Stability in the Deposition of Titanium Dioxide

Ronald R. Willey, *Willey Optical Consultants, Charlevoix, MI*

Abstract

Titanium dioxide (TiO_2 or titania) has been a favored high index material for the visible and near infrared spectrum because of its high index and relative robustness. TiO_2 appears historically to be less popular than other high index materials with some practitioners because of difficulties in obtaining a stable index result. This article reviews the probable causes of instability, how they might be controlled, and related information from the literature.

Introduction

Bennett et al.[1] published the results of many TiO_2 films produced by a great variety of techniques and laboratories. That report shows the range of results which can be obtained by different processes. We believe the root of the problems that cause difficulties for some laboratories/facilities can be seen in the extensive work of Pulker et al.[2] using tungsten boat evaporation. They started with various materials including TiO_2, Ti_3O_5, Ti_2O_3, TiO, and pure Ti. Their results are illustrated in **Figure 1**.
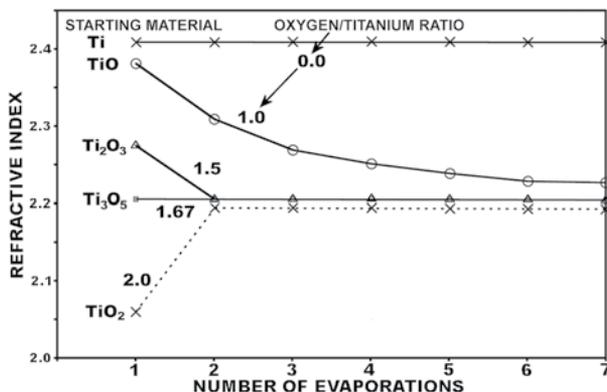

Figure 1. *Index of refraction of TiO_x films as a function of the number of evaporations for various starting materials; taken from the report of Pulker et al[2].*

These represent oxygen-to-titanium atom ratios for the starting materials of: 2.0, 1.67, 1.5, 1.0, and 0.0 respectively. They found that the 1.67 material was stable and gave consistent layers of repeatable index of 2.205 at about 550 nm. However, the first layer of 2.0 material gave an index of about 2.06 followed by layers of nearly 2.20 index. **Figure 1** is adapted from their paper. The 1.5 material gave and index of 2.27 for the first layer and then settled in to nearly 2.205 for subsequent layers. The 1.00 material, on the other hand, required several layers to drop from an index of 2.38 toward 2.2. All of their results were stated to be free from absorption. One criterion for almost any TiO_2 deposition is to have negligible absorption in the working spectral region. This will place a lower limit on the background oxygen pressure and some constraints on temperature and deposition rate. Granqvist[3] also discusses titanium oxide films in his handbook on electrochromic materials. His review is valuable as an additional data source and another point of view.

Our interpretation of their results is that the material being evaporated in the crucible or boat reaches an equilibrium with the background or makeup oxygen in the chamber after some period of being melted or some number of layers of evaporation. The TiO_2 (2.0 material) is releasing excess oxygen until it comes to equilibrium, while the TiO (1.0 material) must take up oxygen from the background to reach equilibrium. This seems to be consistent with the concept of "congruent" vaporization as studied by Chiao et al.[4]. It is also consistent with the findings of Ogura[5]. It can be seen that the TiO process is slower as evidenced by the data of Pulker et al.[2]. where it takes many layers for TiO to approach a stable index.

