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Thermal properties of TiO2 films fabricated by atomic layer deposition

Muhammad Rizwan Saleem¹, ², Seppo Honkanen¹ and Jari Turunen¹
¹University of Eastern Finland, Institute of Photonics, P.O. Box 111, FI-80101, Joensuu, Finland
²National University of Sciences and Technology (NUST), School of Chemical and Materials Engineering (SCME), Sector H-12, Islamabad, Pakistan

Abstract. Thin, amorphous, high index, dense, low scattering & absorption (low extinction coefficient) and optical grade TiO2 films of various thicknesses are prepared by Atomic layer deposition (ALD) technique and investigated in terms of thermo-optic coefficient \( (dn/dT) \) and temperature dependent density \( (d\rho/dT) \). The \( dn/dT \) and \( d\rho/dT \) are calculated by modeling ellipsometric experimental data by developing appropriate optical model such as Cauchy Model. The modeled data was further modeled with Lorentz-Lorenz relation under least-square approach. The \( dn/dT \) of TiO2 films shows negative values for thin and positive values for relatively thicker films and reveals no significant changes in \( dn/dT \) and \( d\rho/dT \) when film thickness increases more than ~ 200 nm. The coefficient values are calculated for a wavelength range of 380–1800 nm. The average values of \( (dn/dT)_{60\,\text{nm}} = -4.2 \pm 0.7 \times 10^{-5}\,\text{C}^{-1} \) and \( (d\rho/dT)_{60\,\text{nm}} = -6.6 \pm 1.1 \times 10^{-5}\,\text{gcm}^{-3}\,\text{C}^{-1} \) at wavelength of 640 nm. The reported coefficients values are measured and calculated for TiO2 film of thickness \( t = 60 \text{ nm} \) and described in detail.

1. Introduction
Thin amorphous TiO2 films are studied increasingly for sub-wavelength optical structures due to their high index of refraction, and transparency within a broad wavelength region [1–3]. Various techniques such as vacuum evaporation and sputtering have been investigated for the deposition of TiO2 coatings [4]. The use of Atomic Layer Deposition (ALD) shows promise for low cost and large scale production of thin, high index, dense and amorphous TiO2 films with high optical quality. These ALD films can be uniformly fabricated on non-flat surfaces having 3D nanoscale structures, with a guided mode resonance filter as an application example [5]. ALD is a unique thin film deposition method based on saturative surface reactions of alternatively supplied precursor vapors [6]. Due to saturative nature of each reaction step, the film growth is self-limiting, provided several practical advantages compared to other deposition techniques: atomic level control of film composition and thickness, uniform coverage of corrugated surface profiles, and large area uniformity.

The refractive index of TiO2 films deposited by different techniques has been investigated and is found to correlate well with the density of the material [7]. Importantly, the films prepared by the same technique but under different growth conditions exhibit different density and refractive index due to phase changes in their microstructure [8,9]. The density of the deposited TiO2 films is approximately directly proportional to the corresponding mechanical properties (Young’s modulus) [10] and refractive index [11]. For amorphous TiO2 films the density changes at different temperatures are not caused by the material undergoing a phase change. These density changes are attributed to the
varying concentration of hydrogen containing species (H$_2$O, OH etc.) which adsorb in the voids or residual oxygen vacancies formed during the growth of the films [7,12]. The temperature dependent refractive index of TiO$_2$ films deposited by different techniques shows a negative thermo-optic coefficient (dn/dT), i.e., the value of refractive index decreases as temperature increases [13]. The microstructure of TiO$_2$ thin films depend on the deposition technique and the nature of the substrate. The film properties show variations in film density (porosity), mechanical properties, refractive index, extinction coefficient etc. For example, dn/dT of TiO$_2$ films deposited by plasma enhanced chemical vapor deposition [14], deposition by electron beam evaporation [15] exhibit different magnitudes due to the nature of the deposition method being employed.

