealing RMS surface roughness of 2.25 nm. Cross-section of scan reveals feature sizes on the order of 50 nm.

As described in chapter 2, some post-deposition surface-processing methods can be used in the future to optimize the surface, such as chemical mechanical polishing or the deposition of amorphous layers over nanostructures.

Next, we calculate the index of refraction and thickness of our rutile sample using ellipsometry and prism coupling. We describe prism coupling in section 3.2. We measure the guiding modes of TiO₂_31 at wavelengths of 633 nm and 826 nm. We set the substrate index to 1.7578, according to the extraordinary axis of sapphire at 633 nm. We identify two modes with effective indices 2.399 and 1.823 during prism coupling measurements at 633 nm, as depicted in Figure 4.4. We find that the thickness of TiO₂_31 is 223 nm and the index of refraction is 2.592 based on solving the mode equation with two modes. We rotate the sample by 90 degrees to investigate the birefringence of this sample. We adjust the index of the substrate to the ordinary index of sapphire (1.7659) and find two modes at 2.374 and 1.8011, resulting in an index 2.570 and thickness of 221 nm. Additionally, we investigate the index at a sample rotation angle of 45 degrees. Setting the substrate index to 1.7619 (equal to $\frac{n_e+n_o}{2}$) and calculate an index of 2.575 and thickness of 223 nm. This result falls in between the result of 0 and 90-degree measurements, as expected.

We perform measurements at a wavelength of 826 nm and find one mode at an effective index of 2.285. We show the plot of intensity vs. effective index for this measurement in Figure 4.5. We use the substrate indices for sapphire at 826 nm ($n_o = 1.75961$; $n_e = 1.7517$) and assume a thickness of 221 nm. This results in an index of 2.564. Additionally, we measure the sample at a 90-degree rotation and find an index of 2.545 for the same assumed thickness. Our measurement results for prism coupling of TiO₂_31 are summarized in Table 4.1.

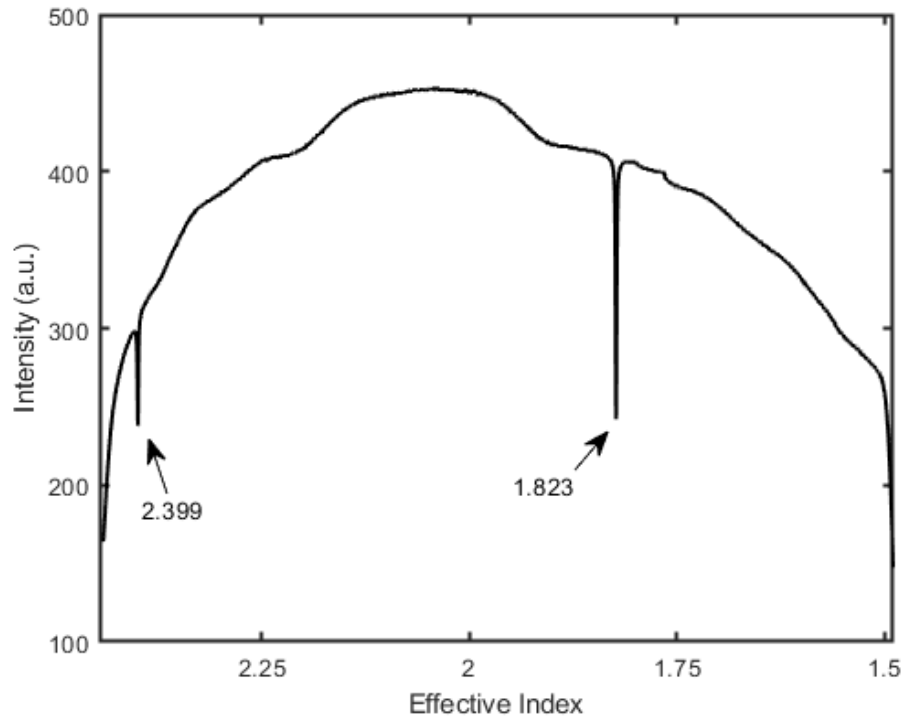


Figure 4.4: Prism coupling measurement at 633 nm for TiO₂_31 oriented at 0 degrees. Two modes are identified, yielding an index of refraction of 2.59.

Table 4.1: Summary of prism coupling results for sample TiO₂_31

Wavelength (nm)	Angle of sample (°)	Index of refraction	TiO ₂ Thickness (nm)
633	0	2.59	223
633	45	2.58	223
633	90	2.57	221
826	0	2.56	221*
826	90	2.55	221*

* assumed thickness.

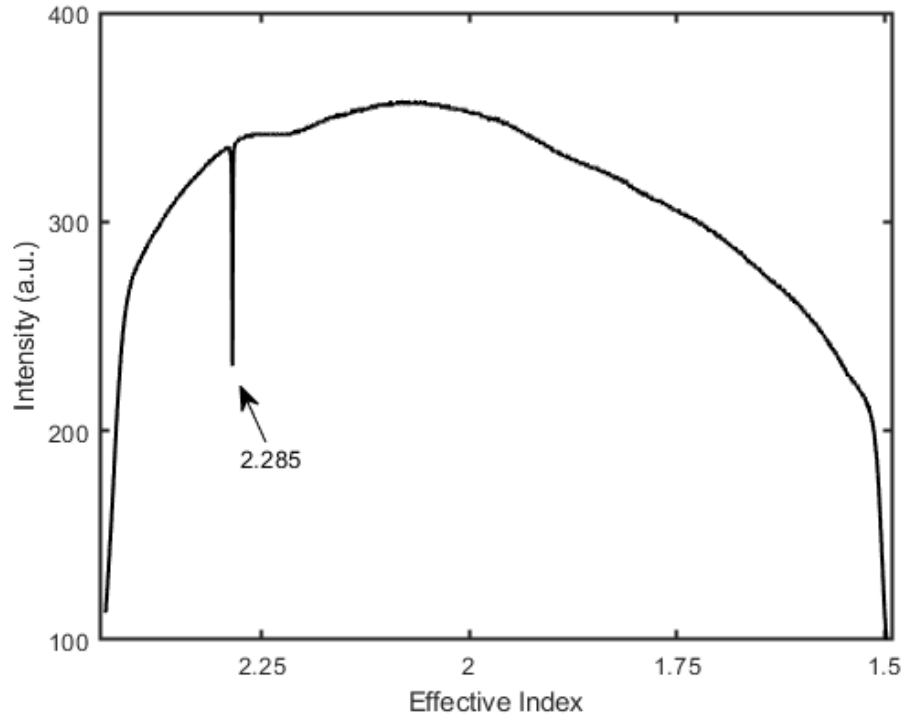


Figure 4.5: Prism coupling measurement at 826 nm for TiO₂_31 oriented at 0 degrees. One mode is identified, yielding an index of refraction of 2.56.

4.2 Rutile TiO₂ Nanofabrication

We use top-down lithographic fabrication methods to define nanostructures in our rutile TiO₂ film. Our fabrication process is adapted from our previous work nanostructuring waveguides in amorphous and anatase TiO₂ grown on a SiO₂/Si substrate. We summarize this process in the diagram of Figure 4.6 and describe each fabrication step in detail in the next sections.

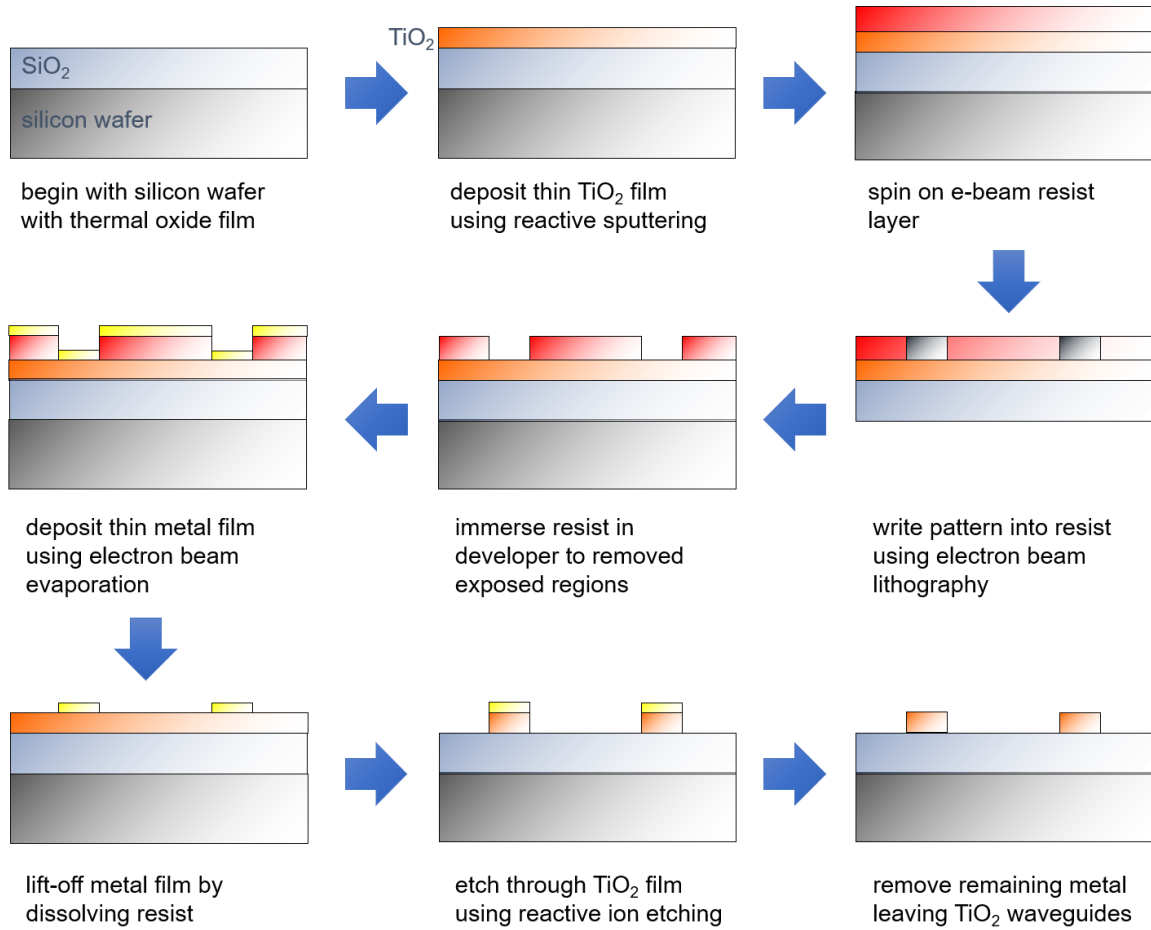


Figure 4.6: Fabrication process for obtaining TiO₂ nanostructures. Adapted from [70]

4.2.1 Defining nanoscale features with electron beam lithography

The first step in the fabrication process is to sputter TiO₂ on the substrate of choice. For rutile TiO₂ deposition, we use an m-sapphire substrate. The sputtering process for TiO₂_31 is discussed in detail in section 4.1. After deposition of rutile TiO₂, we prepare our sample for electron beam lithography (F-125 Elionix), which provides high resolution down to 5 nm structures.

Preparation for e-beam lithography involves cleaning the sample and spinning on e-beam resist. Our sample cleaning procedure for e-beam lithography consists of a piranha clean ($3\text{H}_2\text{SO}_4:1\text{H}_2\text{O}_2$), a deionized water rinse followed by a solvent clean (Acetone and IPA sonication) and N_2 blow dry. Further sample preparation includes dehydrating the sample at $180\text{ }^\circ\text{C}$ for 10 minutes and performing a 2-min O_2 plasma clean at 80 W and 40 sccm.

We use ZEP-520a (Zeon Corporation) resist to define our nanostructure features. This positive resist is well suited for achieving high-resolution nanoscale features (combined with the F-125 Elionix e-beam capabilities). We bake the sample at $180\text{ }^\circ\text{C}$ for 2 minutes and blow dry the sample immediately prior to adding resist to ensure no particles from the environment are on the sample surface. We pipet a few μL of ZEP onto the sample until the sample surface is covered and spin at 4500 rpm for 45 seconds (with 5 second ramp at 1000 rpm). This results in a ZEP-layer thickness of about 320 nm. We then bake the sample with resist for 3 minutes at $250\text{ }^\circ\text{C}$.