An Approach

As a result of the above considerations, our philosophy and practice has been to attempt to achieve the most stable process practical by melting in new tablets of TiO_2 starting material in an E-gun under its shutter with the same background pressure of oxygen which is to be used during the actual process. This is illustrated in **Figure 2**. As the premelt is started, the power to the gun is raised and the material begins to outgas. The power is raised until the pressure is somewhere below that which would cause E-gun arcing (we used $\sim 5 \times 10^{-4}$ torr). The molten material in the crucible (usually with a molybdenum liner and possibly raised on SiO_2 granules to reduce heat loss) is kept at a temperature where little material is actually evaporating, but gas (oxygen) is being driven off, as evidenced by the chamber pressure gauge. After a few minutes, the chamber pressure drops and the power can be increased to keep the material melting and outgassing. When the whole charge in the crucible is well melted and the chamber pressure has come down to the oxygen makeup gas pressure setting to be used in production, a few minutes of additional soaking is allowed, at production deposition power and background oxygen pressure, for the melt to stabilize at its equilibrium with the makeup gas. We believe that this has given us the most stable properties for the deposition of TiO_2.
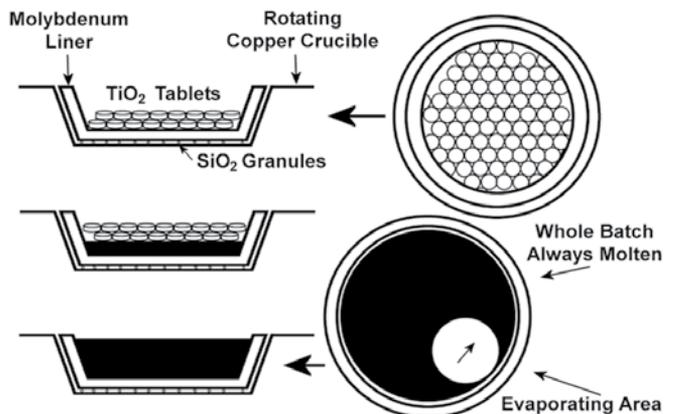

Figure 2. *Melt-in technique to yeild the desired TiO_x for the smooth and reproducible deposition process with approximately Lambertian cloud.*

All of our work has been done by using an E-gun to evaporate titania. Pulker et al.[2]. used both tungsten and tantalum resistance boats as well as an E-gun to evaporate titania. They found that the tungsten boats were attacked by the titania, particularly the TiO_x forms with the higher oxygen content. The films contained ~20 weight % of WO_3 depending on the number of layers of TiO_2 evaporation. The tungsten oxide lowers the index of the films somewhat. They recommend E-guns or tantalum boats instead. It appears from their data and comments that the tantalum boat is not attacked as severely, there is less weight % of its oxide in the films, and the tantalum oxides do not lower the index as much as tungsten. If boats were to be used, it appears from Pulker's results that the boats should be tantalum, and the starting material should be Ti_2O_3 or Ti_3O_5. It is interesting to note, however, that the current Balzers data[6] shows only tungsten boats and E-guns for any of the oxides of titanium.

There are vendors in today's market who can provide Ti_3O_5[5] and Ti_2O_3 (1.67 and 1.5 material) to support the concept pointed to by the work of Pulker et al.[2], Chiao et al.[4], and Ogura[5] wherein no significant change occurs from layer to layer. This material had been quite a bit more expensive than other forms of titanium oxide, but now (2015) seems to be available at a smaller premium. We also think that there may be some small risk of instability if a different background pressure were used (in IAD, for example); under which circumstance a different atomic ratio might be the more stable value. For this reason, we prefer to use the least expensive uncontaminated material available and "melt it in" as described above.

The resulting index of refraction and freedom from absorption is a significant function of the background pressure of oxygen and temperature as shown by Pulker et al[2]. Higher temperatures for the substrates give higher index, for example, 2.63 at 500 nm for 400ºC. However, higher temperatures are usually less desirable for other reasons and IAD has become a popular way to approach the higher indices at lower or even room temperature. It is usually necessary to provide enough O_2 to avoid absorption which reduces transmittance, but it may also be necessary to reduce absorption to increase the laser damage threshold.

Starting from the Ti metal in Pulker's report gives a significantly different index (2.41) from the 2.205 that the various oxides converge upon with increasing numbers of depositions from the same material charge. Pulker et al.[2] allude to this being a case where the Ti deposits in a dense layer with a crystal structure which then oxidizes to the rutile crystal form of TiO_2. Bulk rutile is the most dense form of titania. All forms tend to this stable phase when heated above about 400°C. At low deposition temperatures without energetic processes like sputtering or IAD, the oxide starting materials tend to give amorphous phases and/or the anatase crystalline form as the temperature is increased. These are lower index in the bulk form than rutile, and thin films may be lower still due to packing density per the Thornton Zones 1 and T described above. Jang et al.[7] studied E-beam evaporated TiO_2 with various oxygen flow rates for crystalline structure changes, and they analyzed the films with various new tools such as atomic force microscopy (AFM). At a constant deposition temperature of 250°C, they concluded that increased oxygen flow rate increased the rutile content versus the anatase.