In this paper we report on thermo-optic and temperature dependent density coefficients of ALD coated TiO$_2$ films. We fabricated optical grade amorphous TiO$_2$ films with different thicknesses under the same growth conditions and measured their temperature dependent refractive index and extinction coefficients. The dn/dT values are evaluated from measured experimental results by modeling with Cauchy model and Lorentz-Lorenz relation for wavelengths 380–1800 nm with a least-square approach. These values are further used to calculate the density of TiO$_2$ films and corresponding temperature dependent density changes using Lorentz-Lorenz relation. Theoretical calculations of the electronic polarizability at different temperatures are also carried out.

![Designed optical-model for Wvase software analysis of TiO$_2$ films with layered structure](image)

**Figure 1.** Designed optical-model for Wvase software analysis of TiO$_2$ films with layered structure

### 2. Theory

Spectroscopic ellipsometry measurements are represented in terms of ellipsometric parameters $\Psi$ and $\Delta$ and related to optical constants of TiO$_2$ film, shown in Eqs. (1–4). The refractive index data of TiO$_2$ films is modeled by Wvase32 software by considering layered structure as shown in figure 1. The incident light comes from a residual medium air (layer 0) at an incident angle $\phi_{0,i}$ and reflected from air-film interface, the part of light transmitted through the film (layer 1) is further reflected from film-substrate medium. The refractive indices of air and film materials are $n_0$ and $n$, respectively.

$$\rho = \tan \psi e^{i \Delta} = \frac{\widetilde{R}_p}{\widetilde{R}_s}$$

(1)

where $\widetilde{R}_p$ and $\widetilde{R}_s$ are p and s polarized pseudo-Fresnel reflection coefficients given as:
\[ \frac{\bar{R}_p}{1} = \frac{\bar{r}_{01,p} + \bar{r}_{12,p} e^{-12\beta}}{1 + \bar{r}_{01,p} \bar{r}_{12,p} e^{-12\beta}} \]  
(2)

\[ \frac{\bar{R}_s}{1} = \frac{\bar{r}_{01,s} + \bar{r}_{12,s} e^{-12\beta}}{1 + \bar{r}_{01,s} \bar{r}_{12,s} e^{-12\beta}} \]  
(3)

where \( \bar{r}_{01,p}, \bar{r}_{12,p} \) and \( \bar{r}_{01,s}, \bar{r}_{12,s} \) are the Fresnel reflection coefficients from air-film and film-substrate interfaces for p- and s-polarized lights, respectively and \( \beta \) is the optical thickness (phase thickness), given as [16]:

\[ \beta = 2\pi \frac{t}{\lambda} \sqrt{n_0^2 - n^2 \sin^2 \phi_{0,j}} \]  
(4)

3. Experimental methods and data modeling

3.1. Experiments

Amorphous TiO<sub>2</sub> films of thicknesses 60, 100, 200, 300, 400, and 500 nm are coated on Si-wafers with \(<100>\) orientation by Boneq TFS 500 ALD reactor at a deposition temperature of 120 °C with commonly known TiCl<sub>4</sub> and H<sub>2</sub>O precursor materials [17]. The film growth rate per ALD cycle was also monitored by measuring the thickness and refractive index with ellipsometer PLASMOS SD 2300, Philips Analytical Technology GmbH. The optical constants of the films were measured by a variable angle spectroscopic ellipsometer VASE manufactured by J. A. Woollam C. The thermal dependence of refractive index of the films is measured by a home made heating assembly directly attached with ellipsometer. The ellipsometry reflectance spectra was measured at incident angles 65° and 75° with normal to the stage in wavelength range 380–1800 nm with an interval of 20 nm with a beam spot size of 3 mm. The samples were placed firmly on an aluminum hot plate where the temperature was controlled and monitored carefully. The surface temperature of the samples was measured with Convir ST8811 Handheld Infrared Thermometer by Calex Electronics Limited Company with an accuracy of ± 2 °C. The heating rate was 0.5 °C / min with accuracy of ± 0.1 during each measurement interval. The specular and diffused reflectances are measured with PerkinElmer LAMBDA 1050 Spectrophotometer by scanning the wavelength with steps of 1 nm in the visible wavelength range.

