Structural and optical investigation of brookite TiO₂ thin films grown by atomic layer deposition on Si (111) substrates

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HIGHLIGHTS

• TiO₂ thin films with brookite phase successfully deposited on Si(111) using ALD.
• Correlated Structural and optical properties perceived and studied.
• Reduction of refractive index observed for films with ultra-small thicknesses.

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ABSTRACT

In this paper, titanium dioxide (TiO₂) thin films, deposited on single crystal Si (111) substrates under different temperature conditions by Atomic Layer Deposition (ALD), have been systematically studied by X-ray diffraction, photoluminescence spectroscopy and spectroscopic ellipsometry methods. X-ray diffraction analysis showed that the prepared films have a polycrystalline brookite phase over a growth temperature range of (150–300 °C). Increasing the growth temperature resulted in systematic increase of texturing the polycrystalline films along the (200) direction, with the film at 300 °C having the highest textur along the (200) direction. This was accompanied by improved photoluminescence of the TiO₂ films with the increasing growth temperature. The improved crystallinity at higher temperatures was also reflected by higher refractive indices, which were deduced from spectroscopic ellipsometry measurements carried out on the grown films.

1. Introduction

In recent years, Titanium oxide (TiO₂) thin films have been widely used in the field of solar cells [1,2], gas sensors [3] and protective coatings [4,5]. TiO₂ is considered as one of the most promising and suitable photocatalytic materials for energy conversion and environmental remediation due to its excellent properties such as non-toxicity and high surface reactivity [6,7] and chemical stability [8,9]. In addition, TiO₂ thin films have been widely studied for optical applications due to its high transparency and a very small absorption coefficient in the visible range [5,10–13]. For example, in dye-sensitized and perovskite solar cells, a compact thin transparent layer of TiO₂ on the conductive glass is essential to prevent the back transfer of electrons between the conductive glass and the hole transport material [5,11–13]. Therefore, it is important to determine the optical and structural properties of grown TiO₂ thin films such as refractive index, extinction coefficient, film thickness and surface roughness. In addition to that, the surface properties of the grown TiO₂ film can have major impacts on subsequently deposited films [14,15]. In this regard, the structural phase and growth direction must be carefully determined for the grown TiO₂ film. A variety of techniques have been used to deposit ultrathin TiO₂ films so far. These include, suspension coating [16], sputtering [17,18], electrochemical deposition [19], pulsed laser deposition (PLD) [20] and atomic layer deposition (ALD) [21–26]. Among these, atomic layer deposition (ALD) is an advanced chemical vapour deposition technique that is capable of producing high quality thin
films with excellent atomic level control of layer thickness and uniformity.

TiO$_2$ can form in three crystalline phases: rutile, anatase and brookite. While rutile is the most stable phase for bulk TiO$_2$, anatase is more stable for TiO$_2$ nanostructures. In all cases, the TiO$_2$ brookite phase is usually difficult to produce. D-H Kim et al. [27] used plasma enhanced ALD to fabricate brookite TiO$_2$ thin films on (110) yttria-stabilized zirconia (YSZ) substrates. M. Reiners et al. [28] used liquid injection ALD to fabricate TiO$_2$ thin films with mixed anatase/brookite phases. In this work, and for the first time, we show that TiO$_2$ thin films with pure brookite phase can be deposited on Si(111) substrates using conventional ALD technique.

