Investigation of Inhomogeneity of TiO$_2$ Thin Films Using Spectroscopic Ellipsometry

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Abstract. Titanium dioxide thin films have been deposited on silicon wafers (100) substrates by pulse DC reactive magnetron sputtering. The spectroscopic ellipsometry is the method used to determine the degree of inhomogeneity of titanium dioxide thin films. The effect of operating pressure on the micro-structural and optical properties of inhomogeneity titanium dioxide thin films were characterized by grazing-incidence X-ray diffraction, spectroscopic ellipsometry, field emission scanning electron microscopy and high resolution transmission electron microscopy. The optical properties of the films were examined by variable-angle spectroscopic ellipsometer. Several spectroscopic ellipsometry models, categorized by physical models, were proposed based on the ‘simpler better’ rule and curve-fits, which were generated and compared to experimental data using regression analysis. It has been found that the triple-layer physical model with the Cody-Lorentz dispersion model offered the most convincing result. Titanium dioxide thin film was found inhomogeneous and a more detailed analysis of high resolution transmission electron microscopy and field emission scanning electron microscope are discussed.

1. Introduction
The titanium dioxide (TiO$_2$) exists in three different crystalline forms: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic), rutile being the most stable of the three, and the formation of its phase depends on starting material, calcinations temperature and deposition method. There are many techniques were used to compare the optical properties of TiO$_2$ thin films. In case of classical reactive evaporation, the large dispersion of the values for the refractive index and the extinction coefficient is observed, caused by small changes in the process conditions. The influence on the optical properties of the deposition parameters has been studied by several authors in the case of evaporation [1], of DC reactive magnetron sputtering [2], etc. They usually focus at the effects of the deposition parameters, O$_2$ pressure, deposition rate, and substrate temperature [3-7] which influence the packing fraction, the crystallinity and the optical properties of the films. Only few groups are
2. Experiments
The TiO\textsubscript{2} thin films were prepared by pulse DC reactive magnetron sputtering in both high purity argon (99.999%) and oxygen (99.999%) ultra-high vacuum system (AJA International, Inc. ATC 2000-F), using a Titanium (99.995%; KJ. Lesker) target of 2 inch-diameter. The distance between the substrate holder to target was 90 mm, and the incline angle of the gun was 40° with respect to the plane of substrate holder. The base pressure of the deposition chamber was about 1 x 10\textsuperscript{-7} Torr. The operating pressure was selected as a variable parameter. The gas flows of argon and oxygen were set at 10 and 20 sccm, respectively. The discharge was generated with a 400 W pulsed DC power. The silicon wafers (100) substrate were prepared by ultrasonic washer with isopropanol and acetone successively, and dried in nitrogen atmosphere, before loaded into the deposition chamber. Prior to deposition, the substrate was cleaned by Ar plasma ion for 5 minutes to remove surface contamination of the substrate.

Crystal structures of the films were studied using Rigaku TTRAX III grazing-incidence X-ray diffraction (GIXRD). The Cu-K\textalpha\textsubscript{α} radiation was operated at 50 kV, 300 mA with scanning speed of 20 per minute at 20 step of 0.020. The measurements were conducted from 20-60° incident angles. The morphologies of the TiO\textsubscript{2} thin films were investigated using high resolution transmission electron microscopy (HRTEM) experiment performed on a JEM-2010 electron microscope (JEOL) with an acceleration voltage of 200 kV. The optical parameters, i.e. the index of refraction, the extinction coefficient and the film thickness, were calculated from ellipsometric measurements using a variable-angle spectroscopic ellipsometer (VASE, J.A. Woolam). The VASE measurements were done at 70° incident angles, in the photon energy range of 0.75-6 eV, with autoretarder activated.

3. Results and Discussion
3.1. Grazing-incidence X-ray diffraction
It is well known that operating pressure is the main parameters for the formation of different TiO\textsubscript{2} crystal structures. The structural of sputtered 120 nm thick TiO\textsubscript{2} thin films strongly depend on operating pressure (Figure 1). TiO\textsubscript{2} thin films deposited at high operating pressure (OP: 5-7 mTorr) exhibit pure anatase phase (Fig 2(c)). For TiO\textsubscript{2} thin films prepared at low operating pressure of 3 mTorr composed of a mixed anatase-rutile phase. The higher losses of particles energy in collisions causes decrement on the crystallinity of the rutile phase, that it could form at high temperature and activation energy. From the previous study of M. Yamagishi et al. [9], the rutile phase on unheated film at low operating pressure due to the higher energy of the particles impinging on the growing film surface.