The final step prior to e-beam writing is to spin-on Espacer (Showa Denko). This conductive polymer is necessary to counteract the effects of charging that occur during e-beam lithography when working with insulating samples (such as titanium dioxide, sapphire and diamond)[71]. Insulating properties cause electrons from the electron beam to accumulate on the sample, leading to possible sample damage and affecting how the resist is exposed, making it difficult to achieve the desired feature shapes and resolution. Espacer is water-soluble and easy to spin onto samples just prior to e-beam writing. This makes it advantageous over other approaches to the charging problem, such as depositing a $\sim 10\text{-nm}$ metal film under or over the resist layer. These techniques require further time-consuming fabrication steps (typically a low-temperature metal deposition technique such

as e-beam evaporation) and potentially sample-damaging removal of the anti-charging layer (e.g. chemical or dry etching without affecting the rest of the sample). Therefore, we use Espacer for anti-charging as the simplest approach, requiring the least adjustments to sample fabrication and preparation for e-beam lithography.

To begin e-beam writing, we choose a beam current. The choice in beam current balances time required for e-beam writing (faster writing achieved with higher beam currents) with resolution (where electrons are exposed can be better controlled with lower beam currents, giving higher resolution). It can also be easier to optimize the focus of the beam with higher currents, since there is more contrast under SEM. Our chosen range of beam current is 0.5 – 1.0 nA, which allows for relatively fast pattern-writing with high-resolution and high focusing-quality. We use the lower beam current primarily for writing nanopillar structures and the higher current for waveguides, which occupy a larger area of the sample and take longer to write.

We perform dose tests to determine the best dose for achieving the desired feature sizes. In the case of writing pillar structures, this allows for a variation in the size of pillars to be fabricated. For waveguides, we obtain robust results for waveguide dimensions when using a dose around $480 \mu\text{C}/\text{cm}^2$. We use a 250- μm writing window for pillars and a 500- μm writing window for waveguides, since the latter benefits from less stitching errors along the length of the waveguide.

After writing the pattern we rinse the sample in DI water to remove the Espacer layer. Next, we develop the resist in ortho-xylene (o-xylene) for 30 seconds with light agitation, followed by an IPA stop bath[27]. ZEP-520a is a positive resist; therefore, the regions where the electron beam was exposed are removed during development. As an additional

precaution in case the sample is slightly underdeveloped, we expose the sample to 30 seconds of low power O_2 plasma. This removes a small amount of resist from the entire sample, ensuring complete removal of resist from the regions that were patterned. This is an important step to improve control over the lift-off step (see next section), where a metal mask is removed if it is deposited on top of resist.

4.2.2 Nanostructure etching with metal mask

Our e-beam lithography process results in the nanostructuring of ZEP resist on top of TiO_2 . Next, we follow steps to define a metal mask to etch TiO_2 into the desired structures. We use a metal mask to define features prior to etching. The positive-tone resist used during the e-beam step leaves behind trenches. By depositing metal using directional techniques, we can achieve thin layers within the bottom surface of the trench and the top surface of the remaining resist, but not on the resist sidewalls (as seen in the diagram of Figure 4.2.1). After metal deposition, the resist can be removed in a chemical etch, lifting off the metal that was deposited on top of the resist, but leaving behind the metal deposited within the trenches. This lift-off technique results in a thin metal layer covering the region where the TiO_2 nanostructure will be located after dry-etching away the remaining TiO_2 .

We choose Cr as our metal mask given its high etch-selectivity ($s \approx 9$) over TiO_2 in a fluorine environment. A directional deposition is necessary to avoid depositing metal on the resist sidewalls. Full coverage of the resist and exposed TiO_2 regions would make it difficult for the chemical etch to reach the resist and would provide less control over which Cr regions stay on the sample and which are left behind. The O_2 plasma step after

developing the sample ensures that no resist is left on the bottom of the trenches. This would cause some of the Cr in these regions to also be lifted off, causing irregular patterns to be left behind by the Cr.

We deposit Cr onto the TiO₂ sample with structured ZEP using a Denton electron beam evaporator. E-beam evaporation is a directional deposition technique, making it suitable for lift-off. We deposit 60 nm of Cr at 2 Å/sec in three rounds of 20 nm to obtain the highest quality deposition from the target. Prolonged evaporation of the Cr target can lead to instabilities in the deposition rate and less control over the final thickness or quality of the Cr mask.

We lift-off the unwanted Cr by etching the resist. We perform several etching steps using Remover PG (MicroChem). First, we leave the sample at 90 °C. This accelerates the etch and allows it to expand to difficult to reach parts of the resist. We gently swirl the sample, lifting off a majority of the Cr and move the sample to new PG remover (without Cr + resist debris). We continue to apply a gently swirl until all Cr has been visibly removed. We clean the sample with IPA for 30 seconds and dry it with nitrogen.

We use an Oxford Instruments PlasmaPro 100 Cobra 300 reactive ion etcher (RIE) to define TiO₂ nanostructures. TiO₂ that is unprotected by Cr is etched by fluorine chemistry, combined with ion bombardment. We test three etch recipes for TiO₂ nanostructures, outlined in Table 4.2. As a starting point, we use our previous TiO₂ etch recipe for amorphous and anatase TiO₂[27], [29], which was performed in a Nexx Systems Cirrus 150 RIE. We use a Veeco AFM to measure the height of samples before and after dry-etching and after removing the Cr mask (using a Cr-etchant for 2 min).

Table 4.2: Summary of etch recipes tested for rutile TiO₂ nanofabrication development.

Parameter	Original recipe[27]	Recipe 2	Recipe 3
CF ₄ flow rate (sccm)	16	16	16
H ₂ flow rate (sccm)	4	4	4
Pressure (mT)	5	5	5
μ W Power (W)	300	500	600
RF Power (W)	150	100	50

We find that the original recipe etches TiO₂ at 59 nm/min and Cr at 9 nm/min. In addition, we take SEMs of our sample, which contains pillars and a waveguide with bend. The SEMs are shown in in Figure 4.2.2. We achieve quite straight sidewalls but high roughness, resembling grooves. One approach to decreasing the observed sidewall roughness is to use a thicker metal mask so that the roughness of the Cr layer becomes less pronounced and doesn't lead to similar roughness in the TiO₂ structure. Another approach consists of decreasing the strength of ion bombardment, which contribute to accelerating the etch and forming grooves faster.

In order to avoid changing our lift-off process dramatically by increasing the thickness of Cr from about 60 nm to >100 nm, we test a different etch chemistry with lower DC bias to decrease the strength of ion bombardment. To this end, we increase the μ W power and decrease the RF power. Table 4.2.2 shows different DC bias voltages obtained for different combinations of the μ W and RF powers.

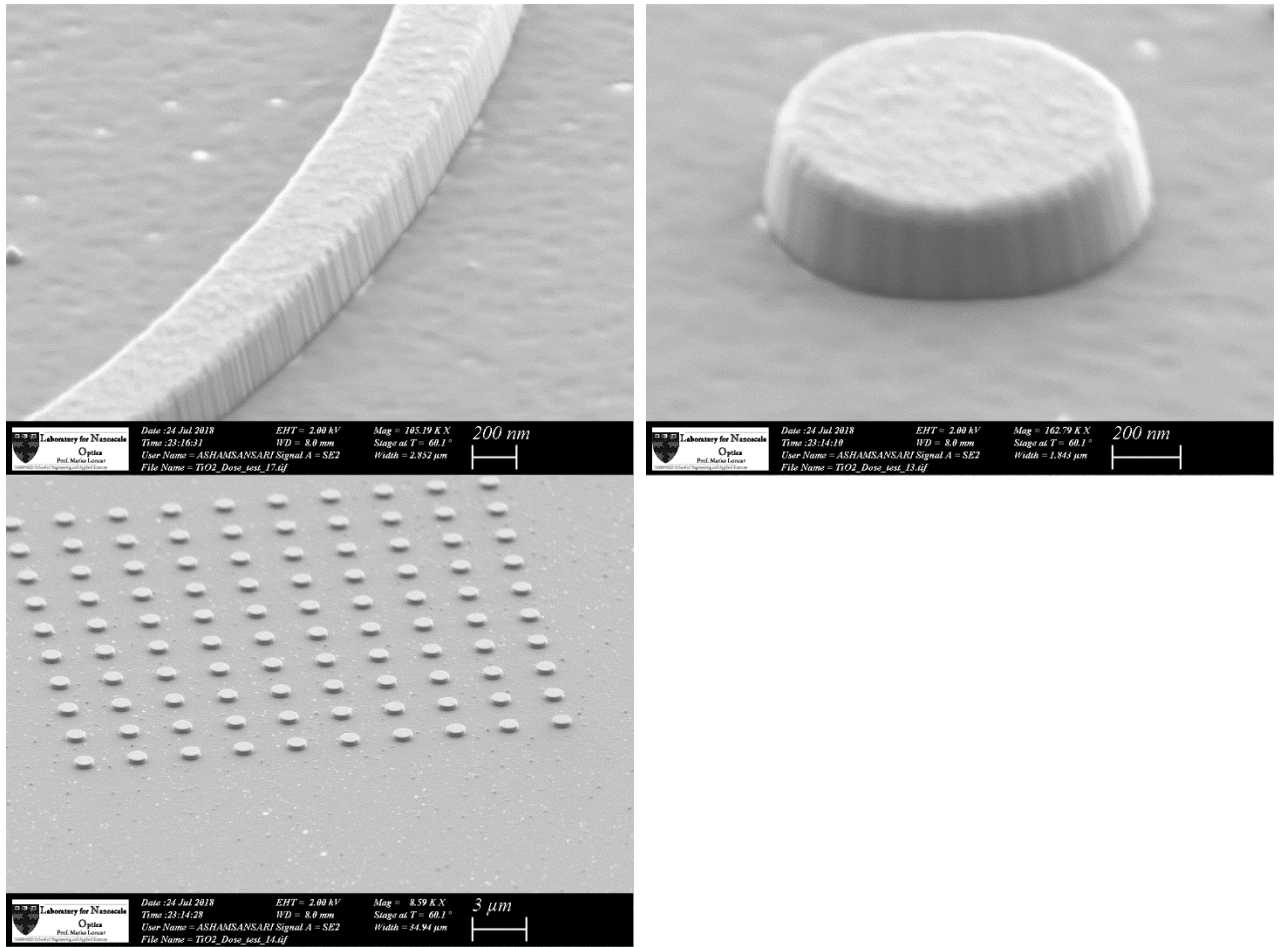


Figure 4.7: SEMs of TiO₂ structures fabricated with the original etch recipe.

Table 4.3: Change in DC bias voltage as a function of the RF and μ W powers.

	Original	Test 0	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7
μW	150 W	100 W	100 W	100 W	50 W	50 W	50 W	70 W	70 W
RF	300 W	500 W	400 W	600 W	600 W	550 W	500 W	500 W	550 W
DC Bias	380 V	255 V	270 W	240 V	125 V	130 V	140 V	190 V	180 V

We use the conditions in Test 0 and 3 to etch two samples fabricated in the same way as our original sample (recipes 2 and 3 in Table 4.3, respectively) and characterize the samples under SEM and AFM. We find that the roughness appears to be smoother for the new samples. AFM measurements show that the sample at 258 V DC bias achieves the smallest sample features at an etch rate of 61 nm/min for TiO_2 and 6 nm/min for Cr, resulting in an etch selectivity of 10.

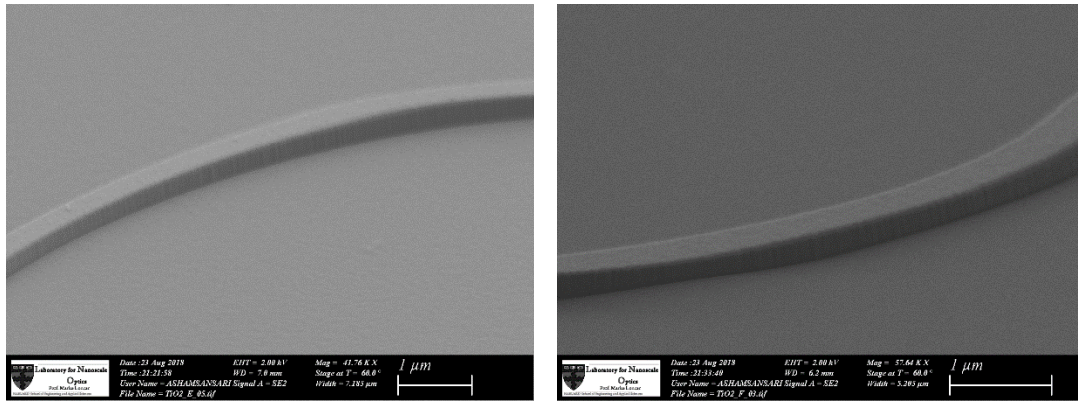


Figure 4.8: (a) Sample at 127 V DC Bias and (b) sample at 258 V DC Bias.