2. Experimental details

In the present work, TiO$_2$ thin films were deposited on Si (111) wafers by atomic layer deposition (ALD) (Beneq TFS 200). The Si wafers were cleaned prior to deposition using ethanol and acetone in an ultrasonic bath for ~30 min. Film deposition was carried out under different temperature of 150 °C, 200 °C, 250 °C, and 300 °C and a base pressure of ~17 mbar. Titanium tetrachloride (TiCl$_4$) and deionized water were used as precursors for the deposition process. The evaporation temperature of TiCl$_4$ was kept at 25 °C while it was 20 °C for deionized water. High purity (99.9999%) nitrogen gas was used as a purging and carrying gas. The flow rates of the carrier gas through TiCl$_4$ and deionized water were kept at 150 and 200 standard cubic centimeters/minute (sccm) respectively, and their pressures were respectively kept at 9 mbar and 8 mbar. For each deposition process, successive purge cycles of reaction precursors (TiCl$_4$ and de-ionized water) were performed, while keeping the Si substrate at the required growth temperature. Each cycle consists of two half-cycles; in the first half, TiCl$_4$ vapour pulse is injected to the reaction chamber by the nitrogen carrier gas until self-terminating reactions occur on the substrate. The non-reacted reactants along with the reaction by-products are purged out from the chamber. In the other half cycle, a pulse of deionized water is brought to the reaction chamber, which chemically reacts with the substrate in a self-terminating manner as well. Dry pulses of nitrogen intervene between TiCl$_4$ and de-ionized water pulses. The pulsing scheme for TiCl$_4$/N$_2$/H$_2$O/N$_2$ gases during one cycle was set with time durations of 0.1s: 3s: 0.1s: 4s. Two sets of samples were prepared. The first set was prepared, using the above-mentioned pulsing scheme, at different growth temperatures of 150 °C, 200 °C, 250 °C and 300 °C using 1000 coating cycles. The second set consists of thin films prepared using the same pulsing scheme at 300 °C but with different thicknesses, which was achieved using different number of coating cycles of 200, 600, 1000 and 1500 cycles.

The structural properties of the grown films were investigated by a Field Emission Scanning Electron Microscope FE-SEM (model: JEOL JSM-7600F) and X-Ray Diffractometer XRD (PANalytical X'pert MPD) in the 2θ mode. CuKα radiation was used in XRD measurements at 45 kV and 40 mA, and the scanning angle was changed between 2θ = 20° - 50° in steps of 0.01°. Spectroscopic ellipsometry measurements (model: WVASE- J. A. Woolam) were carried out to determine the thickness and optical constants in the wavelength range of 500–2500 nm at an angle of incidence of 50°. The optical constant and the thickness of TiO$_2$ thin films deposited on Si(111) substrates were fitted using the Cauchy model. Photoluminescence spectra of the films were carried out with a luminescence spectroscopy system (Perkin-Elmer, LS45).

3. Results and discussion

3.1. Structural properties

Fig. 1 shows a cross-sectional image for a film grown at 300 °C using 600 cycles. As expected, the grown film shows a highly uniform thickness of 25 nm over the Si substrate. To determine the crystal structure and possible phase changes of the films, X-ray analysis was performed. Fig. 2 shows the XRD pattern for the four samples deposited under different temperatures in the range between 150° to 300°. Interestingly, all samples show diffraction peaks that can be well indexed with the crystal structure of the pure brookite phase TiO$_2$ (JCPDS card no. 29-1360). It can be noticed that the film grown at 150 °C is highly untextured where XRD peaks correspond to different lattice planes in the XRD pattern. When the growth temperature is increased from 150 °C to 300 °C, texture along the (200) direction was observed, and it was improved until almost a full texture along (200) direction is achieved for a growth temperature of 300 °C. This texture improvement explains the strong effect of growth temperature on the structural properties of ALD grown films.

The (200) peak was further analyzed in order to estimate the lattice constant (d$_{200}$) in the grown films, which can be estimated using Bragg’s formula:

$$2d_{200}\sin\theta_{200} = \lambda$$  

(1)

and the results are shown in Table 1. For the 150 °C sample, the (200) peak was absent, and estimation of d$_{200}$ value could not be performed. For the other samples, it can be noticed that the (200) peak position systematically shifts from 32.99° to 33.13° when the temperature is increased from 200 °C to 300 °C. This implies a contraction behavior of the crystalline lattice, for which the lattice constant of (200) planes
(d_{2θ}) decreased from 2.713 Å at 200 °C to 2.702 Å at 300 °C. This decrease of lattice constant can be explained by the reduced strain at higher growth temperatures [29].