![Figure 1 GIXRD pattern of TiO\textsubscript{2} thin films deposited at different operating pressure](image-url)
3.2 Spectroscopic Ellipsometry (SE) Analysis

3.2.1 SE Modelling for Pure Anatase TiO$_2$ Thin Films

In this experiment, we use three physical models in analyzing the ellipsometric data of pure anatase TiO$_2$ thin films prepared at 5 and 7 mTorr. Three fitting models, namely, single-layer model (containing a native oxide and homogeneous layer of TiO$_2$ thin film (Figure 2(a) top), double-layer model (containing a native oxide, TiO$_2$ void free layer and TiO$_2$ with void layer (Figure 2(a) middle) and triple-layer model (containing a native oxide, TiO$_2$ void free layer, TiO$_2$ with void layer and surface roughness (Srough) (Figure 2(a) bottom). An interfacial layer native Si oxide which assumed thickness of 2 nm was included because the Si substrate not etched by HF before film deposition. The optical properties of TiO$_2$ were modeled by a single Cody-Lorentz Oscillator [5, 10-11]. Bruggeman effective medium approximation (BEMA) is used to determine of optical constant of the composition. The proposed physical model corresponding to each film sample was generated based on appropriate generalized oscillator for the optical dispersion, and eventually curve-fitted with the experimental data. The goal is, by a regression algorithm for the ellipsometry equation, to minimize the mean square error function:

$$\text{MSE} = \sqrt{\frac{1}{2N-M} \sum_{i=1}^{N} \left( \frac{\Psi_{i}^{\text{mod}} - \Psi_{i}^{\text{exp}}}{\sigma_{\Psi,i}^{\text{exp}}} \right)^{2} + \left( \frac{\Delta_{i}^{\text{mod}} - \Delta_{i}^{\text{exp}}}{\sigma_{\Delta,i}^{\text{exp}}} \right)^{2}}$$

(1)

$N$ is the number of measured $\Psi$ and $\Delta$ pairs, $M$ is the total number of variable parameters and $\sigma$ is the standard deviations. The ‘mod’ means the theoretical calculation, and the ‘exp’ means the experimentally measured data.

The experimental SE data are plotted in circle symbol, and the solid line is the regression fitting result. In the first attempt, the model of a single homogeneous layer of TiO$_2$ on c-Si substrate was tested. Figure 2(b) shown agreement between the SE data and the fitted data of all TiO$_2$ thin films. It was found that this single-layer and double-layer models were not given a good fit to measured $\Psi$ and $\Delta$ spectra. Obviously, the triple-layer physical model proposed the best curve-fits (low MSE value), confirmed that the TiO$_2$ thin films is far from being homogeneous. The results from these three different models are shown in Table 1. The SE model can be confirmed by cross-section HR-TEM micrograph shown in next section (Figure 3(a)).

3.2.2 SE Modelling for Mixed Phase TiO$_2$ Thin Film

Next is the case of mixture phase (anatase-rutile) TiO$_2$ thin film deposited at 3 mTorr operating pressure on silicon wafer substrate. The best fit of physical model of mixture TiO$_2$ thin film show different structure from previous experiment. These films can be modeled as composed of the native oxide layer, TiO$_2$ with void layer, TiO$_2$ void free layer, and surface roughness (Srough). Figure 2(c) shows the agreement between the experimentally observed $\Psi$ and $\Delta$ spectra. Notice that the order off void free and the voided layer is different from the films prepared at higher operating pressure. The reason of the phenomenon will be discussed in the next section.
Figure 2 (a) Best-fit single layer model (SLM), double layer model (DLM) and triple layer model (TLM) of TiO$_2$ thin film on silicon substrate. (b) Measured and calculated ellipsometric $\Psi$ and $\Delta$ spectra for the TiO$_2$ thin films deposited at operating pressure 5 and 7 mTorr on silicon wafer substrate of Angle of incident 70°. (c) Measured and calculated ellipsometric $\Psi$ and $\Delta$ spectra for the TiO$_2$ thin films deposited at operating pressure 3 mTorr on silicon wafer substrate of Angle of incident 70° (inset figure is best-fit model of mixture TiO$_2$ thin film on silicon substrate)

Table 1 Summary results of the spectroscopic ellisometry characterization from inhomogeneous pure anatase TiO$_2$ thin films.