There have been interesting applications made of the chemically active properties of titania. There have been many studies of the use of TiO_2 as a photocatalyst to treat air, water, etc., through the photolysis of organics and toxic gases[8-10]. Street light glazing, etc., have been coated with TiO_2 to breakdown organic road and smog deposits. The concept is that UV light activates the photocatalytic action of TiO_2 to break down organic deposits which then evaporate or wash away. The action is also proported[11-13] to make the surfaces "superhydrophilic" so that water droplets lie very flat on the surface with near zero contact angles. The combination of these effects is highly desirable for automotive mirrors, windows, and also architectural glazing. There are ongoing discussions of the relative potency of the various crystalline phases of TiO_2 with respect to these effects. Anatase seems to be the most effective, it has been said that it is exclusively so. However, others have reported that both anatase and rutile are needed for maximum effect. The production of a specific phase is a function of substrate temperature or other energy added to the deposition (such as IAD), etc.[14,15]. Chen et al.[16] concluded that rutile formation in a coating was enhanced by substrates with an Al_2O_3 content, while it was reduced by a Na2O content. The determination of which phases exist in a coating are best done by Raman spectroscopy, X-ray diffraction (XDS), and IR analysis[17-20]. Such coatings are found on the external rear-view mirrors of some production automobiles.

Pulker's Results

Before we deal with the use of IAD for TiO_2, let us first examine the valuable results provided by Pulker et al.[2]. We have taken the data published there and applied the tools of the Design of Experiments (DOE) field to develop the equation below and the graphics of **Figure 3** of how the index of TiO_2 might be expected to vary with oxygen pressure, substrate temperature, and deposition rate. We took the data from the Pulker et al.[2] Tables I and II and performed a least squares fit to first and second order equations for a plane. The second order effects were found to be negligible to within the experimental error. **Figure 3** shows the index of refraction from their data as a function of temperature and pressure. It can be seen that the highest index occurs at the highest temperature and lowest pressure and that there are fairly linear relationships of the variables.

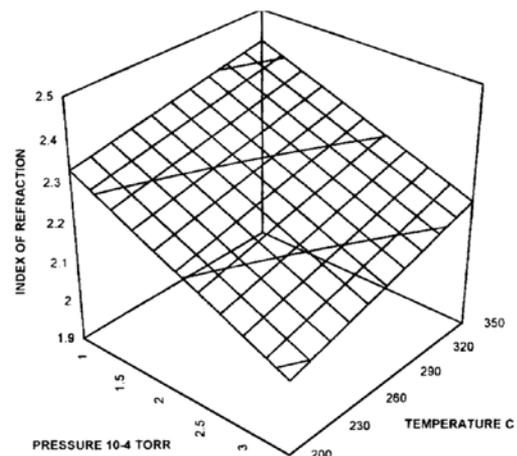$$n_t = 2.28 - .119P + .518 \times 10^{-3}T + .11 \times 10^{-3}PT + .0107R$$

Figure 3. *The index of refraction as a function of temperature and pressure from the data of Pulker et al.[2].*

Using the equation, we can predict what the index of refraction at 530 nm will be as a function of pressure, temperature, and rate. The pressure (P) is entered in units of 10^{-4} torr, the temperature (T) in degrees Celsius, and the rate (R) in Å/second.