As mentioned above, the rutile and anatase phases are the most stable for TiO₂. The brookite phase is usually more difficult to produce, with different growth models and assumptions regarding how the brookite phase is formed during the growth. For the hydrothermal solution growth of TiO₂, it has been well established that the presence of sodium (Na⁺) or other alkali ions has a strong effect on driving the crystallization process into the brookite phase, and there have been different reports proving this fact [30]. For thin films, however, the presence of Na⁺ ions is not always available and other growth models have to be proposed. In fact, different thin film deposition techniques were reported to grow brookite TiO₂ films, but in most of them the brookite phase was mixed with rutile/anatase phases. For a pure brookite thin film, D-H Kim et al. reported the epitaxial growth of brookite TiO₂ on yttria-stabilized zirconia (YSZ) substrates by using plasma enhanced ALD. This success is attributed to the small lattice mismatch between YSZ and brookite lattices [27]. Other successful attempts on the epitaxial growth of brookite were also reported using other techniques [31–33]. The question whether non-epitaxial growth of brookite is also possible, which is confirmed by our work for reporting pure brookite films and by many previous articles reporting mixed phases, has been recently studied by J. Haggerty et al. where 95% brookite thin films could be grown on different substrates using pulsed laser deposition (PLD) [34]. Their work confirms a previous report by M. P. Moret et al. who succeeded to grow brookite rich thin films on Si(111) and other substrates using PLD as well [35].

Table 1
Lattice constants of TiO₂ films grown at different growth temperature.

<table>
<thead>
<tr>
<th>Growth Temperature</th>
<th>2θ200 (degrees)</th>
<th>d2θ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 °C</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>200 °C</td>
<td>32.99</td>
<td>2.713</td>
</tr>
<tr>
<td>250 °C</td>
<td>33.07</td>
<td>2.707</td>
</tr>
<tr>
<td>300 °C</td>
<td>33.13</td>
<td>2.702</td>
</tr>
</tbody>
</table>

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3.2. Photoluminescence spectroscopy

Unlike anatase and rutile, brookite has a direct bandgap, and thus emission activity is expected to be higher than anatase and rutile polymorphs because charge carriers do not need additional phonons for the recombination process [36]. Fig. 3 shows fluorescence spectra of brookite TiO₂ thin films deposited at different temperature from 150 to 300 °C, using an excitation wavelength of 370 nm. From the fluorescence spectra, two main emission peaks appear at 408 nm and 421 nm, being equivalent to 3.03 eV and 2.94 eV respectively. Considering the brookite bandgap of 3.14 eV [37,38], both peaks lie in the near-band-edge (NBE) region of the brookite phase. These two NBE emission lines at 408 nm and 421 nm could be assigned respectively to band-to-band transition [37,39] and to shallow defect levels in the bandgap [36,40].

It can be noticed that the intensity of the PL emission at the band edge was highly improved when the growth temperature was increased to 300 °C. In addition to that, a broad defect band started to appear (above 450 nm). The two observations clearly indicate that the radiative channels, both NBE and deep level, in the brookite crystal improved with temperature. This can be attributed to the improvement of crystalline structure with annealing. A similar behavior was also observed by W. F. Zhang et al. [41]. Generally, there are two ways for the relaxation of electrons in the conduction band. The first way is the radiative recombination, either from the band edge or a shallow defect level, to the valence band. The second one is the non-radiative recombination at imperfect lattice points or surface sites. Our results indicate that the radiative recombination channels generally improve when the growth temperature is increased, manifested by improved NBE emission as well as the development of radiative defect emission band at 300 °C.

3.3. Spectroscopic ellipsometry

Spectroscopy ellipsometry is one of the most important characterization optical techniques which is widely used to determine film thickness, refractive index (n), surface and interface roughness of thin films on solid surface. Spectroscopy measurements were carried out using a polarized light with angle of incidence of 50° on the TiO₂ front surface. A three-layer-model was assumed in order to fit the measured ellipsometric constants (Ψ and Δ). Each sample was assumed to consist of Si substrate/a native TiO₂ layer/TiO₂ layer/TiO₂-air mixed layer. The TiO₂-air mixed layer is a virtual optical layer mixed of 50%-50% air and TiO₂, and is proposed to estimate the film roughness. The thickness of the SiO₂ native oxide layer was introduced with a value of 1 nm. The ellipsometry reflection data were collected and fitted, assuming the above-mentioned architecture, using the Cauchy dispersion model [42,43], which is given by:

\[
n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}
\]

where A, B, and C are Cauchy parameters and λ is the wavelength. Further details on the fitting model along with the best fits to the measured ellipsometric constants Ψ and Δ of all deposited films can be found in the Supplementary Materials (Figs. S1–S3). The thickness and the wavelength-dependent refractive index of TiO₂ thin films deposited on Si substrates could subsequently be extracted from the fitted data.