4.3 Rutile nanophotonics

We perform measurements of rutile TiO_2 waveguides and pillars. To measure waveguides, we must first dice the sample and polish the facet. Dicing is necessary since cutting sapphire with a diamond pen does not offer enough control to avoid destroying the nanostructures on the sample, due to the hardness of sapphire. We therefore use a Disco Corp. automatic dicing saw with 0.3 mm blade to cut away material from the sample,

bringing the facet up to the waveguides. Since our TiO_2 pillars can be coupled into from above, we do not need to dice these samples. To avoid cracking of the TiO_2 and sapphire layers during dicing, we initially dice 0.1 mm into the sample. We then repeat the cut in the same location down to 1 mm away from the bottom of the sample. This provides a clean cut, but not devoid of roughness from the dicing saw.

We polish the waveguide rutile TiO_2 sample using diamond lapping films (Allied High Tech Products Inc.) of varying grating sizes: 30, 15, 6, 3, 1, 0.5 and 0.1 μm . We mount the sample with crystal bond on the top and bottom of the sample to ensure adhesion to the sample holder and to provide some protection to the waveguides from polishing debris. We polish samples beginning with the largest grating size to remove larger roughness first and then decrease the size of the gratings in order. We polish with each film for approximately 5 minutes and then characterize the facet of the sample. Figure 4.9 shows a microscope image of the polished facet of a TiO_2 _31 nanostructured sample.

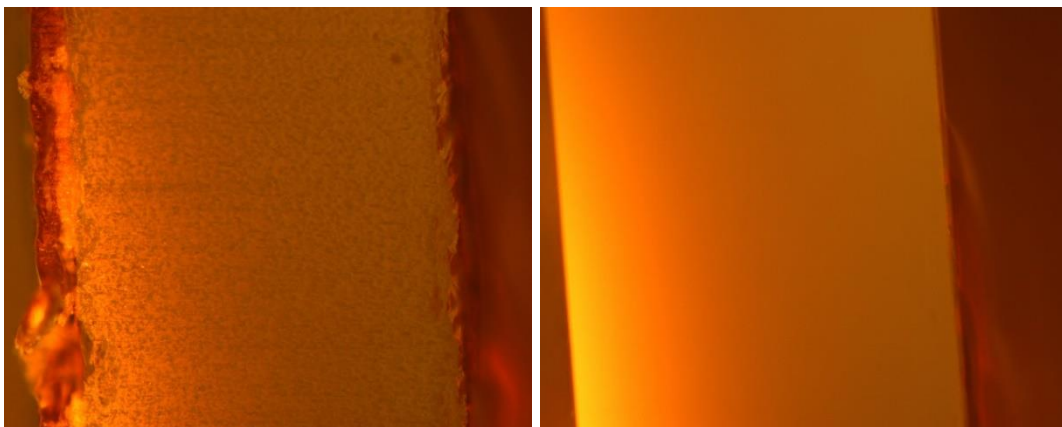


Figure 4.9: Microscope image (20x) of the TiO_2 _31 waveguide facet after 30 μm polish (left) and after 100 nm grating polish (right).

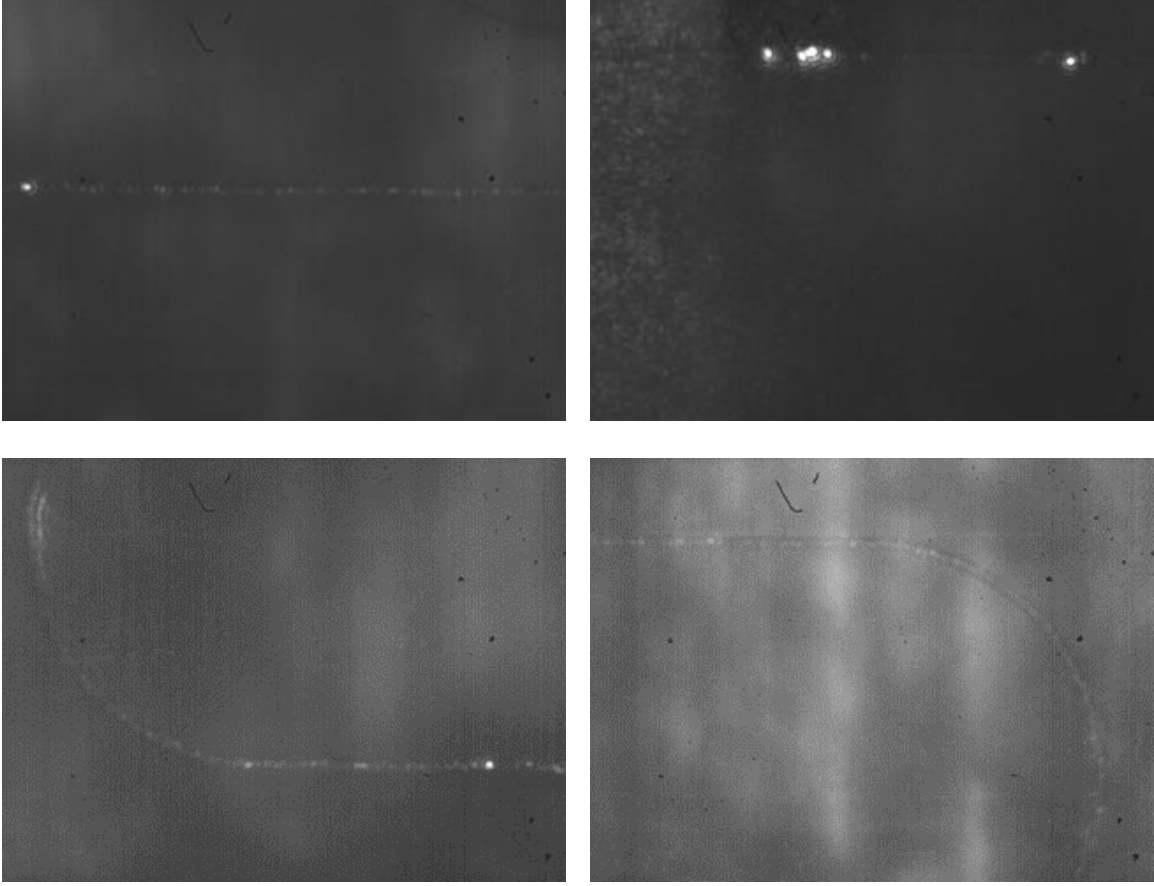


Figure 4.10: InGaAs camera images of 1310 nm light coupled into sapphire waveguide: waveguide input and faint scattering off the top of the straight waveguide (top, left), strong scattering at damaged part of waveguide (top, right), scattering at waveguide bends with light damage for comparing the brightness of scattering (bottom, left), faint scattering on upper s-bend region of waveguide (bottom, right).

After polishing the facet, we couple into a 5 μm and a 600 nm waveguides using a fiber coupling setup. We inject light at 1500 nm wavelength and observe an output loss of about 40 dBm. We attribute this high loss to the large surface roughness measured in TiO₂_31

thin films with AFM. To mitigate this problem, we clad the sample in silicon dioxide (SiO_2). We clad the sample with 4 μm of chemical vapor deposition (CVD) low frequency deposited SiO_2 . Upon remeasuring the sample with a 1310 nm 1-mW source by coupling into a 1 μm lightly damaged waveguide, we can observe bright light at scattering centers where visible damage to the sample occurred (e.g. scratches). However, we observe very faint scattering off the top of the waveguide, indicative of low loss in the waveguide. Figure 4.10 illustrates this. We conclude that adding the cladding layer is essential for minimizing roughness in waveguides fabricated from TiO_2 _31.

Finally, we measure TiO_2 _31 nanopillars (detailed description in chapter 5). We measure the scattering from pillars of varying diameter and find white light scattering with to vary with the diameter of pillars.

CHAPTER 5 STRUCTURAL COLOR FROM TiO_2 NANOSCALE PILLARS

5.1 Introduction

Structural color, the effect of filtering visible light based on interference using nanoscale structures has long been present in nature, with examples including scales in butterfly wings and peacock tail feathers. This method of coloration differs from using dyes, pigments and metals, that reflect specific wavelengths, which become the color we see by eye, and absorb the rest. The benefits of structural color include brighter appearance of the color, and possible control of the angle at which colors are scattered. The theory of structural coloration is much like the theory of x-ray diffraction, discussed in section 2.2.1, where constructive and destructive interference of thin films allow certain wavelengths to be reflected, while suppressing other wavelengths, based on the order of the structures. Such techniques are made use of in devices such as distributed Bragg stacks, where thin films are stacked together based on designs that reflect and transmit specific wavelengths for applications such as lasers and solar cells. By defining sub-nanometer features in thin films we can observe additional effects, such as Mie scattering. This scattering regime occurs when the structures are on the order of the wavelength of light. This scattering is stronger than Rayleigh scattering, which occurs for particles much smaller than the wavelength of light, and therefore can be harnessed for applications requiring strong, directional color filtering. Here, we investigate the structural color produced by nanoscale rutile and anatase TiO_2 pillars.

Nanopillars and nanoparticles have been used for various applications, including quantum optics, where smaller dimensions enable probing of quantum effects. In addition, research with semiconducting materials, producing quantum dots and nanowires is another field of intense research, for instance for photovoltaic applications. In this work, we explore the optical properties of nanopillars. Significant research has been performed in the area of metallic nanostructures for producing structural color. Although spatial resolution of about 100,000 dpi has been obtained with such approaches, the use of metals has the drawback of leading to losses in the visible wavelength region, causing broadening of the reflected spectrum. Previous work with silicon metasurfaces by Proust et al. demonstrated an all-dielectric approach to obtaining high spatial resolution of color filters using isolated Mie resonators. Silicon has a high index of refraction around 3.5 but is absorbing in the visible wavelength region. The high optical contrast of TiO_2 (~ 2.55 for rutile and 2.4 for anatase) and transparency in the visible regime (absorption edge around 400 nm), combined with our developed nanofabrication technique, promises to provide efficient color filtering.

In previous work, Sun et al. explored color printing with TiO_2 metasurfaces using e-beam evaporation of TiO_2 . In this work, TiO_2 squares of about 200 nm in side length were placed close to each other to allow for proximity resonance effects to enhance reflection. In the absence of Fano resonances, resonances from individual TiO_2 structures were difficult to distinguish from the reflected substrate (ITO coated glass). Here we demonstrate visible color filtering in for pillars spaced 5 m apart, without the need for Fano resonances to enhance the process.

5.2 Experimental Method

We structure nanoscale pillars from rutile and anatase TiO_2 thin films grown on m-sapphire and a silicon substrate with thick oxide layer, respectively. We characterize each film with ellipsometry and determine the thickness and dispersion. We use the fabrication methods described in section 4.2 to structure pillar arrays in the CAD pattern shown in Figure 5.1. The pattern consists of 10×10 pillar arrays, with pillars separated by $5 \mu\text{m}$ and arrays separated by $25 \mu\text{m}$. These distances ensure that the pillars are non-interacting. We fabricate arrays instead of individual pillars in order to visualize the repeatability of the diameter and reflection measurement result for pillars of the same designed size. We write patterns using ZEP resist and matrix the pattern shown in Figure 5.1 over a range of 40 to $1150 \mu\text{C}/\text{cm}^2$. Anatase TiO_2 films are about 250 nm thick and rutile films are at a similar thickness of 220 nm.

We perform reflection measurements of the pillar arrays using hyperspectral imaging, which allows us to characterize the spectrum achieved for each pixel. We measure our devices in the 400 – 800 nm wavelength range using a Cytoviva hyperspectral imaging system incorporated into a Horiba XploRA system. We focus unpolarized light onto the pillars using a 50x objective (Olympus, $\text{NA} = 0.5$) and scan 696 lines to obtain the full pattern for a given dose (a region of about $0.2 \times 0.2 \text{ mm}$). We characterize the size of pillars using scanning electron microscope (SEM) measurements. We perform 2D electromagnetic mode and 3D scattering simulations using COMSOL and FDTD, respectively.



Figure 5.1: CAD pattern design for pillar samples showing 10 x 10 pillar arrays with the diameter of the pillars indicated in yellow at the center of each array. A cross at the top right serves to help distinguish the pillars during measurements.

