

Optimizing Anatase-TiO₂ Deposition for Low-loss Planar Waveguides

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ABSTRACT

Polycrystalline anatase-TiO₂ thin film possesses desirable properties for on-chip photonic devices that can be used for optic computing, communication, and sensing. Low-loss anatase-TiO₂ thin films are necessary for fabricating high quality optical devices. We studied anatase-TiO₂ by reactively sputtering titanium metal in an oxygen environment and annealing. By correlating key deposition parameters, including oxygen flow rate, deposition pressure, RF power, and temperature to film morphology and planar waveguiding losses, we aim to understand the dominant source of propagation losses in TiO₂ thin films and achieve higher quality, lower-loss films.

Keywords: anatase TiO₂ thin film, reactive sputtering, anatase, TiO₂, non-linear devices, low optical loss, deposition, optical devices

1. INTRODUCTION

Recent advances in laser and fiber-optic technology have expanded the capacity of existing communications networks. Electronic switching and routing are expected to become inefficient at future data rates, leading us to ask if we can design photonic devices capable of switching and routing data completely in the optical domain. Ongoing research into photonic devices has opened up new aspects of various fields, including optical computing, communication, and sensing [1-8].

To fabricate optical devices, we first deposit thin films of TiO₂, 700 – 1500 nm thick, on a substrate, and then pattern using electron beam lithography followed by reactive ion etching. TiO₂ possesses a unique balance of materials properties. It combines a high nonlinearity [9-11] with extended transparency from 400 nm to the infrared and low two-photon absorption for wavelengths longer than 800 nm [9]. Because TiO₂ can be deposited at low temperature, it is highly integratable with other materials including silicon and diamond, and can provide a link to single photon sources and detectors [12-14]. TiO₂ exists in three naturally occurring polymorphs: anatase, rutile and brookite [15]. Among them, anatase can be achieved using a wide range of deposition parameters, is more stable than amorphous TiO₂, and is therefore promising for photonic devices. Bradley et al. reported fabrication of channel waveguides in polycrystalline anatase TiO₂ thin films for on-chip photonic devices using reactive radio frequency (RF) magnetron sputtering [16]. However, improving the losses observed in these films remains a challenge.

There are three main sources of optical loss for TiO₂-based optical devices. First, there is potential absorption of the bulk material, which is intrinsic to the material. Second, there are losses caused by the morphology of the deposited film, which may be controlled during the deposition. Lastly, the e-beam lithography step introduces further losses, notably from side-wall roughness. Our project aims to reduce the second type of loss, optical loss from thin film deposition. The result of this study can also illuminate the source of optical loss of thin films composed of other materials.

Sputtering is a technique used to create a high quality thin film by first creating oxygen plasma and then accelerating ions from the plasma to eject neutral particles from the source material (target) to coat the substrate [17]. To control the crystalline phase and other properties of a thin film, users can change sputtering pressure, oxygen flow rate, temperature and power. Sputtering high optical-quality anatase TiO₂ is a fairly slow process (0.3 nm/min) relative to amorphous TiO₂ (1.5 nm/min), mainly because of the high oxygen flow rate needed. Improving both the deposition speed and film quality of the sputtering process are therefore the main objectives of this research.

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Alternatively, we can anneal amorphous TiO₂ thin films to transform them into anatase TiO₂. The advantage of annealing is that amorphous thin films are much faster to deposit by sputtering than anatase, and heating in a furnace is a less expensive, simpler, and more accessible method than sputtering. One of our goals is to test whether annealed anatase TiO₂ thin films can achieve the same optical quality as sputtered ones.

In this study, we present an optimal deposition method for anatase TiO₂ thin-films for on-chip photonic devices with low loss and reasonable deposition speed using sputtering and annealing methods. Additionally, we investigate the relation of pre-deposition cleaning procedure and deposition parameters including power, oxygen flow-rate, and substrate temperature on the observed planar optic losses to improve the quality of our thin films.