Now that we have seen the way that the index of TiO_2 can vary with deposition conditions, it becomes easy to imagine why some practitioners have been less than enthusiastic about index stability of the material. From the partial derivatives of the equation, it can be seen that a 0.01 variation in the index of TiO_2 would result from a change of any of the following deposition parameters: 0.1×10^{-4} torr of oxygen pressure, $17°C$ in substrate temperature, or 1Å/second of deposition rate. The pressure seems to be the most sensitive and may be the most difficult to maintain. The material would have to be well outgassed so that no pressure bursts occur. It would also be desirable to be sure that some makeup oxygen was needed to achieve the desired background (such as 1×10^{-4} torr) so that a steady pressure could be maintained by a gas pressure controller. Melt conditions in the crucible would need to be fairly steady to keep the rate constant also. These conditions can be achieved with today's technology and some care and understanding. We therefore have found TiO_2 to be our preferred high index material in the visible and near IR spectrum.

The use of IAD with TiO_2 can generally give the same benefits as with SiO_2 such as reduced/eliminated humidity shift, higher density, etc. Some time ago, we developed a TiO_2/SiO_2 process using Argon IAD by a Kaufman gridded ion source with an oxygen background in the chamber. We were able to get rid of the humidity shift in a laser blocking filter with very tight edge requirements. We found that the SiO_2 (evaporated from an E-gun) could accommodate 600 eV bombardment without ill effects. However, the TiO_2 would have absorption if the ions (from the Kaufman gridded ion source) were at much more than 200 eV. We used 600 eV for the silica layers and 200 eV for the titania layers. It was found that the silica layer after a titania layer could only use 200 eV for about the first 1/10th of the layer or there would be absorption. Our interpretation of this was that the higher energy (600 eV) ions would cause absorption producing damage to the titania and even penetrate some layer thickness of silica before the SiO_2 was thick enough to protect the TiO_2. We concluded that IAD for TiO_2 should be in the 200 eV range from a gridded source and 333 eV or less from a gridless source where the mean energies are estimated to be about 60% of the drive voltage. This has been consistent with our subsequent experience.

Most of our more recent TiO_2/SiO_2 processes have used 300 eV drive voltage or less as the goal for gridless sources for both types of material. This avoids changing drive voltage with each layer, and it has been found satisfactory for both types of material. The drive voltage is then chosen as high as the TiO_2 would allow, and the deposition rates of the material can be chosen to be as high as allowed by full densification with no absorption.

Once the TiO_2/SiO_2 process parameters have been optimized for a given chamber with or without IAD, any design for the appropriate spectral region can be adapted to that chamber by proper number of layers and thicknesses. If the process chosen was at an elevated temperature, the influence of different substrates might have to be taken into account. The optimum process with IAD might be done at near ambient temperature, at high deposition rates (1 nm/second), and would normally be one with little or no humidity shift or absorption and scattering. It might also be optimized for the best laser damage threshold. We would expect to use such a TiO_2/SiO_2 process for the 400-2000 nm spectral region and perhaps to 3000 nm or beyond. The materials have good environmental durability and are not expensive or toxic.

From the Literature

An interesting study was reported by Hsu and Lee[21] using single and dual-ion-beam sputtering. Although their processes were relatively slow and mostly used post baking, the study shows various properties and interactions that are useful for insight. Zöller et al.[22] reported using their APS (IAD) system and a starting material of Ti_2O_3 to produce "fully" densified films of index 2.38 at 550 nm. The best results were obtained at a discharge voltage between 100 and 130 volts.

Albertinetti and Minden[23] found evidence that diffuse scatter is intrinsic to the TiO_2 coating itself. The scatter sites are granules in the TiO_2 layers. They concluded that the granularity (crystallization) was minimized if the substrates were kept below 85°C. They discuss the crystallization process.

Zöller et al.[24] used an APS system to compare the temperature stability of TiO_2/SiO_2 and Ta_2O_5/SiO_2 filters. They preferred TiO_2/SiO_2.

Chen et al.[16] found that the properties of a BAP800 deposited TiO2 layer depended on the substrates. Al_2O_3 in the substrate enhanced the rutile phase formation in the film, and Na_2O in the substrate retarded the rutile phase formation in the film. The index at 450 nm on fully oxidized films (no absorption) varied from about 2.45 to 2.53, depending on the substrate.