5.3 Experimental Results

We find the diameter of fabricated pillars using SEM and summarize the dimensions obtained in Table 5.1. is stable and varies by only about ± 25 nm for a given CAD design size, independent of the dose tested. We find that the top of pillars generally are within 7.5 % of the design dimensions. The base of pillars is larger by about 170 nm on average. Figures 5.2 and 5.3 show SEM images for two pillars that were measured by hyperspectral imaging and have design dimensions of 50 nm and 250 nm in diameter, respectively.

Table 5.1: Summary of average SEM dimensions obtained for pillars (across all doses).

We observe that the top of the pillar has dimensions typically within 7.5% or less of the design dimension. The base of the pillars have dimensions averaging about 170 nm above the dimensions of the top of the pillars, forming a conical shape.

Design dimensions [nm]	Top of pillar [nm]	Bottom of pillar [nm]
400	401	579
350	357	519
300	319	470
250	252	414
200	215	366
150	150	295
100	96	257
50	-	177

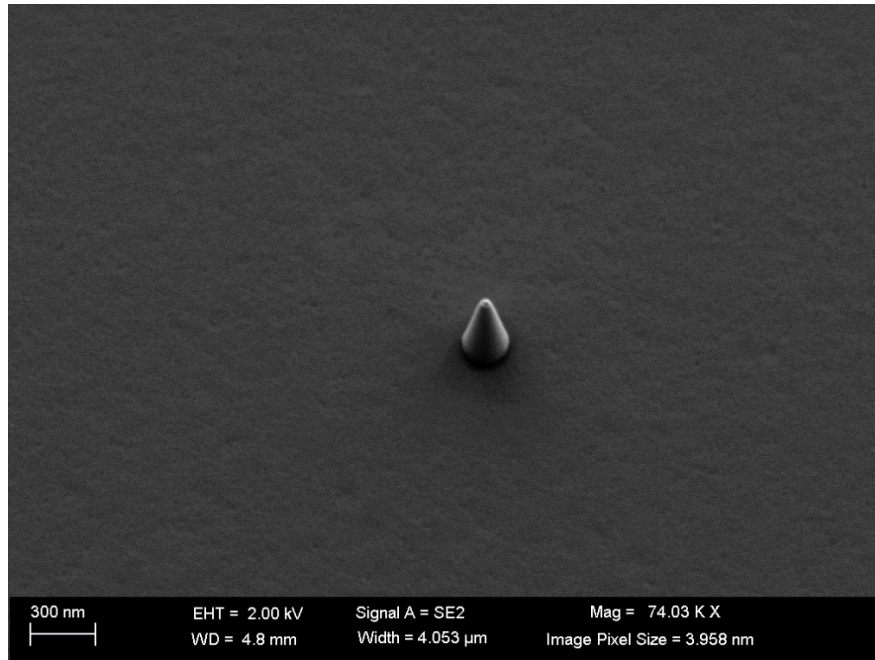


Figure 5.2: SEM image for smallest pillar size with dimensions 63 nm (top) and 223 nm (base). Clear indication of conical shape is seen.

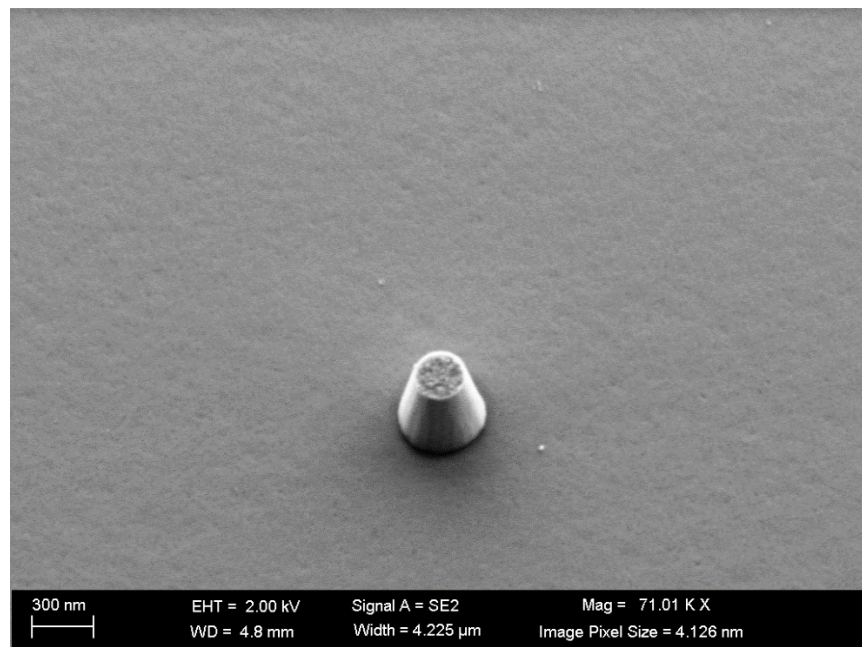


Figure 5.3: SEM image of 250-nm-design pillar with dimensions of 268 nm (top) and 441 nm (base).

We image rutile and anatase samples via hyperspectral dark field imaging. The images are shown in Figures 5.4 and 5.5 below.

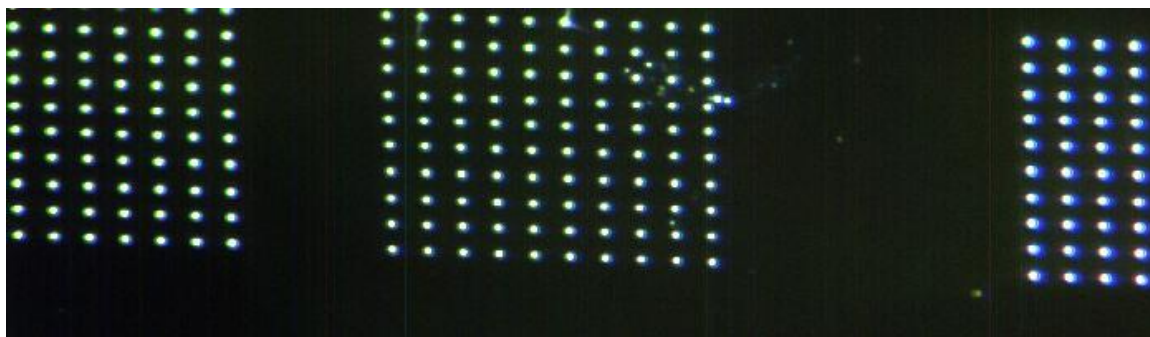


Figure 5.4: Hyperspectral dark field image for rutile TiO_2 pillars.

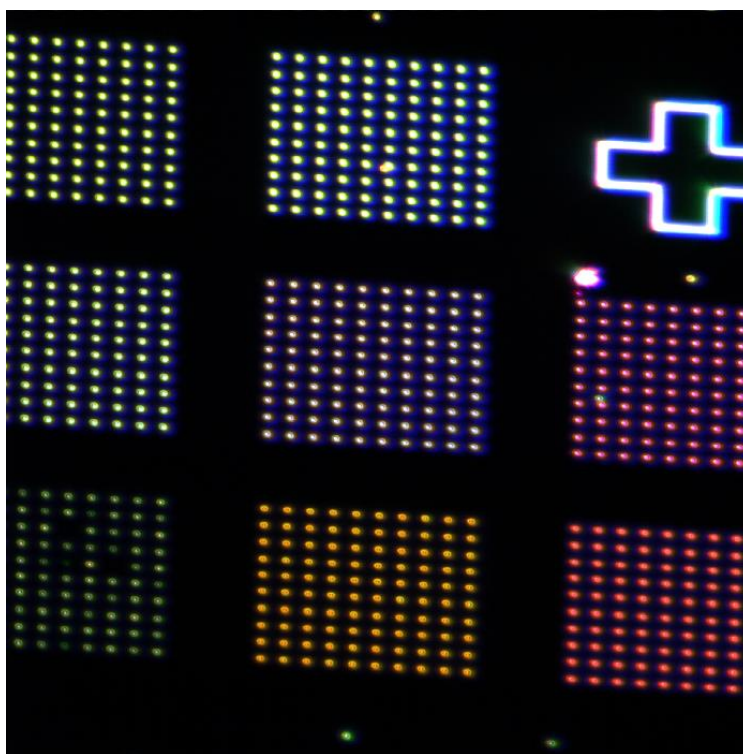


Figure 5.5: Hyperspectral dark field image anatase TiO_2 pillars.

We measure the reflection spectrum for the spatial region depicted in the image. Visual inspection of the different arrays in the patterns show that the diameter of the pillars affects the scattered color, most visibly in the anatase TiO_2 sample. We extract reflection spectra averaging a matrix of 2x2 pixels from the center of pillars located in the center of each array. The results are shown in Figures 5.6 and 5.7.

The reflection spectra for rutile TiO_2 pillars indicate that some variation of the light is occurring; however, the spectrum is broad, resulting in white light with different spectral distributions. We expect this result is due to the high surface roughness of the rutile film, measured via AFM and shown in section 2.3. Similar to the obtained improvement in performance with waveguiding from cladding, we expect that coating the pillars in a TiO_2 or silica layer may decrease the effect of Rayleigh scattering from roughness.

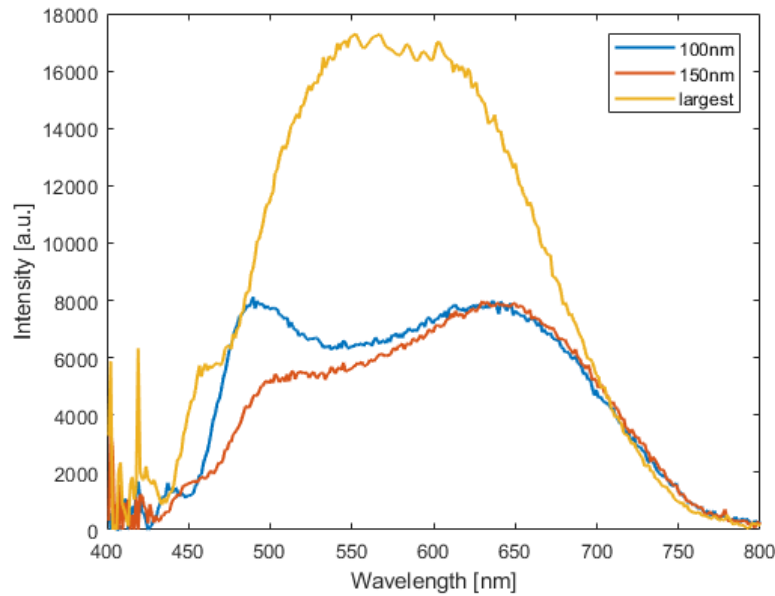


Figure 5.6: Reflection spectrum for rutile pillars from the center of each array. The spectrum is selected from the center of the pillar and averaging 2x2 pixels.

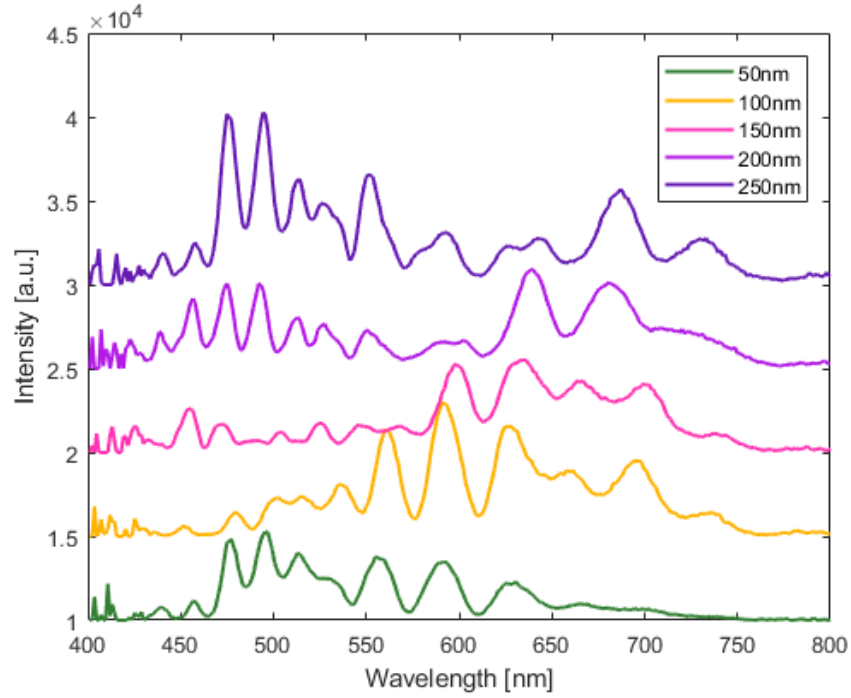


Figure 5.7: Reflection spectra for anatase TiO₂ pillars with design dimensions ranging from 50 to 250 nm in steps of 50 nm.