2. MATERIAL AND METHOD

Before each deposition, we cleave a strip from the thermally oxidized silicon substrate, and place it in a sonicator for 5 minutes; we dry the surface with nitrogen and repeat the same procedure with isopropanol. The purpose is to remove organic impurities on the substrate surface. After the second drying, we place it on a hot plate at 180 °C for 5 minutes to evaporate any remaining liquid droplets from the surface. An oxygen plasma barrel asher is then used to remove any remaining organic contamination. Directly before deposition, we blow the surface again with the nitrogen gun.

We deposit our film using an AJA International Sputterer (model: ATC) in the Harvard Center for Nanoscale System (CNS) to sputter titanium (Ti) from an RF gun in the oxygen environment. The AJA sputterer we use for the purpose of our experiment has a turbo-pumped main chamber that can be pumped down to 10⁻⁸ Torr and a load lock chamber. In our depositions, we set the propeller height at 36 and rotation speed at 40. The temperature for anatase deposition is usually set at 350 °C. We perform a pre-deposition using a test wafer to reduce contamination from any previous depositions and estimate the deposition rate given the current condition of the sputtering target.

We use a single point ellipsometer to measure the thickness of the deposited films and a commercial prism coupler to measure planar optical propagation loss [18]. In the prism coupler, an incident laser light hits a rotating prism; at certain angles (based on the modes in the film) the light is coupled into the film and will propagate along the film, appearing as a “streak” of light. A primary detector collects deflected light that is not coupled into the film. The dips that occur during an angular scan, as measured by the primary detector, correspond to the angles in which light can be coupled into the planar waveguide, each corresponding to a mode of the waveguide. Using a series of modes, both the film index and thickness can be calculated. If the film is single mode, the thickness or index of refraction can be measured externally and the other parameter can be calculated from prism coupling. To measure the planar waveguiding losses, we first couple light into the film and then we scan a secondary detector along the streak of propagation. A short streak should be observable with the naked eye for measurements in the visible range, or using an IR viewer in the near infrared range and by an InGaAs camera in the infrared range. If the incident light is in mode (as indicated by the primary detector) yet no streak is observed, the loss of the film is very likely to be too high to be measured by prism coupling.

Lastly, we determine the morphology of our films, such as the nanocrystal size, using scanning electron microscopy (SEM) and commercial image processing tools. Additionally, we use Raman spectroscopy with a laser wavelength of 633 nm to infer the crystalline structure of our TiO₂. During these Raman measurements, we reduce the background signal caused by the silicon substrate by depositing TiO₂ on a glass substrate with identical deposition parameters.

3. RESULTS AND DISCUSSION

3.1 Annealing

Figure 1 shows the Raman spectrum of an amorphous TiO₂ sample that was annealed at 500 °C for one hour. We observe Raman peaks consistent with the anatase crystalline phase (a strong Raman peak at 144 cm⁻¹ and four weak Raman peaks at 197, 399, 516, and 639 cm⁻¹ [16, 19]). Note that the rising tail in Figure 2b might be caused by fluorescence of the glass slide. Based on Raman spectroscopy, we determine that at 500 °C, amorphous TiO₂ can be annealed to anatase.

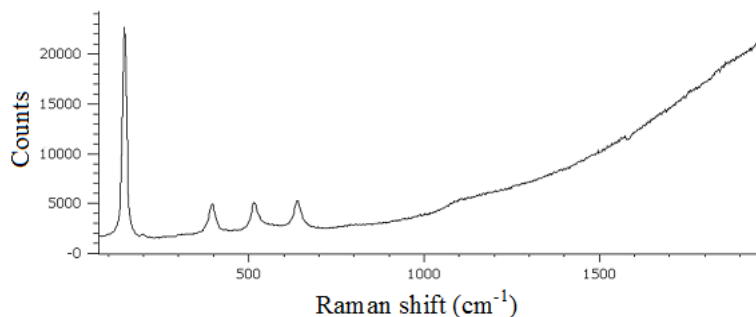


Figure 1. Raman spectrum of a annealed TiO₂ thin-film deposited by reactive RF magnetron sputtering at an O₂ flow rate of 4.4 sccm, an Ar flow rate of 40 sccm, and a power of 156W at ambient temperature. The deposition results in an amorphous film that we subsequently annealed at 500 °C for one hour. The Raman spectrum shows peaks corresponding to the reported peaks of the anatase crystalline phase of TiO₂ at 144, 194, 399, 514, and 639 cm⁻¹, indicating that at 500 °C, amorphous has already been annealed into anatase.