| Operating Pressure (mTorr) | Dense Layer (nm) | TiO$_2$ with void layer (nm) | Srough layer (nm) | MSE |
|---------------------------|------------------|-----------------------------|-------------------|-----|
|                           | d1               | d2                          | %Void            | d3  | %Void |
| 5                         |                  |                             |                   |     |       |
| SLM                       | 114.2 ± 1.3      | -                           | -                 | -   | -     |
| DLM                       | 102.2 ± 0.3      | -                           | -                 | 11.8 ± 0.2 | 31.9 ± 0.5 |
| TLM                       | 32.7 ± 4.0       | 71.8 ± 4.1                  | 2.9 ± 0.4         | 10.6 ± 0.2 | 35.6 ± 0.9 |
| 7                         |                  |                             |                   |     |       |
| SLM                       | 120.2 ± 2.5      | -                           | -                 | -   | -     |
| DLM                       | 98.7 ± 0.5       | -                           | -                 | 19.0 ± 0.2 | 36.3 ± 0.4 |
| TLM                       | 54.6 ± 1.1       | 46.7 ± 1.2                  | 5.2 ± 0.1         | 18.0 ± 0.1 | 37.9 ± 0.2 |

Table 2 Summary results of the spectroscopic ellisometry characterization from inhomogeneous anatase-rutile TiO$_2$ thin films.

| Operating Pressure (mTorr) | TiO$_2$ with void layer (nm) | Dense Layer (nm) | Srough layer (nm) | MSE |
|---------------------------|-----------------------------|------------------|-------------------|-----|
|                           | $d_1$                       | %Void            | $d_2$             | $d_3$ | %Void |
| 3                         | 23.4 ± 3                    | 7.6 ± 1          | 82.4 ± 3          | 11.2 ± 0.2 | 24.4 ± 0.6 | 8.36 |
3.3 Depth Profiles of Inhomogeneous TiO$_2$ Thin Films

These observed inhomogeneities in the growth direction depend on the plasma conditions. Figure 3(a), shows the depth profiles of the refractive index at 550 nm wavelength for the films deposited on silicon substrate. All films show triples layer with different index properties, due to the difference in films crystallinities. Films deposited at high operating pressure (5 and 7 mTorr) show higher refractive index at the bottom layer than top layer. Films deposited at 3 mTorr show lower refractive index at the bottom layer than top layer. In the case of 3 mTorr, the crystallization at the top layers is increased due to higher energy from substrate temperature which results from deposition condition. At low operating pressure, the high energy gas particles are able to reach the substrate without inter-collision due to the longer mean free path. Higher concentration of the ionized or excited species resulting from the higher electron temperature in the plasma and the higher energy of the particles impinging on the growing film surface leads to the formation of mixture phase and high refractive index at low operating pressure. As an example, HRTEM image (OP 5 mTorr) clearly shows the film microstructure matching with the layers and their thickness in the SE model (Figure 3(a)). From depth profile ellipometric analysis, a dense structure at the bottom of the film was indentified to have higher refractive index from the triple layer model. The middle part of the film that shows a columnar structure has a slightly lower refractive index compared to the dense region at the bottom. On top of the films, a very thin rough layer which its index was calculated from BEMA.

![HRTEM Image of TiO$_2$ Thin Film](image)

**Figure 3** (a) Cross section HRTEM of TiO$_2$ thin film deposited at 5 mTorr (b) Depth profiles of the refractive indices for the sample (OP 3-7 mTorr) at 550 nm wavelength

3.4 Analysis of Inhomogeneous TiO$_2$ Films by Scanning Electron Microscopy

Figure 4 shows the surface morphologies and the cross-sectional structures of three samples. The film prepared at lower operating pressure (OP 3 mTorr) has a more compact structure, the film prepared at higher operating pressure (OP 7 mTorr) has a more porouse structure, and the films prepared at intermediate pressure (OP 5 mTorr) has a mixed compact and porous structure. That is, the film structure changes gradually from compact into porous as the operating pressure increase. We can explain these qualitatively properties by the Thornton structure zone model [11] with HR-TEM.

4. Conclusion

We characterized the inhomogeneous TiO$_2$ thin films by SE. The results were compared with field emission scanning electron microscope (FE-SEM) and high resolution transmission electron microscopy (HRTEM). Three physical models were used in analyzing the ellipsometric data. First, the single-layer model contained only the homogeneous TiO$_2$ layer. Second, the double-layer model has an additional surface roughness on top of the homogeneous layer. Third, the triple-layer model proposed the homogeneous TiO$_2$ layer, TiO$_2$ with void layer and a surface roughness. From the study, the triple-layer model suggested the best fits. In addition, it is confirmed that the TiO$_2$ thin films is far from being homogeneous, when compared with the results from the cross-sectional FE-SEM and HRTEM micrographs.
Figure 4 FE-SEM micrograph of TiO$_2$ thin film eposited at different operating pressure: top view and cross-section.

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