We plot the results for anatase pillars of the design dimensions of 50 to 250 nm diameters, which had clear visible light variations. The green curve on the bottom corresponds to the smallest square design and the subsequent curves are in increasing order of square size design. We see from the graph that each spectrum shifts slightly. Initially, there is a red shift from the 50 nm green curve to the 150 nm pink curve. At this diameter, we have peaks primarily in the red region and we begin to see additional peaks forming in the blue region. For larger diameters, we observe the blue region peaks increasing in relative intensity and a broadening of the spectrum. This results in a purple reflection, which eventually becomes a broad white light reflection (for larger diameters, observable in Figure 5.5).

To further investigate why we observe visible color filtering for smaller pillars, we zooming-in further to the hyperspectral image obtained for anatase pillars. We find that the reflected colors have spatial dependence. The center of the pillars has a mixture of reflected colors, approaching white light, whereas the outer edge has a clear preferentially reflected color.

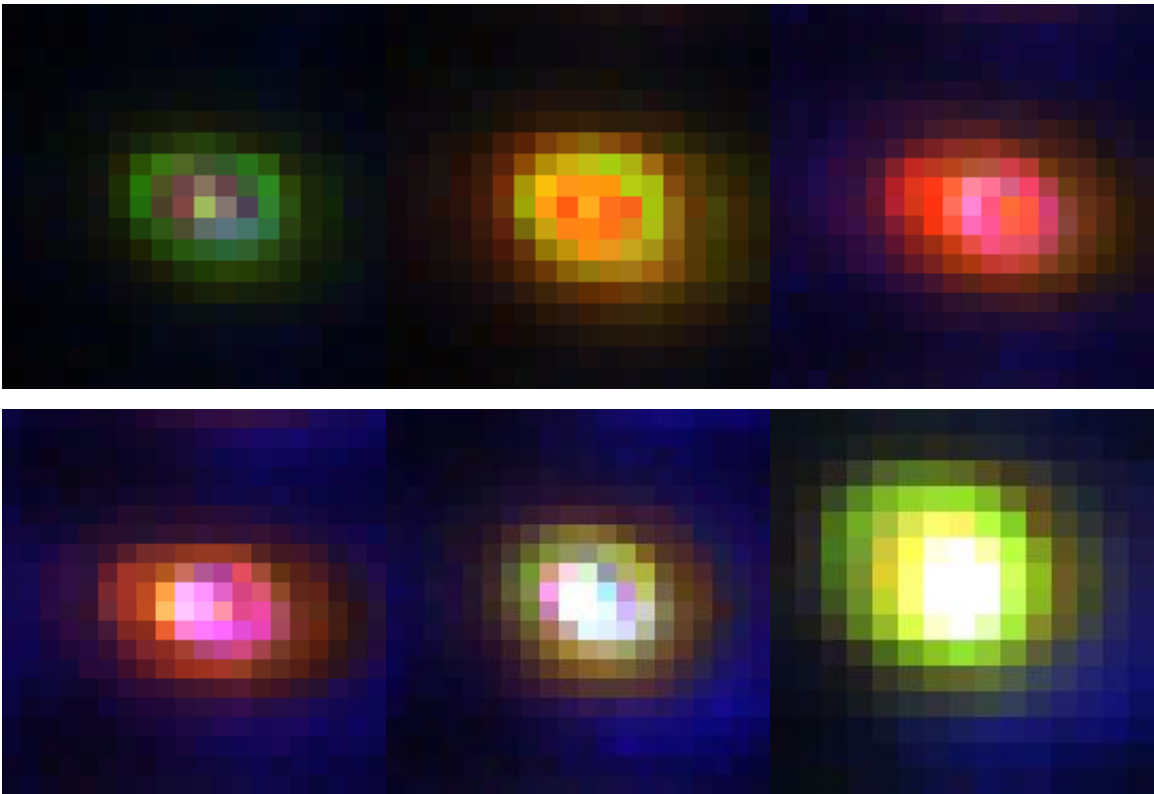


Figure 5.8: Zoomed in image of hyperspectral imaging data showing the pixels containing spectral measurements. Pillar design dimensions, from left to right: (top) 50, 100 and 150 nm, (bottom) 200, 250 and 350 nm. Image shows the spatial variation of reflected light from pillar varying with the diameter size.

To further investigate this spatial variation of the reflected light, we measure the anatase sample with different objectives. This varies the resolution of the pixels and the collection cone of light, based on the different numerical apertures (NA) of the objectives. We perform measurements of the anatase sample with a 10X objective (NA = 0.25) and 100X objective (NA = 0.9).

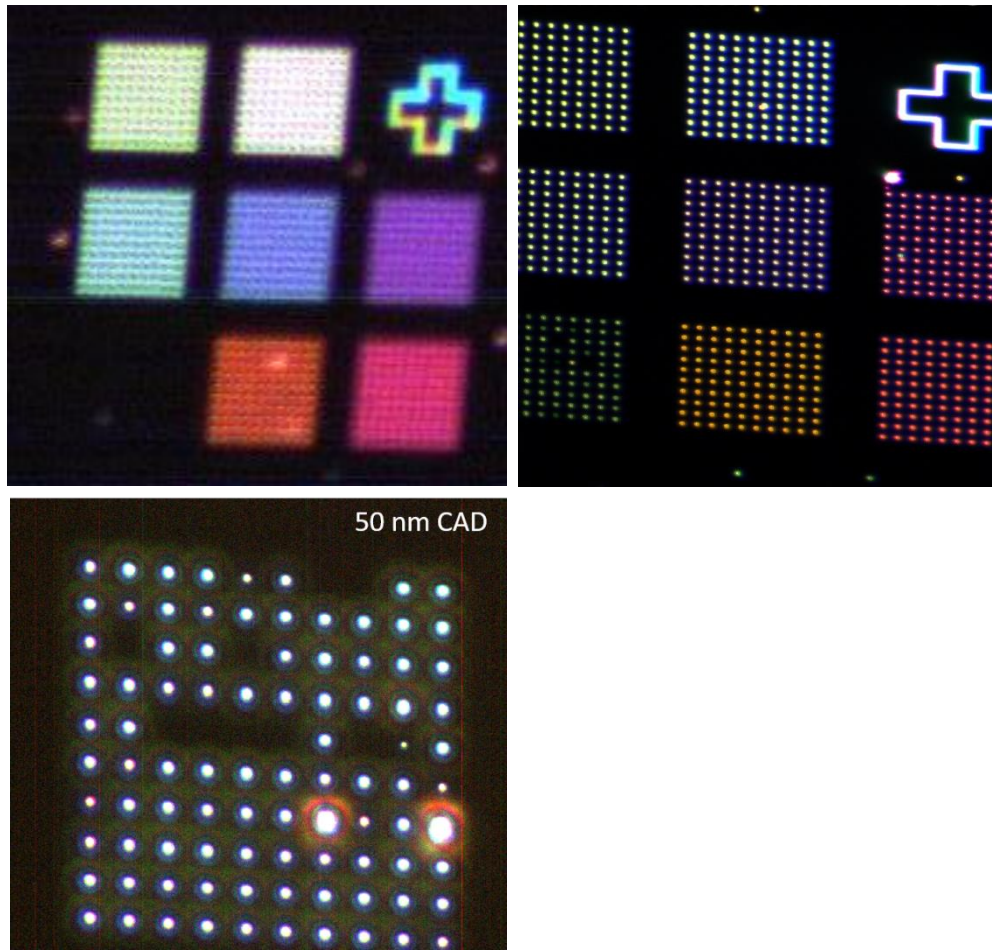


Figure 5.9: Hyperspectral dark field imaging results using 10X (top, left), 50X (top, right) and 100X (bottom, left) objectives. The 100X measurement region is smaller and is centered about the 50 nm CAD designed pillars.

We observe a difference in the reflected light based on the objective. This result points toward an angular dependence of the reflected light. We zoom into the regions for each measurement and find that at 10X, the white light (or color mixture) obtained at the center of pillars during 50X objective measurements cannot be resolved. On the other extreme, the spectra collected with the 100X objective only has the white light source. We combine these observations with information regarding the morphology of our anatase pillars using SEM (Figures 5.2 and 5.3). The top of the pillars has evidence of surface roughness, whereas the pillar wall grooves appear smoother in comparison. This may result in Rayleigh scattering off the top of the pillars, leading to white light at the center of pillars.

5.4 Simulations of pillar modes

We perform 2D simulations of the electromagnetic modes of pillars with different diameters. We use a 633 nm source and model the media surrounding the pillar as air. We find that for smaller pillars, such as the 200 nm pillar simulated in Figure 5.10, the fundamental mode probes the outer region of the pillars. For larger pillars, light is more strongly confined within the pillar, decreasing the interaction with the pillar outer surface, as seen in Figure 5.11.

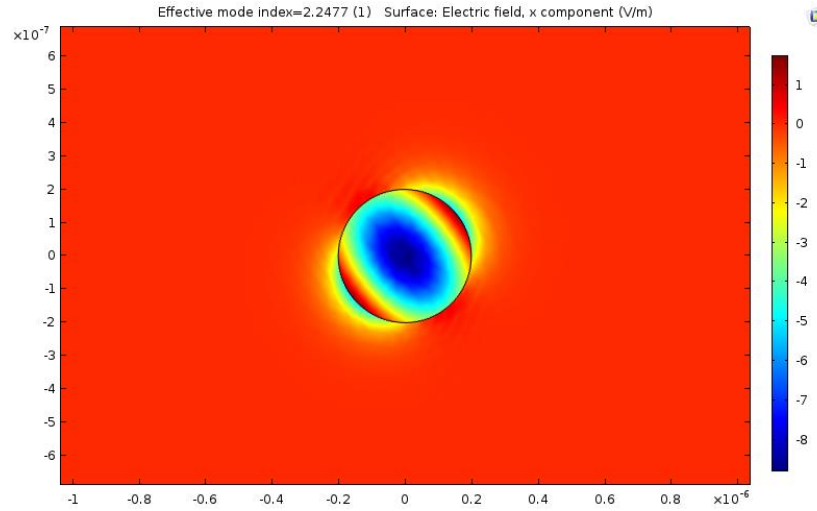


Figure 5.10: 2D COMSOL simulation of 633 nm plane wave coupling into 200-nm-diameter pillar. The lobes on the outer side of the pillar demonstrate that smaller pillars experience more interaction of light with the outside angled surface of the pillar.

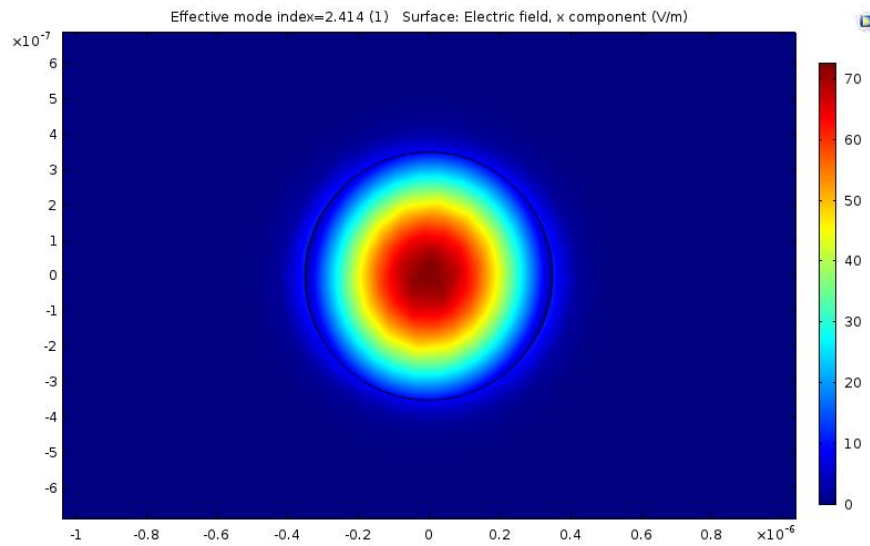


Figure 5.11: 2D COMSOL simulation of 633 nm plane wave coupling into 350-nm-diameter pillar. The absence of lobes on the outer side of the pillar demonstrate that the light is confined more strongly within the pillar.

5.5 Conclusion

We fabricate nanoscale pillars in rutile and anatase TiO_2 and observe a change in the reflected light depending on the diameter. We achieve better color filtering with anatase films, likely because the surface roughness of the anatase film was lower than for the rutile film. In addition, the anatase film was slightly thicker (250 vs. 220 nm). Rutile pillar color filtering performance can likely be improved with coating with TiO_2 or SiO_2 , to decrease surface roughness.