Given the phase changing temperature, we anneal a 240 nm thick amorphous TiO₂ film on a thermally oxidized silicon substrate deposited with O₂ flow rate at 4.4 sccm, Ar flow rate at 40 sccm, power at 142 Watt, and temperature at ambient (17 °C) for 190 min. Without annealing, we measure a loss of 1.6 dB/cm at 1550 nm. The sample is annealed at 500 °C for 2 hours. The loss of the annealed sample is significantly higher and could not be measured (we estimate the losses are higher than 30dB/cm)

The SEM image of the sample provides us with more insight into the reason for the increased loss. Figure 2 compares the sample before and after annealing. Figure 2 (a) is an SEM image of the sample before annealing; notice that no crystallites can be observed, consistent with the amorphous phase. Figure 2 (b) shows the sample after annealing; there are cracks across the surface, and the cracked islands have diameters around 1000 nm, possibly arising from the disparity of thermal expansion coefficient between the oxidized silicon substrates (2.2- μ m-thick SiO₂) and anatase TiO₂. The size of the cracked islands is comparable to the wavelength of our incident light for loss measurement (1310 nm and 1550 nm). We conclude that annealing appears not to be a feasible option to improve film quality, at least with the parameters used in this study.

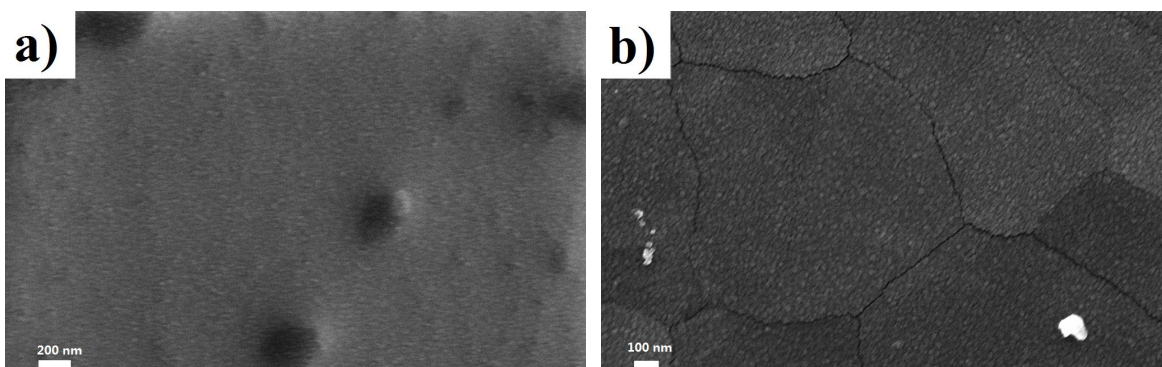


Figure 2. A comparison of TiO₂ thin film morphology before and after annealing. a) before annealing: amorphous TiO₂; b) after annealing: densely packed nanocrystals, together with the Raman data, we infer a polycrystalline anatase phase. Note the cracks across the surface of the annealed films with diameters around 1000 nm.