**Figure 2.** Ellipsometric experimental data of TiO<sub>2</sub> film with thickness \( t = 60 \) nm and Cauchy Model fitting. (a) \( \Psi \) values and wavelength \( \lambda \). (b) \( \Delta \) values and wavelength \( \lambda \).
3.2. Data modeling

The optical constants are obtained by fitting the ellipsometry measured data of $\Psi$ and $\Delta$ with Cauchy model using Wvase 32 software at particular film thickness as shown in figure 2. The refractive index data is measured at incidence angles of 65° and 75° under isotropic depolarization conditions. The refractive index data of dielectric amorphous TiO$_2$ films obtained from Cauchy model is further modeled by Lorentz-Lorenz relation [18], owing to evaluate $dn/dT$ and density via the relation.

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \alpha_e \rho N_A \frac{n}{m}$$  \hspace{1cm} (5)

where $n$ is the refractive index of TiO$_2$ films at room temperature, $\alpha_e$ is the electronic polarizability at optical frequencies in (cm$^3$), $\rho$ is density in (g/cm$^3$), $N_A$ is Avogadro number $6.023 \times 10^{23}$ (electrons mol$^{-1}$) and $m$ is the molecular weight 79.9 (g mol$^{-1}$). The electronic polarizabilities of Ti$^{4+}$, O$^{-2}$ and TiO$_2$ molecule are $0.19 \times 10^{-24}$, $2.4 \times 10^{-24}$ and $5 \times 10^{-24}$ cm$^3$, respectively [16]. The electronic polarizability connects dipole moment $\mathbf{p}$ to applied field $\mathbf{E}$ by the relation [19].

$$\mathbf{p} = \alpha_e \mathbf{E}$$  \hspace{1cm} (6)

Eq. (6) is commonly used for non-polar molecules at high frequencies so that permanent dipole moments do not follow the electric field. The $\alpha_e$ in Eq. (5) is assumed a scalar polarizability (isotropic case) due to insignificant difference in the scattered light in various directions.

3.2.1. Index data

To modal the thermal properties of refractive index of TiO$_2$ films, reciprocal of left hand side of Eq. (5) is calculated from temperatures 25 to 155 °C with interval of 5 °C and wavelengths 380 to 1800 nm for all TiO$_2$ films thicknesses. All data points follow a parabolic curve after plotting the function $(n^2 + 2)/(n^2 - 1)$ against temperature $T$ as shown in figure 3. The calculated data points at 640 nm wavelength are fitted with least square approach with a characteristic average $dn/dT= -4.2 \pm 0.7 \times 10^{-5}$ °C, as calculated from Eq. (8).

$$\frac{n^2 + 2}{n^2 - 1} = 5.8 \times 10^{-8}(T)^2 + 1.8 \times 10^{-5}T + 1.6$$  \hspace{1cm} (7)

Differentiation of Eq. (7) with respect to $T$ gives

$$\frac{dn}{dT} = \frac{-1}{6} \frac{(n^2 - 1)^2}{n} [11.6 \times 10^{-8}(T) + 1.8 \times 10^{-5}]$$  \hspace{1cm} (8)

Here, $n$ is expressed as a function of temperature $T$ and wavelength $\lambda$. The $dn/dT$ value is evaluated at each wavelength for TiO$_2$ film thickness and is repeated for other film thicknesses, similarly.