We investigate the source of the color filtering in anatase nanostructures and observe that it is likely from interaction of the light with the outer surface of the pillars. Pillars that confine the incident light well result in bright white light, likely from Rayleigh scattering from surface roughness at the top of pillars (imaged with SEM in Figure 5.3). We find that color filtering is achieved by Mie scattering, without proximity effect resonances.

Increased color filtering capabilities via investigating pillars in closer proximity and with dimensions below 100 nm, may result in further interesting phenomena. We find that the conical shape of our pillars may enhance the preferential reflection of visible light and creates an angular dependence of the scattering. This angular dependence can be useful in applications that require precise control of the directionality of filtered light.

CHAPTER 6: PERFECT ABSORBER

We develop a broadband absorber using amorphous TiO₂ devices. A broadband absorber is capable of absorbing light efficiently for a wide range of wavelengths. This is in contrast with devices or materials (e.g. metals) that are nearly perfectly absorbing (100%) but at a specific wavelength [4,5]. The benefits of broadband absorption include several applications, such as hiding objects from radar or infrared detectors [6] and preventing crosstalk between optical interconnects in optoelectronic devices [5,6]. Another example consists of collecting solar energy for photothermal and photovoltaic devices. The solar spectrum ranges from about 250 to 2500 nm. Efficient absorption over this broad range is challenging from the theory and fabrication perspectives.

Recently, metamaterial-based broadband absorbers consisting of metal-dielectric structures have been investigated [7–17]. Efficient absorption in the visible spectrum was achieved for a device design consisting of a stack of metal (Au) and nanocomposite (Au/SiO₂) layers [7,8]. Metallic nanostructures surrounded by a dielectric medium in a double-layer scheme were shown to have narrow resonance peaks in the absorption spectrum [9,10]. In addition, devices achieving broadband absorption in the infrared [14], microwave [15] or visible [17] ranges with angular selective thermal emission properties [16] have been proposed using saw-toothed anisotropic metamaterial designs.

We build on the work in Lobet *et al.* [72], which presents a theoretical framework for using multilayer Au/Ge pyramidal structures [14,17] to achieve nearly perfect (> 90%) broadband absorption over the spectral range. The approach is demonstrated to make use of plasmon hybridization of dipolar modes in the layers, which act as resonators. This leads

to ultra-broadband operation ranging from 200 nm to 5.8 μm , encompassing the UV-visible, the near-infrared and mid-infrared regions. Although the design achieves nearly perfect absorption, it consists of 20 layers of metal-dielectric stacks, making it impractical for fabrication. We use a genetic algorithm optimization approach outlined in Mayer *et al.*[73] to significantly simplify the design. In the following sections we present an overview of the theory describing the absorption in multilayer dielectric-metal stacks with pyramidal shape, our reasons for design modifications and new theoretical results, and new device fabrication and measurement.

6.1 Broadband Absorber Theory and Design

Absorption $A(\lambda)$ is related to transmittance $T(\lambda)$ and reflectance $R(\lambda)$ by the energy conservation law:

$$T(\lambda) + R(\lambda) + A(\lambda) = 1$$

We can achieve a perfect absorbing device by minimizing transmittance and reflectance. We can suppress transmittance by using a metal layer that is thicker than the skin depth (propagation within media) for the spectral range. This can be achieved with a thick layer of gold on a glass substrate. We can prevent reflection by using an anti-reflection layer. Anti-reflection layers often take on a pyramidal shape to achieve gradual transition of the refractive index to minimize Fresnel reflections. Finally, coupled plasmonic resonators can maximize absorption within the device. This can be achieved by metal-dielectric structures placed near to each other to achieve resonance. We calculate Absorption (η) for the

bandwidth of interest ($\lambda_f - \lambda_i$) by integrating and normalizing the absorptance over this bandwidth, as shown in Equation 6.2:

$$\eta = \frac{\int_{\lambda_i}^{\lambda_f} A(\lambda) d\lambda}{\lambda_f - \lambda_i}$$

The perfect absorber device is designed as an array of pyramids, formed by stacking metal-dielectric squares with incrementally smaller sizes stacked on top of each other. The pyramidal shape minimizes the reflectance from light arriving at the device, as observed in anti-reflection coatings. The pyramid itself functions as a plasmonic resonator, where metal layers with high conductivity interact between the dielectric spacer. The physical phenomena that allows for high absorption in such devices is the formation of localized surface plasmons (LSP) on dielectric-metal-dielectric slabs. LSPs spectrally aggregate via electromagnetic coupling and lead to the absorption spectral broadening.

The design in Lobet Optics Express paper with 20 layers, is the starting point of our design. It consists of 20 stacked square metal-dielectric layers, achieving 98% absorption integrated over the range of $0.2 - 5.8 \mu\text{m}$. The design features gold as the metal of choice for the substrate (thickness of 200 nm to be above skin depth) and metal-dielectric stack (thickness of 15 nm to be lower than skin-depth). The dielectric material chosen is germanium (35 nm). Each square has length 600 nm at the base and 150 nm at the top layer. The lateral period of the squares in the array is set to 800 nm. As mentioned in the paper, the choice of material is quite versatile, as the only requirements include choosing

a metal with high conductivity to ensure resonant plasmonic behavior. The design is optimized using Rigorous Coupled Wave Analysis (RCWA).

Stacking multiple layers of metal-dielectric structures represents a non-trivial fabrication challenge. Vertical integration for integrated devices is an active area of research and optimization, often requiring planarization techniques to fill-in each layer prior to initiating fabrication of the next layer. In addition, fabrication steps such as dry and chemical etching can affect previously fabricated layers by reacting with them chemically or even etching them partially or completely away. On the other hand, depositing new layers of material must be done strategically in order to avoid etching steps that would affect previous layers. We investigate decreasing the number of layers of the perfect absorber device to decrease the fabrication complexity and enable more easily scalable adoption of this platform. We investigate reducing the complexity of designs by an order of magnitude to obtain three or less layers. This decreases the fabrication steps required and the possibility of errors from theory and fabrication. We use absorption over the 400 – 1600 nm window as the figure of merit for each design.

To begin, we choose TiO_2 and Cr as the materials for the metal-dielectric stacks. This is schematically depicted in Figure 6.1. TiO_2 can be easily deposited on a gold substrate and structured into square arrays with Cr on top using our readily developed top-down fabrication technique outlined in Chapter 4. The transmission window for TiO_2 above 450 nm allows for the localized surface plasmon excitations to dominate the obtained broadband absorption. Depositing TiO_2 on gold leads to amorphous growth, given the lack of crystalline order for lattice matching. The design does not have strict requirements for the dielectric medium; however, the lower index of amorphous TiO_2 over anatase or rutile

can be beneficial in decreasing Fresnel reflections, as the device is designed to be anti-reflecting. In addition, the lower scattering losses from the absence of grain boundaries in amorphous TiO_2 optimizes this layer for facilitating the plasmonic resonance effects that dominate the absorption mechanism in this device. A future area of investigation could compare the effects of scattering coupled with resonant behavior, as it is possible that scattering could be beneficial instead of detrimental to the absorption mechanisms in this device.

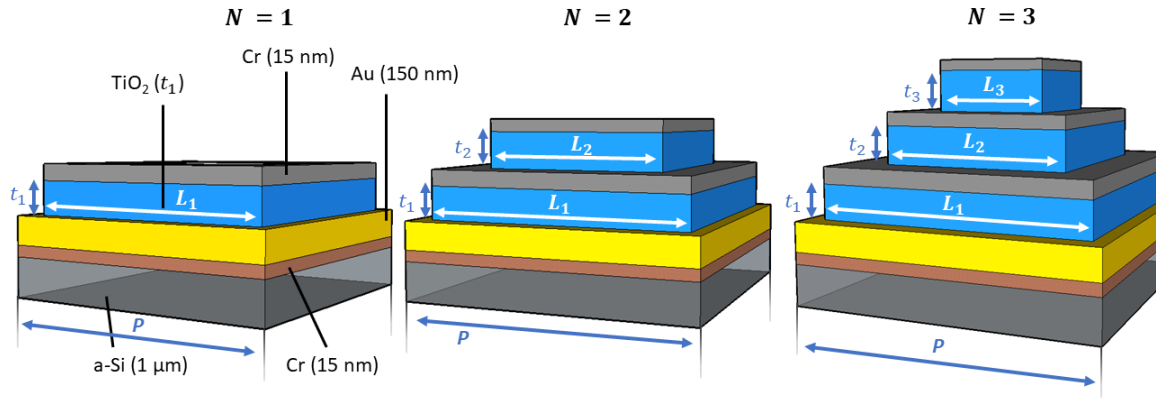


Figure 6.1: Perfect absorber designs for $N = 1, 2$ and 3 layers of Cr/TiO_2 stacks on a gold substrate. Adapted from Mayer *et al.*[73]

We choose Cr since our TiO_2 fabrication makes use of a Cr mask in nanofabrication. This is given to the etch selectivity of Cr over TiO_2 in a fluorine dry-etch environment. Not having to remove the Cr layer from on top of the TiO_2 structures as in our typical fabrication process leads to one less fabrication step. One potential drawback of using Cr is that it is more lossy than Au, which was used in the original design. Nevertheless, it is a

cheaper material with high conductivity, making it feasible as an absorber and more cost-effective.

We simulate a three-layer structure of Cr/TiO₂ square arrays on a gold substrate. We limit the thickness of Cr to 15 nm and optimize the dimensions (thickness, length) of each TiO₂ layer. The Cr length is set to be the same as TiO₂. We also optimize the period between the three-layer pyramids in the array. We initially investigate restricting the period to be at least 40 nm greater than the base length dimension. This facilitates fabrication (as discussed in section 6.2). Absorption is calculated using numerical methods for the 400 – 1600 nm wavelength range. Optimization of the design is achieved with a genetic algorithm following the procedure in Mayer *et al.*[73]

Table 6.1: Results for N = 1, 2 and 3-layer devices using Cr/TiO₂ stacks. L₁ and t₁ are the bottom layer length and thickness, respectively. L₂ and L₃ correspond to the second and third layers, respectively. P corresponds to the period between square structures in the array. η corresponds to the absorption of each device over the 400 – 1600 nm wavelength region.

Cr/TiO ₂								
	L ₁ (nm)	t ₁ (nm)	L ₂ (nm)	t ₂ (nm)	L ₃ (nm)	t ₃ (nm)	P (nm)	η
N=1 stack L ₁ ≤ P	317	124	-	-	-	-	444	84.9%
N=2 stacks L ₁ < L ₂ ≤ P	201	131	368	91	-	-	412	97.5%
N=3 stacks L ₁ < L ₂ < L ₃ ≤ P	176	127	331	65	351	50	414	98.9%
N=3 stacks L ₁ < L ₂ < L ₃ L ₃ + 40 nm ≤ P	175	127	329	66	353	50	415	98.9%

We summarize our optimization results in Table 6.1. We find that the absorption (η) for the optimized three-layer TiO_2 -Cr device is 98.9%. This is comparable to the result obtained with 20 layers in Lobet *et al.* The wavelength region investigated here (400 – 1600 nm) is narrower than the 0.2 – 5.8 μm bandwidth in Lobet *et al.* This is due to lack of standard refractive index data for this wider window for TiO_2 and Cr. By extending the wavelength region, it is possible that the absorption percentage would increase further for the TiO_2 /Cr device. The dimensions obtained for the new design are also included in Table 6.1, where L1 always represents the square length of the top layer of the stack and t1 is the thickness of this layer. L2 and L3 represent the square length for the middle and bottom squares in the stack, respectively. P is the period between adjacent pyramids.

We further investigate decreasing the complexity of the device to two and one layer using the same materials and constraints. We find that the absorption for a two-layer TiO_2 -Cr device is 97.5% and for a one-layer device is 84.9%. Therefore, we observe that our design is quite robust, achieving absorption above 80% for as simple as a one-layer device.

We plot the absorptance, transmittance and reflectance spectra of each design in Figure 6.2. The bottom row spectra are nearly identical since the designs have the same number of layers and similar dimensions. A significant improvement in absorptance is observed when increasing the number of layers from $N = 1$ to $N = 2$.