3.2 Thickness

We have previously observed that the film thickness affects the planar optic loss of thin films; however, the exact correlation remains obscure. Qualitatively, there are two counteracting factors that can account for the effect of film thickness on loss. On the one hand, a thicker film implies that for incident light of the same angle, there are fewer reflections of light when the light propagates along within the film, leading to lower optical loss. On the other hand, as

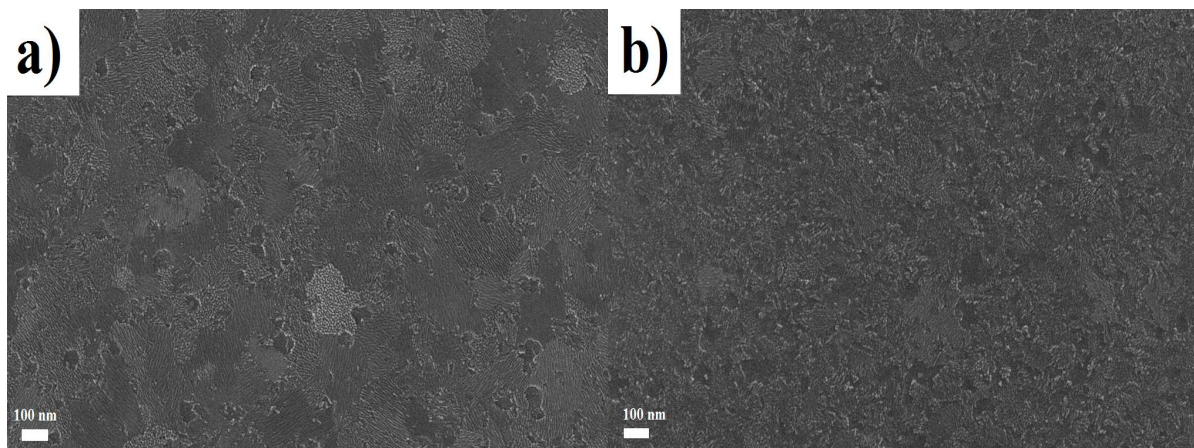
film becomes thicker, column growth of nanocrystals becomes increasingly difficult; more misaligned layers of nanocrystals lead to higher loss within the domain.

In order to confirm the effect of thickness on losses, we prepare two samples cleaved from the same wafer with the exact same cleaning procedure and deposit them with the same deposition parameters: O₂ flow rate of 12.5 sccm, Ar flow rate of 2 mT. Sample 1 has a thickness of 92.7 nm and Sample 2 has a thickness of 183.4 nm; both are polycrystalline anatase TiO₂. The average of ten loss measurements of Sample 1 and 2 using prism coupling are 5.15 dB/cm and 9.69 dB/cm, respectively. We observe that the average loss of Sample 2 is about twice as high as that of Sample 1. In this limited case study, the thicker film has much higher loss. It may be possible that as thickness further increases, the planar optical loss decreases. Thus, a more thorough investigation on the relation between thickness and planar optical loss should be carried out in future studies.

3.3 Cleaning procedure

Before each deposition, we clean the oxidized silicon substrate in sonicator with isopropanol, methanol, and in an oxygen plasma barrel asher. We also use a diamond pen to cleave a strip off the oxidized silicon substrate if the thin film to be deposited is only needed in a small size. Empirically, it had been shown that proper cleaning and cleaving of the substrate before deposition is crucial to guarantee the optical quality of the film. We aim to understand how the cleaning procedure affects the optical loss at a more fundamental level.

We deposit three samples with all the other parameters kept the same except for the cleaving and cleaning procedure. We treat the first sample with no cleaning at all; the second one with cleaning first and then cleaving; the third one with cleaving first and then cleaning. It is shown that the sample with no cleaning exhibits uneven surface with patches of nanocrystals oriented in different directions and large crystalline size (Figure 3a); the sample with cleaning and then cleaving has a less uneven surface and medium crystalline size (Figure 3b); the sample with cleaving and then cleaning has the finest grain size and smoothest surface under SEM. The reason that there is a preferred order of cleaving and cleaning is that there are particles scattered on the substrate surface from cleaving; cleaning after cleaving thus ensured a less contaminated substrate surface. The results show that the inappropriate pre-deposition cleaning and cleaving process affects the film quality in two ways: first, it leads to uneven surface; second, it results in a larger grain size. Neither is normally desirable for low-optic-loss thin films.