Yamada et al.[25] deposited high-quality TiO_2 films by an oxygen-radical beam-assisted evaporation (RBE) with good success on substrates at 100°C or less. It is interesting that this process imparts no kinetic energy to the growing film, but the ionized oxygen reacts with the depositing Ti metal to produce a dense film of high index (>2.4) and low absorption. This seems to be an accelerated version (because the oxygen is ionized) of the Pulker et al.[2] Ti to TiO_2 with non-ionized background gas which seem to go directly to rutile of index >2.4 at low temperatures. There is a small effect of higher temperature, but most of the densification seems to come from the chemical reaction.

Selhofer et al.[26] extended the work of Pulker et al.[2] some 26 years later. They characterized the various oxides of titanium from the metal to TiO_2 from a molybdenum liner in an e-gun with a controlled oxygen background from 2.25 to 3.0×10^{-4} torr with substrate temperatures of 25° and 250°C. For all cases, the oxygen and deposition rates were chosen for no absorption. At 25°, they got indices at 550 nm from 2.06-2.23, depending on the starting material. They recommended Ti_3O_5 as the best for unheated substrates. At 250°, the spread in index was smaller at 2.395 to 2.405, independent of the starting material. They found the eraser-rub hardness to be good for all indices >2.21, but decreased rapidly for lower indices (densities). The stresses can be near neutral for room temperature substrates, but is highly tensile at 250°C.

Tachibana et al.[27] improved the sputter deposition rate of TiO_2 by 8 times for large area coatings by the use of TiO_{2-X} targets rather

than the metal targets.

Vergöhl et al.[28] deposited TiO_2 by reactive High Power Impulse Magnetron Sputtering (HiPIMS) by the use of a linear double magnetron from metal targets.

Szeghalmi et al.[29] used ALD for titania and alumina multilayer and AR coatings. They reported that the TiO_2 refractive index at 633nm increased from 2.1 to 2.5 with increasing substrate temperature from 80 to 200 °C. TEM micrographs show that the film is amorphous when deposited at 120 °C. At higher temperature (>165 °C), the anatase phase is formed, and one can observe a relative increase of the refractive index for the films deposited around 150–200 °C compared with the 120 °C deposition.

Kääriäinen, et al.[30] investigated TiO_2 films deposited by ALD with respect to their structure and its effect on their photo-activity and photocatalytic properties.

Horáková et al.[31] also studied the photocatalytic activity of TiO_2, but in this case using PECVD.

Chen et al.[32] studied the effect of annealing on stress and optical properties of TiO_2 films deposited by e-beam with IAD, DIBS, and magnetron sputtering. They found that the e-beam films, which were the least dense of the three methods, would go from amorphous films to anatase when annealed at 300°C but not at 250°C. The DIBS films did not change with annealing up to 300°C, but remained amorphous.

Conclusions

Titanium dioxide is widely used as a high index material in the visible and near infrared spectrum and its earlier perceived instabilities can be overcome by better process control. Pressure, temperature, and deposition rate are the primary parameters to be tightly controlled in order to give reproducible results, particularly pressure.

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About the Author Ron Willey

Ron Willey graduated from the MIT in optical instrumentation, has an M.S. from Florida Institute of Technology, and over 40 years of experience in optical system and coating development and production. His current activities are primarily teaching courses and consulting. He is very experienced in practical thin films design, process development, and the application of industrial Design Of Experiments methodology. He is the inventor of a robust plasma/ion source for optical coating applications. He worked in optical instrument development and production at Perkin-Elmer, Block Associates, United Aircraft, Martin Marietta, Opto Mechanik, Hughes, and formed Willey Corporation which serves a wide variety of clients with consulting, development, prototypes, and production. He has published many papers on optical coating design and production. His recent books are "Practical Design of Optical Thin Films", 4th Ed. (2014) and "Practical Production of Optical Thin Films," 3rd Ed. (2015). He is a fellow of the Optical Society of America and SPIE and a past Director of the Society of Vacuum Coaters.
For further information, contact Ron Willey, at ron@willeyoptical.com.