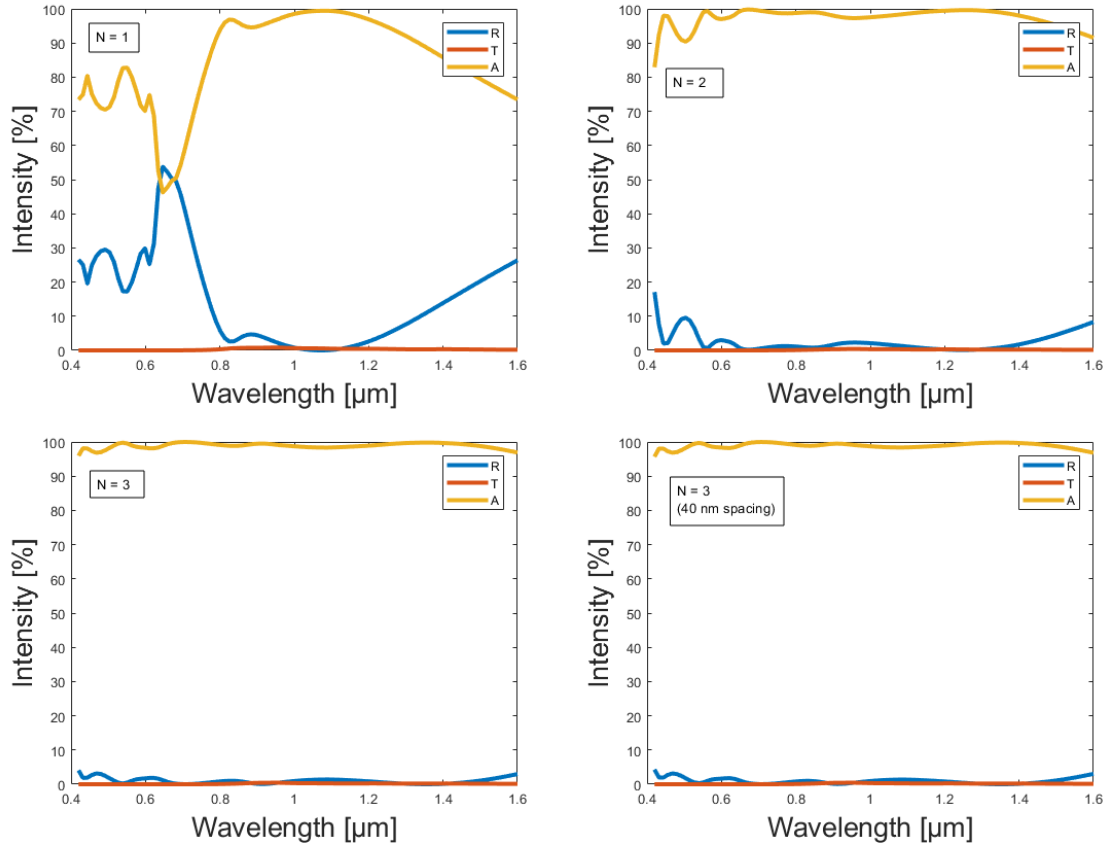


Figure 6.2: Absorptance (yellow), transmittance (red) and reflectance (blue) of Cr/TiO₂ designs from Table 6.1: N = 1 design (top, left), N = 2 (top, right), N = 3 (bottom, left) and N = 3 with 40 nm spacing between squares (bottom, right).

6.2 Perfect Absorber Fabrication

We fabricate the one-layer absorber device using the fabrication procedure for TiO₂ devices described in section 4.2 with minor modifications. Here, we use a substrate of Au on glass. We use a AJA International ATC sputtering system to sputter a thin 18-nm Cr adhesion-layer on a glass slide, followed by 150 nm of Au. Standard cleanroom recipes are

used for these layers. We characterize the substrate with spectroscopic ellipsometry and a spectrophotometer reflection scan.

Amorphous TiO_2 is sputtered at room temperature, at 2 mT, at 10% O_2 , 195 W based on our previous optimization of amorphous TiO_2 sputtering[27]. We confirm the thickness of TiO_2 using spectroscopic ellipsometry. We use the substrate model to obtain an accurate fit of the TiO_2 layer and confirm a thickness of 92 nm.

Square array structures are written using ZEP-520a resist in an Elionix ELS-F125 electron beam lithography system, at 125kV and beam current of 500 pA. We write a pattern consisting of ten 60 x 50 square arrays. We maintain the period of the squares at 419 nm for all arrays but test square lengths between 300 – 400 nm (one length assigned to each array) in order to reach the target length of 372 nm. We matrix this pattern to perform an e-beam dose test of the square arrays for doses between 340 to 680 $\mu\text{C}/\text{cm}^2$ in steps of 20 $\mu\text{C}/\text{cm}^2$.

The remaining fabrication steps follow the same procedures in Chapter 4 for developing the resist, depositing and lifting off Cr (2 x 20nm), and etching the TiO_2 with reactive ion etching. The dry etching step is performed for 95 seconds and removes about 9 nm of the Cr. We simulate varying the thickness of Cr and determine that the Cr can vary up to about 50 nm before becoming detrimental to the device operation. We use a thicker Cr layer than 15 nm to aid in the dry etching step: a thicker metal mask can lead to less roughness in the TiO_2 structures.

We characterize the structured one-layer device using a Zeiss Ultra scanning electron microscope (SEM). We measure our patterns using 2kV and a working distance of 7.7 mm.

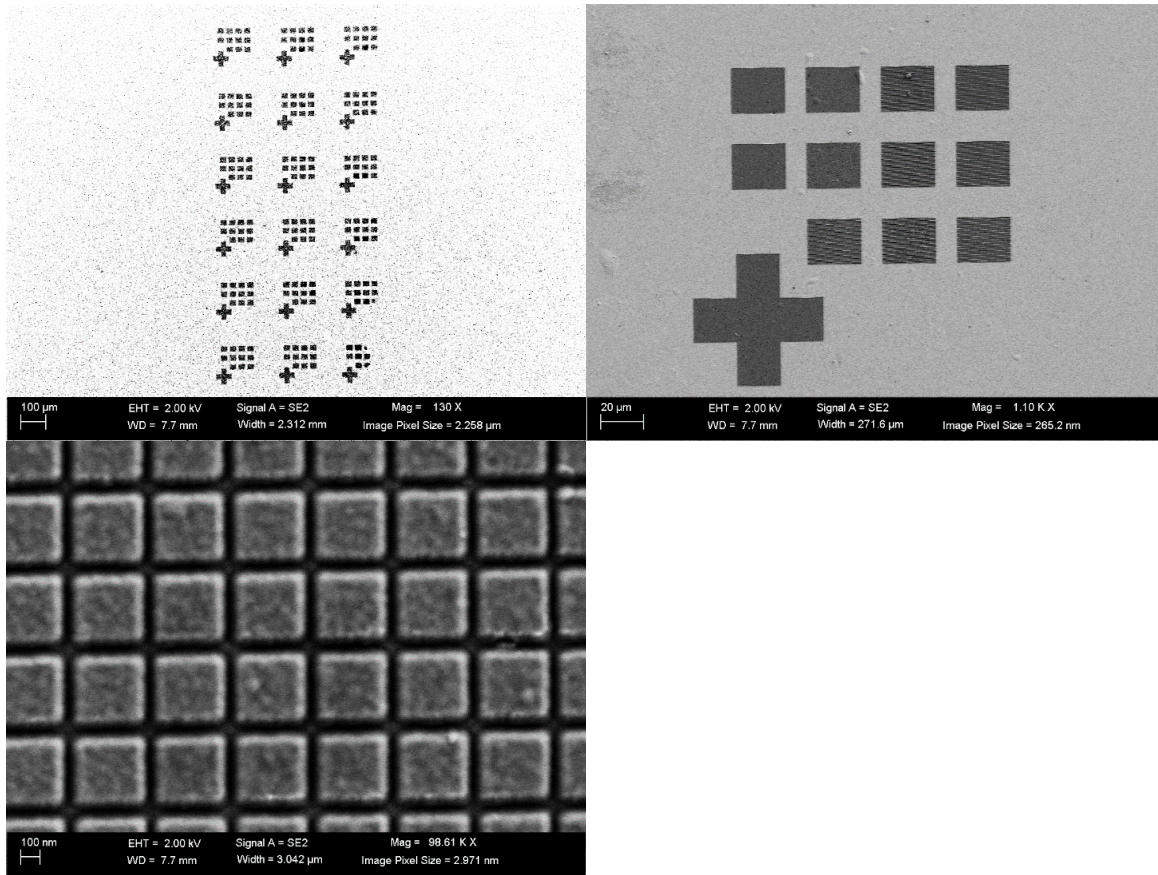


Figure 6.3: Scanning electron micrographs of one-layer perfect absorber device: (top, left) overview of 6 x 3 array of surviving patterns fabricated at different doses; (top, right) overview of design pattern fabricated for a single dose of $420 \mu\text{C}/\text{cm}^2$; (bottom) zoom in to pattern with squares of length 371.7 nm, meeting 372 nm design dimensions.

The top-left image in Figure 6.3 shows an overview of the matrixed patterns written at different e-beam doses. The top-right image in Figure 6.3 shows the pattern written at a

dose of $420 \mu\text{C}/\text{cm}^2$, with square arrays designed with square length sizes varying between 300 and 400 nm in steps of 10 nm. Figure 6.2c shows a square array with sides measured to be 371.7 nm, meeting the target size of 372 nm. We see some morphology on the squares, mostly from the Cr layer that sits on top of TiO_2 .

6.3 One-layer Broadband Absorber Reflection Measurement

We perform reflection measurements of perfect absorber square arrays using hyperspectral imaging, which allows us to characterize the spectrum achieved for each pixel. The resolution of each pixel is determined based on light passing through a diffraction grating and spectrometer. We measure our devices using a Cytoviva hyperspectral imaging system incorporated into a Horiba XploRA system. Using a 50x objective, we focus on the regions of interest and can perform measurements in the small 50×60 square array areas ($25.2 \times 21 \mu\text{m}$).

Visual inspection of the square patterns shows that the smallest designed squares appear dark, whereas the larger designed squares become lighter in color, eventually approaching a pink-like color. Figure 6.3 shows the optical microscope image of square arrays fabricated at $420 \mu\text{C}/\text{cm}^2$.

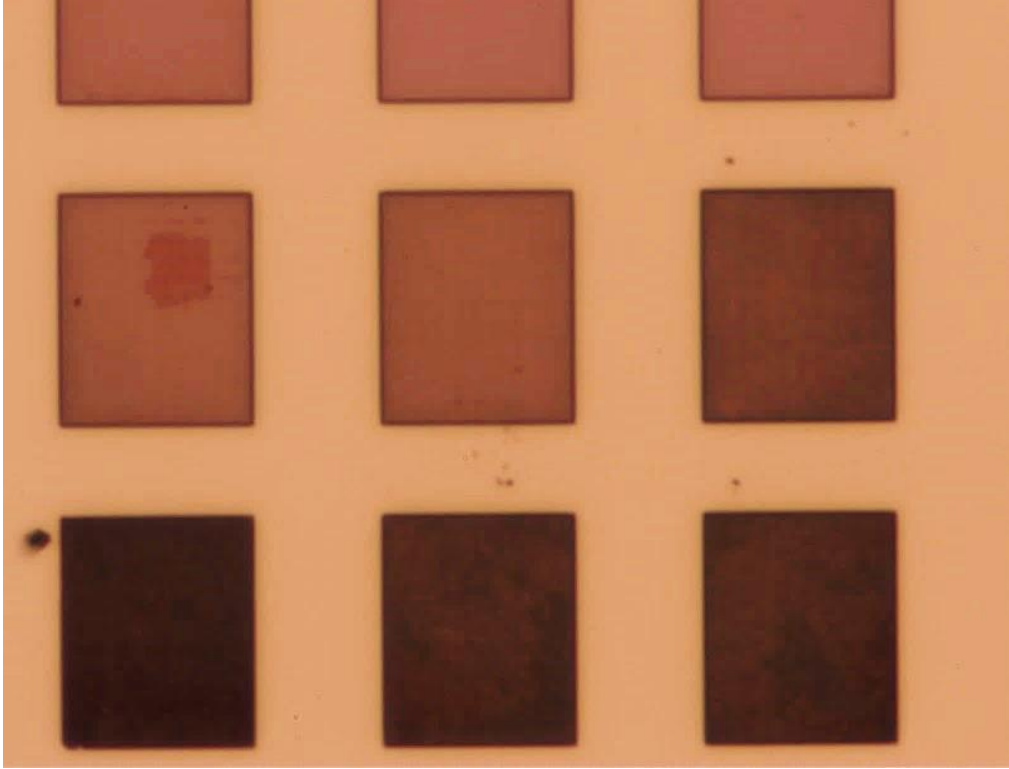


Figure 6.3: Optical microscope image of 9 square arrays of size 25 x 21 μm .