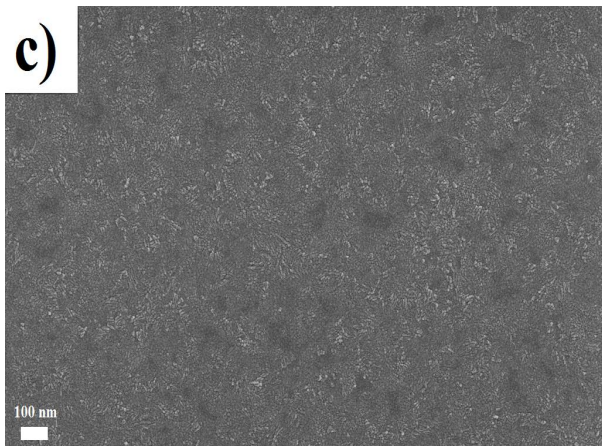


Figure 3. SEM images of three samples of anatase TiO_2 deposited oxidized silicon substrates. a) no pre-deposition cleaning: uneven surface with patches of crystalline orientating in different direction and large crystalline size; b) pre-deposition cleaning and then cleaving: less uneven surface and medium crystalline size; c) cleaving and then cleaning: most uniform surface and finest crystallines.

3.4 Oxygen flow rate

We deposit anatase TiO_2 using a titanium target in an oxygen environment in an RF sputtering system. The oxygen flow is responsible for the oxygen component of the TiO_2 thin film. Of all the controllable sputtering parameters (power, oxygen flow rate, argon flow rate, temperature and chamber pressure), the oxygen flow rate has a largest effect on the deposition rate and planar optical losses. In order to find the optimal oxygen flow rate setting that gives us a reasonable deposition rate with low loss, we keep all the other variables the same and change the oxygen flow rate only.

Figure 4 gives the relation between oxygen flow rate (sccm) and deposition rate. It can be seen that as the oxygen flow rate increases, the deposition rate decreases exponentially.

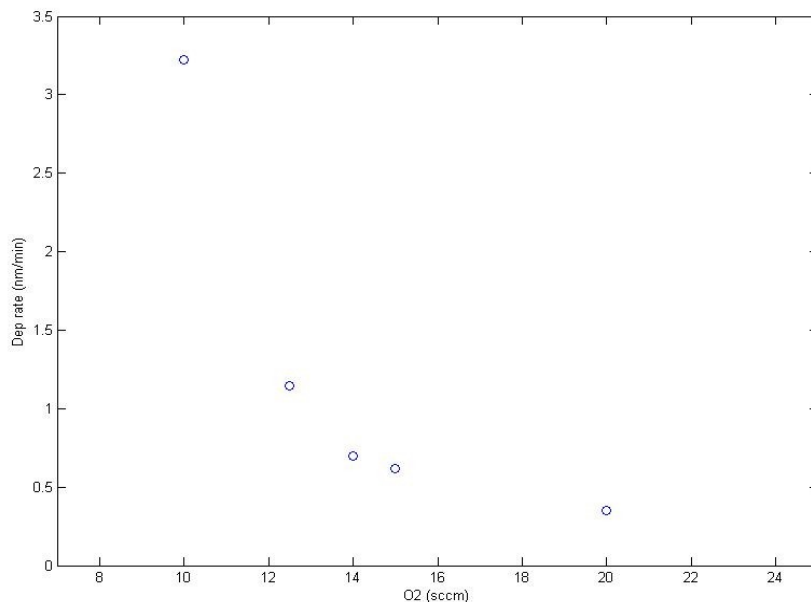


Figure 4. The relation between oxygen flow rate and deposition rate: as oxygen flow rate increases, the deposition rate decreases exponentially.

Figure 5 gives the relation between oxygen flow rate and crystalline size. It shows that lower oxygen flow rate gives smaller crystalline size. From experience we know that smaller crystalline size usually yields low loss thin films.

