

Achieving Stable Results with Titanium Dioxide

R.R. Willey, Lexalight International Corporation, Charlevoix-the-Beautiful, MI

Keywords: TiO₂; Optical thin films; Ion assisted deposition
Index of refraction; Optical properties

ABSTRACT

Titanium dioxide has been a favored high index material by some, but it appears to be less popular with others because of difficulties in obtaining a stable result. We discuss what we think is the root of the problem and how it may be rectified. The need to have negligible absorption places a lower limit on the background oxygen pressure and some constraints on temperature and deposition rate. Our interpretation of reported results and our own experience is that the material being evaporated reaches an equilibrium with the background oxygen in the chamber after some period of being melted. The oxygen rich material is releasing excess oxygen until it comes to equilibrium, while the oxygen poor material must take up oxygen from the background to reach equilibrium. As a result, our philosophy and practice has been to achieve the most stable process practical by the techniques and material choices which we use in "melting-in" starting material. An equation derived from our experience and others' is given for the index of refraction of titania as a function of background oxygen pressure, temperature, and deposition rate without ion-assisted deposition (IAD). The effects of IAD are also discussed.

INTRODUCTION

Titanium dioxide (TiO₂) has been our favored high index material for the visible and near infrared spectrum because of its high index and relative robustness. It appears historically to be less popular with some practitioners because of difficulties in obtaining a stable result. We believe the root of the problem can be seen in the extensive work of Pulker et al.¹. They started with various materials including TiO₂, Ti₃O₅, Ti₂O₃, TiO, and pure Ti. 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 2.21 at about 550 nm. However, the first layer of 2.0 material gave an index of about 2.06 followed by layers of nearly 2.21 index. The 1.5 material gave an index of 2.27 for the first layer and then settled in to nearly 2.21 for subsequent layers. The 1.00 material, on the other hand, required several layers to drop from an index of 2.38 toward 2.21. All of their results were stated to be free from absorption. One criteria from almost any TiO₂ 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.

A PREPARATION PROCEDURE

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 TiO₂ (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. It can be seen that this latter process is slower as evidenced by the data of Pulker et al.¹ where it takes many layers for TiO to approach a stable index. As a result, our philosophy and practice has been to attempt to achieve the most stable process practical by melting in new tablets of TiO₂ starting material in an E-gun under its shutter with the background pressure of oxygen which is to be used during the actual process. 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 5×10⁻⁴ torr). The molten material in the crucible (usually with a molybdenum liner to reduce heat loss) is kept at a temperature where little material is actually evaporating, but gas is being driven off, as evidenced by the chamber pressure gage. 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 TiO₂.

All of our work has been done by using an E-gun to evaporate titania. Pulker et al.¹ 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 and the films contained up to 70 weight % of WO₃ after many layers of TiO₂ 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. It is interesting to note, however, that the current Balzers data² shows only tungsten boats and E-guns for any of the oxides of titanium.

There are vendors in today's market who can provide Ti₃O₅ (1.67 material) to support the concept pointed to by the work of Pulker et al.¹ wherein no change occurs from layer to layer. This material has been quite a bit more expensive than other forms of titanium oxide, however. We also think that there may be some small risk of instability if a different background pressure were used; 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.

Another approach (which we do not agree with) was taken some years ago by engineers at Leybold Heraeus. They made a 19-pocket E-gun. At the beginning of each run they placed one or two pellets of new material into each pocket. Each new layer used another pocket with fresh material. In our view, the stability of this is like trying to balance on a tight-rope as opposed to standing flat on the floor (with the 1.67 material)!

PREDICTING THE INDEX OF REFRACTION

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.¹. Higher temperatures for the substrates give higher index, for example, 2.63 at 500 nm for 400°C. However, higher temperatures are usually less desirable for other reasons and IAD has become a popular way to approach the higher indices at low or even room temperature. It is usually necessary to provide enough O₂ to avoid absorption which reduces transmittance, but it may also be necessary to reduce absorption to increase the laser damage threshold (LDT).

Before we deal with the use of IAD for TiO₂, let us first examine the valuable results provided by Pulker et al.¹. We have taken the data published there and applied the tools of the Design of Experiments (DOE) field described by Schmidt and Launsby³ to develop a formula and graphics of how the index of TiO₂ might be expected to vary with oxygen pressure, substrate temperature, and deposition rate. We took the data from Pulker's 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 1 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. Figure 2 is an interaction plot of the same surface where we have added the raw data points from Pulker et al.¹ The fit can be seen to be reasonable where the standard deviation shown in Table 1 is .0116 index units.

Table 1 is the DOE data input and results from which Eqn. 1 for the index of refraction of the titania film (n_t) was derived. Using Eqn. 1, 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.

$$n_t = 2.275 - .1193P + .5177 \times 10^{-3}T + .1098 \times 10^{-3}PT + .01067R \quad (1)$$

The data from Pulker et al.¹ in Tables I and II are not consistent with the data in their Table III for the index of refraction as a function of deposition rate. We have derived the slope of the rate portion of the equation from Table III, but the offset has been determined from the data in Tables I and II. It is not clear as to the source of the inconsistency of Table III; perhaps there is a typographic error in the temperature or pressure conditions reported by Pulker et al.¹ for that set of experiments.