We measure the reflection spectrum for 400 – 800 nm wavelengths for the entire region depicted in the image. We extract reflection spectra from the center of each square array, averaging a matrix of 5x5 pixels. The results are shown in Figure 6.4 where we plot the results for all squares on the same graph. The lowest curve corresponds to the smallest square design and the subsequent curves are in increasing order of square size design. It is clear visually and from the graph that the smaller squares achieve the lowest reflection. The larger arrays have a clear reflection peak in the red wavelength region. This explains the slight pink appearance of these arrays in the microscope image. Since several of the

smaller arrays achieved absorbing behavior, this indicates a level of robustness in the approach for achieving broadband absorption.

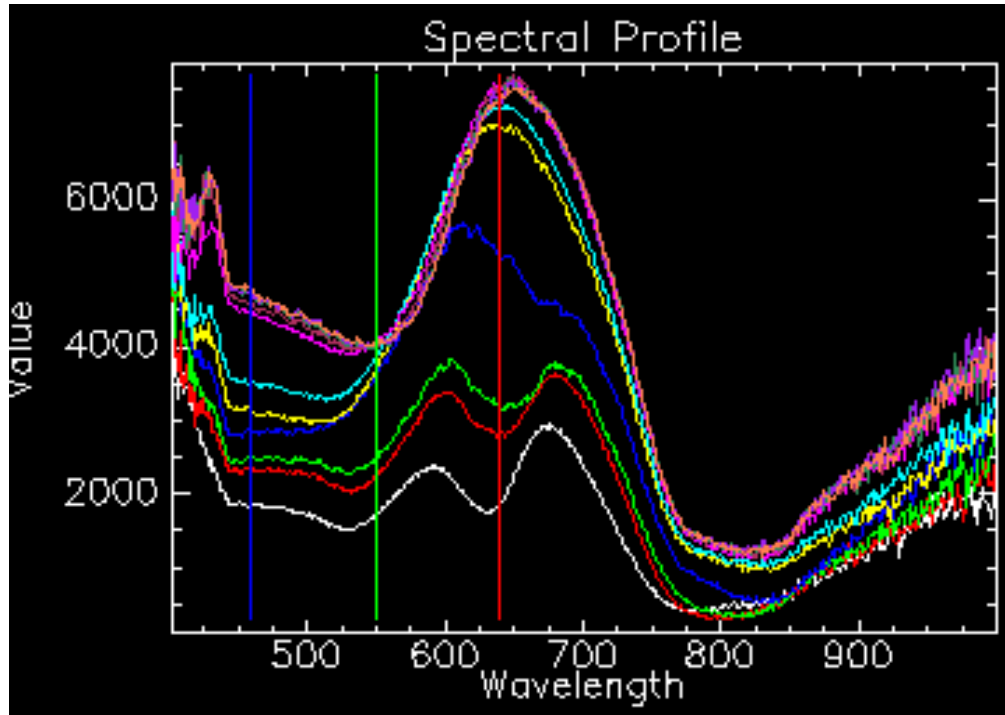


Figure 6.4: Hyperspectral dark field imaging result for squares in Figure 6.3. The bottom curve (white) is taken from the array with the smallest squares and subsequent curves are stacked vertically in the graph for increasing square size. Data is for 5x5 pixel averaging. Double peak shape for lower three curves evolves to large peak centered about the red wavelength region (indicated by red vertical line). Blue and green regions of the spectrum are also indicated by vertical lines.

6.4 Two-layer perfect absorber design

We investigate an approach to fabricate a two-layer broadband absorber. A fabrication challenge of stacking structures vertically is how to planarize each layer in order to add material for the following layer without damaging the existing structures[45], [74], [75]. This planarization process and material must meet several criteria, including making it possible for the material for the next layer to be deposited, being able to withstand the temperatures and chemicals used during subsequent fabrication steps, and (in our case) being able to be removed once the fabrication is complete. Our design calls for air in between the arrays and therefore requires that we remove the planarization material. It can be challenging to etch away material in high aspect ratio spaces such as the 40 nm gap vs. 91 nm height spaces in between adjacent bottom layer squares. An approach not used here is to keep the dielectric or resist layer that acts as the planarizer in the final version of the device. In order to minimize Fresnel reflections as the light is impinging on the device, we investigate methods where we do not embed our absorbing device in another material.

We consider how to use TiO_2 for the second layer in two ways: (1) we follow the same TiO_2 sputtering and top-down fabrication technique as for the first layer; (2) we create hole structures using positive e-beam resist and fill them in with TiO_2 using sputtering or atomic layer deposition (ALD)[31]. In order to use approach one, it would be necessary to planarize the first layer with a material that can be easily removed at the end of the fabrication (this includes resists or silica). Both sputtering and ALD are conformal fabrication techniques, so adding TiO_2 with these techniques would cover the entire sample, making it challenging to remove the planarization material. It could require adding

a dicing step to expose the planarization material for etching. It is also important to consider how this planarization material might chemically react during the lift-off and dry etching steps. Our TiO_2 and Cr depositions occur at room temperature; however, the lift-off process (using PG Remover) and dry etching steps (using fluorine chemistry) require careful selection of the material in order to avoid chemical reactions. At the same time, this material must be easily etched away to maintain the device in air. Therefore, there are several constraints to the materials that can be used in this approach. Altogether, this approach consists of 2 full rounds of fabrication, plus the steps for adding and removing the planarizing layer, resulting in undesirable high fabrication complexity.

We now evaluate the second approach to determine if the fabrication process would result in less complexity. This approach would allow us to use a positive resist, such as ZEP or PMMA, to both planarize the device for the second layer and serve as the e-beam resist for creating the trenches for TiO_2 to be filled in. After writing the pattern, the trenches could be filled in with TiO_2 via sputtering or ALD, followed by a blanket etch to remove excess TiO_2 from the top of the resist. However, depositing a metal layer only on the TiO_2 structures becomes a challenge. Simply depositing Cr after the blanket etch and performing lift-off would likely lead to removal of all Cr from the sample, since the Cr layer would be at the same level on top of the resist and on the TiO_2 . An approach to fix this requires that the resist layer be thicker than the TiO_2 layer, so that the metal is deposited at different levels and lift-off can be successfully performed. In this case, a directional deposition technique is required for both the metal and the TiO_2 , to avoid covering the resist sidewalls. This could be achieved by e-beam evaporating Cr and TiO_2 using targets of these materials. An advantage of this fabrication approach is that the blanket etch could be skipped. This

fabrication requires less fabrication steps than approach number one, but involves optimizing new fabrication techniques, such as depositing TiO_2 with e-beam evaporation into trenches.

Based on analyzing the above two approaches, we investigate alternatives to replace TiO_2 as the second layer dielectric material and make some minor changes to the design. We choose to replace TiO_2 with HSQ (Hydrogen silsesquioxane, Dow Corning), a negative resist that becomes SiO_2 after e-beam exposure and development. In this case, we use the resist to planarize the sample and write the second layer pattern (as in approach 2). We write the patterns in the square regions, so that after development they become SiO_2 squares. In this development step, the remaining HSQ planarizing the rest of the sample is removed automatically. We can then cover the SiO_2 squares in a thin layer of Cr. In this step, we compromise the original design by allowing Cr to also be deposited on the substrate and first (TiO_2/Cr) layer. By using e-beam evaporation to deposit Cr directionally, we avoid covering the sidewalls of each layer, which would suppress the plasmonic resonator effect that dominates absorption in this device. Adding a thin 15-nm layer of Cr to other parts of the device (1st layer Cr and substrate) does not significantly impact the design since these parts of the device are already covered in metal (Cr and Au, respectively) and simulations of varying the Cr thickness have shown found minimal decreases in the efficiency of the device up to 50 nm thickness.

We simulate the absorption in a device with HSQ and Cr on the second layer and TiO_2 and Cr as the first layer (keeping the dimensions of the bottom TiO_2 layer fixed). The results for this optimized two-layer device design are shown in Table 6.2 below and indicate an absorption of 98.3%. This high absorption is only an additional 0.6% away from the result

for a three-layer Cr/TiO₂ device, demonstrating once again how simplifications to the theoretical design can be achieved to approximate a perfectly absorbing device.

Table 6.2: Dimensions (length and thickness) for 2-layer device with Cr/TiO₂ as the bottom layer (L_1 , t_1 , respectively) and Cr/HSQ as the second layer (L_2 , t_2). Bottom layer and period P are kept fixed based on the 1-layer devices design.

Cr/TiO ₂ (bottom) + Cr/HSQ (top)						
	L_1 (nm)	t_1 -HSQ (nm)	L_2 (nm)	t_2 -TiO ₂ (nm)	P (nm)	η
$N=2$ stacks $L_1 < L_2 \leq P$	232	134	372	94	419	98.3%

6.5 Two-layer device fabrication steps and outlook

We fabricate square arrays of SiO₂ on a TiO₂/gold/glass substrate. We investigate the e-beam dose and CAD design size required to achieve the target dimensions of 232 nm for the square side length. The substrate is chosen to imitate the conditions the one-layer device. We clean our substrate gently with Acetone and IPA and dehydrate the sample on a 180 °C hot plate for 10 minutes. We O₂ plasma treat our sample with at 100 W and 40 sccm for 2 minutes and bake the sample again for 2 minutes at 180 °C prior to spinning HSQ resist. We choose the HSQ spin speed according to the spin curve for XR-1541 6% solution. A speed of 2000 rpm results in 134 nm thickness, which corresponds exactly to our optimized design thickness. We bake the sample for an additional 5 minutes at 90 °C after spinning on the resist.

We use the same pattern as for the one-layer device to perform a dose test of HSQ. We choose a beam current of 500 pA and test doses ranging from 860 to 2240 $\mu\text{C}/\text{cm}^2$. After exposure, we develop the patterns using TMAH for 20 seconds. We characterize the dimensions of our sample using SEM. We find that we obtain dimensions of 221 nm using a dose of 860 $\mu\text{C}/\text{cm}^2$ and CAD size of 300 nm. The SEM image for this device, taken at 2 kV and 4.4 mm working distance, is shown in Figure 6.5 below.

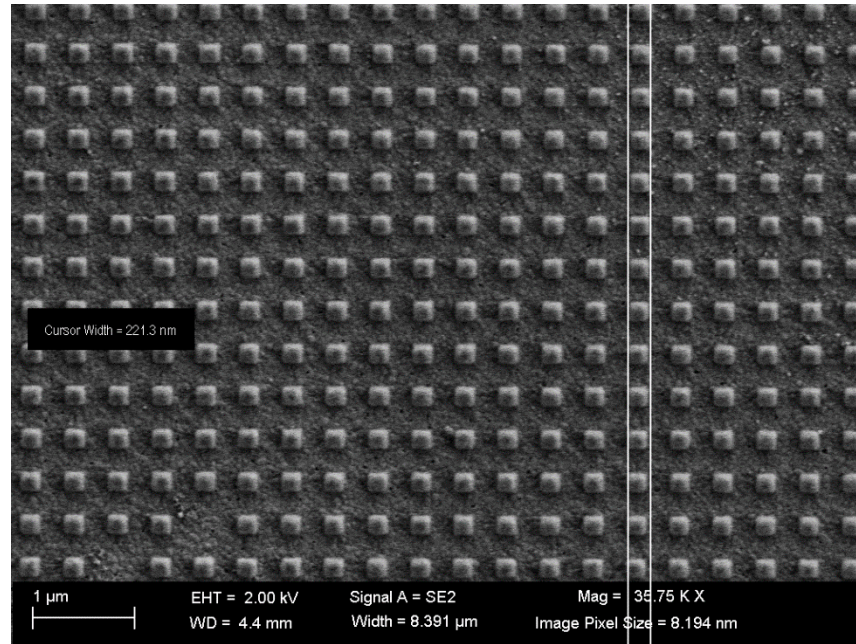


Figure 6.5: Scanning electron micrograph of SiO_2 square array on $\text{TiO}_2/\text{Au}/\text{Glass}$ substrate. Measurement indicates length of squares is 221.3 nm, very near the 232 nm target.

Our results indicate the conditions for fabricating a two-layer device. Our design modifications demonstrate that it is possible to simplify the complexity of fabrication and

still achieve designs with nearly perfect absorbing behavior of $>98\%$. We also demonstrate experimentally that a one-layer device is quite robust to fabrication tolerances and achieves significant absorption over the visible region. A larger scale device can be used to investigate the IR absorption properties via spectrophotometer measurements. Future work in this area will enable the experimental realization of our two-layer device design.

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