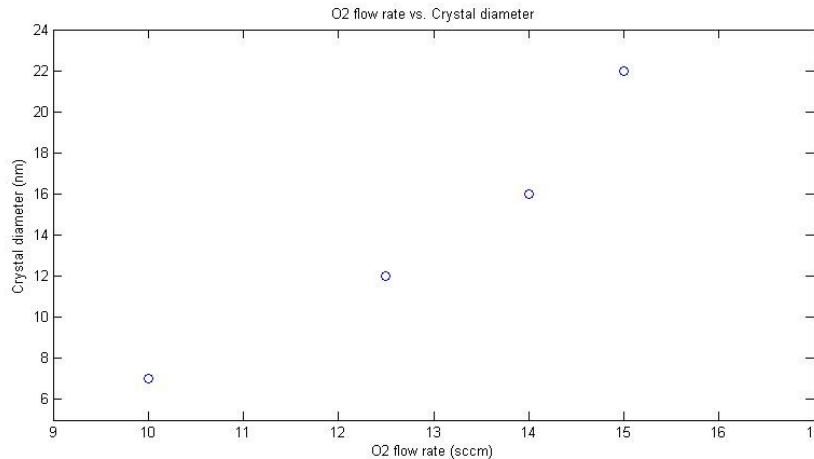


Figure 5. The relation between oxygen flow rate and crystalline size: lower oxygen flow rate gives smaller crystalline size.

Figure 6 gives the relation between oxygen flow rate and planar optical loss at 1550 nm measured by prism coupling. The film deposited at 10 sccm does not guide light. We made multiple measurements on each film with oxygen flow rates of 12.5, 14, 15 and 20 sccm; their average values and error bars are shown in the figure. The figure shows that there is no simple correlation between oxygen flow rate and planar optical loss. Another noticeable feature is that loss measurement by prism coupling at 1550 nm has huge variability. We should note that these measurements were taken using the primary detector to determine coupling as an InGaAs camera was not readily available to observe the propagation streak. Subsequently, we obtained an InGaAs camera and observed only a very short (1-2 cm) streak in the film with a 20 sccm oxygen flow rate and ever shorter for the film with a 12.5 sccm. In other words, the loss is so high that the light can only be guided for a short distance before its intensity drops down to near zero. Therefore, the loss measurement data by prism coupling at 1550 nm is not entirely conclusive.

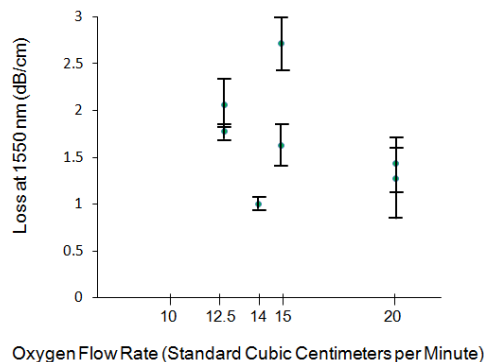


Figure 6. The relation between oxygen flow rate and planar optical loss: no clear correlation between oxygen flow rate and planar optical loss is observed.

4. CONCLUSION

Our study shows that annealing induces nanoscale cracks on the surface of thin film and thus increases the loss. With the current annealing method, annealing amorphous TiO₂ films cannot achieve losses similar to the anatase TiO₂ thin films produced by sputtering with a heated substrate. A case study of a 183.4-nm thick film and a 92.7-nm thick film reveals that thicker film has higher losses; further study is need for a comprehensive relation between thickness and planar optical loss of thin films. Proper cleaning procedure after cleaving the substrates can reduce the island formation on the surface of thin films and result in smaller crystalline size. Decreasing oxygen flow rate results in higher deposition speed and smaller grain size but we observed no significant improvement in losses. Changing the oxygen flow rate from 20

sccm in the standard recipe to 12.5 sccm gives a recipe with a deposition rate three times as high, yet the loss measurement results are still inconclusive.

After changing a wide range of deposition parameters, taking both deposition rate and optical loss into account, we recommend using similar deposition parameters to those previously reported by Bradley et al. with the possible reduction of the oxygen flow (between 12.5–20 sccm) to increase the deposition rate [16].

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