![Figure 3. Ellipsometric measured experimentally fitted data of ALD-TiO$_2$ film with thickness $t = 60$ nm: (a) index variation with temperature, (b) density variation with temperature.](image)
3.2.2. Density data

It is extensively reported that refractive index is approximately proportional to density of TiO$_2$ films [20]. From Eq. (5), we calculated the density $\rho(T)$ of TiO$_2$ films by using index values as a function of temperature. The density values are plotted as a function of temperature in figure 3b, which again shows a parabolic plot after fitting the data points with a fit Eq. (9), an average value of $d\rho/dT = -6.6 \pm 1.1 \times 10^{-5}$ g cm$^{-3}$ K$^{-1}$is computed directly from Eq. (10).

$$\rho = -1.4 \times 10^{-3} (T)^2 - 4.1 \times 10^{-5} T + 3.8$$  \hspace{1cm} (9)

Differentiation of Eq. (9) with respect to $T$ evaluates the value of $d\rho/dT$ term.

$$\frac{d\rho}{dT} = -2.8 \times 10^{-7} (T) - 4.1 \times 10^{-5}$$  \hspace{1cm} (10)

To compute the values of $d\alpha_e/dT$, differentiate Eq. (5) with $T$

$$\frac{dn}{dT} = \frac{2\pi N_e (n^2 + 2)^2}{9 m n} \left[ \alpha_e \frac{d\rho}{dT} + \rho \frac{d\alpha_e}{dT} \right]$$  \hspace{1cm} (11)

use of thermal coefficients $dn/dT$ and $d\rho/dT$ from Eqs. (8) and (10), respectively in Eq. (11) to compute the values of $d\alpha_e/dT$, i.e., about $3.84 \times 10^{-31}$ cm$^3$ K$^{-1}$ which in turn give an assessment of the temperature dependent electronic polarizabilities of ALD coated TiO$_2$ films.

**Table 1.** Measured temperature dependent refractive index $n$, extinction coefficient $k$, and calculated density of ALD-TiO$_2$ film of thickness 60 nm at wavelength 640nm.

| T [°C] | n at 640 nm | K at 640 nm | ρ [g cm$^{-3}$] |
|-------|-------------|-------------|----------------|
| 25    | 2.3705      | 0.001555    | 3.8400         |
| 35    | 2.3702      | 0.001366    | 3.8396         |
| 45    | 2.3698      | 0.001262    | 3.8389         |
| 55    | 2.3695      | 0.001168    | 3.8385         |
| 65    | 2.3691      | 0.001046    | 3.8379         |
| 75    | 2.3686      | 0.000982    | 3.8371         |
| 85    | 2.3684      | 0.000955    | 3.8368         |
| 95    | 2.3681      | 0.000925    | 3.8363         |
| 105   | 2.3670      | 0.000781    | 3.8346         |
| 115   | 2.3672      | 0.000757    | 3.8349         |
| 125   | 2.3665      | 0.000623    | 3.8338         |
| 135   | 2.3664      | 0.000459    | 3.8337         |
| 145   | 2.3653      | 0.000558    | 3.8319         |
| 155   | 2.3650      | 0.000461    | 3.8315         |

3. Results and discussion

Figure 3 shows the refractive index and density of ALD-TiO$_2$ films of thickness $t = 60$ nm at wavelength of 640 nm. It is evident from the curves that refractive index and density of TiO$_2$ films are parabolic functions of temperature. The value of thermo-optic coefficient calculated from Eq. (8) depends on the temperature which gives rise small deviation from the linear behavior with temperature. However, for simplicity (linear dependence), and using a single coefficient value at each wavelength, we approximate the thermo-optic coefficient as the average value. Similar approximations are made to the density of ALD-TiO$_2$ films. Table 1 shows the experimentally measured temperature dependent values of refractive indices, extinction coefficients and calculated density of ALD-TiO$_2$ films. The decrease in index with temperature correspond to an average value of $(dn/dT)_{60nm} = -4.2 \pm 0.7 \times 10^{-5}$ K$^{-1}$ which is about the same order of magnitude reported in (Ref [14]) but an order of magnitude smaller (Ref [15]). This in turn explains the dependence behavior of thermo-optic
coefficient on nature of deposition technique being used. The packing density of TiO₂ films is an important parameter contributing for the index values. More dense films (less porosity) are demonstrated to have low index gradient than high porosity films. This may be attributed to the presence of hydrogenated species in the pores of ALD-TiO₂ films. On heating water vapors desorb from surface with a result of decrease in optical path of TiO₂ films due to replacement of water by air [21]. Since the ALD films are fabricated through a layer by layer deposition process and inherently exhibit high density than other techniques, the value of index gradient is relatively small. Column 4 of Table 1 shows density of ALD-TiO₂ films which are slightly higher than the highest reported values by ion plating method ([10]).