Now that we have seen the way that the index of TiO₂ can vary with deposition conditions, it becomes easy to imagine why some practitioners have been less than enthusiastic about the material. From the partial derivatives of Eqn. 1, it can be seen that a 0.01 variation in the index of TiO₂ 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 1 Å/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 TiO₂ to be our preferred high index material in the visible and near IR spectrum.

ION ASSISTED DEPOSITION

The use of IAD with TiO₂ can generally give benefits such as reduced/eliminated humidity shift, higher density, etc. Some time ago, we developed a TiO₂/SiO₂ 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 blocker with very tight edge requirements. We found that the SiO₂ (evaporated from an E-gun) could accommodate 600 eV bombardment without ill effects. However, the TiO₂ would have absorption if the ions 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 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 en-

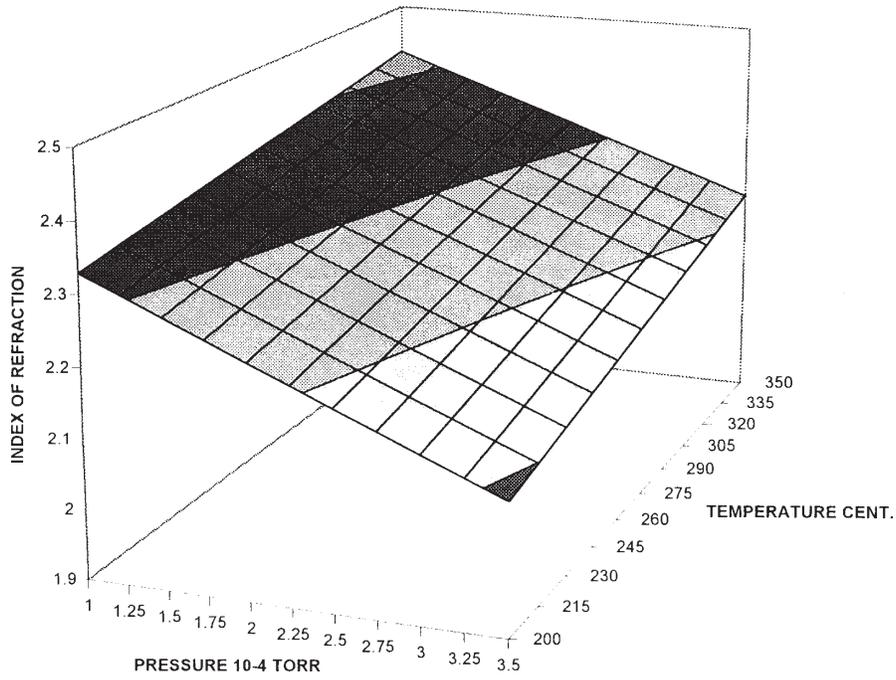


Fig. 1. Index surface plot versus temperature and pressure.

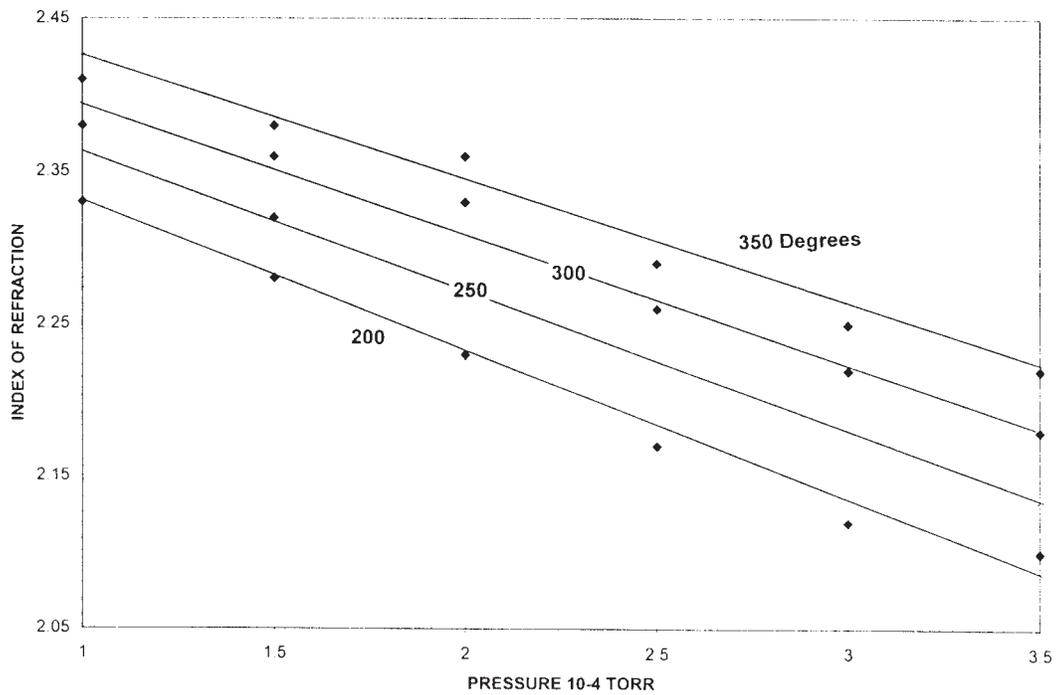


Fig. 2. Index interaction plot versus temperature and pressure.