Figure 4. Ellipsometric measured experimental data of temperature dependent refractive index of ALD-TiO₂ films from 25 to 155 °C of thicknesses: (a) 60 nm, (b) 100 nm, (c) 200 nm, (d) 300 nm, (e) 400 nm, (f) 500 nm.

Figure 4 shows the refractive index changes with temperature for TiO₂ films of various thicknesses. It is evident from these dispersion plots that thermal effect on refractive index is very
small for these films in the spectral range of 380 to 1800 nm. However, the thermal effect is significant to some extent for films of fewer thicknesses. It is observed that as the film thickness increases, the negative thermo-optic effect becomes less pronounced that makes index gradient with a positive value.

Figure 5 shows the temperature dependent refractive index, density and electronic polarizability of TiO$_2$ films as a function of wavelength. It depicts that thermal coefficients ($dn/dT$ and $dp/dT$) follow dispersion relation and the values become more stable with the increase in film thickness. The values of this coefficient possessed large negative values for thin films ($< 150$ nm) and tends to attain a decrease in negative $dn/dT$ values as the film thickness increases at intermediate ranges and becomes positive for relatively thicker films ($> 200$ nm). It is also found that the values of temperature dependent electronic polarizability are so small to contribute significantly to the $dn/dT$. This may be attributed to the fact that thin films ($t = 60$ nm) have pores on its surface being initially filled by hydrogen containing species. The pores become empty on rising temperature that results in a decrease of index due to replacement of water molecules with air. Thereby, the effective refractive index of the material decreases up to a few surface nanometer layers that is scanned by ellipsometry in the form of a change of ellipsometric parameters $\Psi$ and $\Delta$. As the film thickness increases, the proportion of the surface porous area decreases in comparison to the overall thickness of the film and results in a decrease in negative index-gradient that makes $dn/dT$ value to approach towards zero or to have a positive value for relatively thicker films. Figure 6 shows the variation of thermal coefficients ($dn/dT$ and $dp/dT$) with thickness of the films. It is found that the thermal coefficients approach to positive values when thickness increases from 60 nm and after reaching to a certain critical value of ~ 200 nm, the $dn/dT$ remains constant with further increase in film thickness.

Figure 5. Thermal dependence of material properties of TiO$_2$ films of various thicknesses: (a) $dn/dT$, (b) $dp/dT$, (c) $d\alpha_e/dT$.

Figure 6. Variation of thermal properties $dn/dT$ and $dp/dT$ of ALD-TiO$_2$ films with thickness $t$
4. Conclusion
Amorphous, high density, optical grade thin TiO$_2$ films of various thicknesses are coated on silicon substrate by ALD technique. The thermo-optic coefficient and temperature dependent density are calculated for various TiO$_2$ film thicknesses. These coefficients possess negative values for thinner films and tend to attain positive values for relatively thicker films. The measured $dn/dT$ and $d\rho/dT$ are observed to follow the normal dispersion relation. In addition, the values of these coefficients follow parabolic curves that are obtained after fitting with least square approach. The average values of $(dn/dT)_{60\text{nm}} = -4.2 \pm 0.7 \times 10^{-5} \degree\text{C}^{-1}$ and $(d\rho/dT)_{60\text{nm}} = -6.6 \pm 1.1 \times 10^{-5} \text{gcm}^{-3} \degree\text{C}^{-1}$ of ALD-TiO$_2$ film at wavelength 640 nm are presented in detail while calculated over a wide wavelength range from 380–1800 nm.

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