3.3.1. Effect of growth temperature

The estimated spectral variation of the refractive indices for the TiO₂ thin films deposited at different temperatures is shown in Fig. 4. These results are given within the range of wavelength (500–2500 nm) for ellipsometry measurements as a function of growth temperature. As shown in Fig. 4, for each deposited film, the refractive index is almost invariant in the region from ~1000 to 2500 nm. Below ~1000 nm, the
refractive index rapidly decreases with increasing wavelength. Decreasing refractive index with the incident wavelength indicates the normal Cauchy dispersion behavior of the TiO2 thin films. It can be noticed, however, that the refractive index showed a noticeable increase when the growth temperatures increased to 250 °C and 300 °C. This can be explained by the higher crystalline texture of the film at different temperatures. It can also explain the reduced PL at 200 °C in Fig. 3.

Similar results were found by for TiO2 layers using the atomic layer deposition [44] and by other deposition techniques as well [45,46].

Fig. 5 shows the film thickness as well as the roughness (thickness of the virtual layer) data for deposited films. The film thickness for all films has an average value of 42.75 ± 0.98 nm, which corresponds to a growth rate of 0.43 Å per cycle. The small roughness of ~1 nm in all samples indicates the high level of control offered by ALD over a wide range of growth temperatures. It can be noticed that at 200 °C, the film thickness was noticeably smaller (38.7 nm). It has been reported by other works [47,48] that at a growth temperature of ~200 °C anomalous behaviors and phase transitions occur for TiO2 grown by ALD. In this work, this effect was greatly eliminated, and only manifested by a small decrease in the overall thickness. The smaller thickness at 200 °C can also explain the reduced PL at 200 °C in Fig. 3.

3.3.2. Effect of ALD cycles

The second set of samples were deposited at a growth temperature of 300 °C using 200, 600, 1000 and 1500 cycles. The accuracy of our ellipsometry analysis can be remarked by the agreement of estimated film thickness at 600 cycles of 24.8 nm with the FE-SEM image in Fig. 1.

Fig. 6 shows the film thickness and roughness results as a function of the completed number of coating cycles. We observe the expected linear relation between thickness and number of cycles indicating homogeneous growth and linearity effect of the number of cycles on the film thickness. A linear fitting yields a growth rate of 0.44 Å/cycle of the film. Compared to the average growth rate estimated above for samples prepared under different temperatures of 0.43 Å/cycle, it can be concluded that the estimation of film thickness is highly robust and negligibly dependent on the growth temperature. The film roughness is also shown in Fig. 6. Evidently, a systematic increase in the film roughness is observed with increasing the thickness (notice that the roughness at 200 cycles was too small to be detected) until it begins to saturate, at ~5–6 nm, above 1000 cycles.

Fig. 7 shows the refractive index of thin films deposited at different coating cycles. It can be noticed that at small number of cycles, the refractive index undergoes a noticeable decrease over the whole wavelength range, in agreement with others’ works [49,50]. ALD prepared thin films with ultra-small thicknesses were previously reported to show quantum confinement effects [49]. As can be seen in Fig. 6, at 200 cycles, the deposited film has a thickness of ~8 nm, which is within the quantum confinement limit in semiconducting materials including TiO2 (1–10 nm) [51]. Therefore, it is likely to observe the quantum size effect in TiO2 thin films prepared by ALD in similar range of film thickness. However, this conclusion is difficult to be confirmed with the available data especially that the Cauchy model gives no information about the position of the band edge. The sharp decrease in the refractive index can also be correlated to retarded crystallization at very thin layers. At thicknesses below the crystallization threshold, the TiO2 film can be fully amorphous, resulting in TiO2 films with lower density and lower refractive index. Additional analysis is still required to undoubtedly explain the reduced refractive index of ultra-thin TiO2 films.
4. Conclusion

In conclusion, TiO2 films were deposited on Si (111) substrates using ALD technique over deposition temperatures range of 150 °C–300 °C. Purity of the brookite phase in all studied samples has been confirmed with XRD measurements. Spectroscopic ellipsometry measurements for these TiO2 thin films were fitted using the Cauchy model. The refractive index increases with increasing the growth temperature, and a noticeable reduction in the refractive index is observed for ultrathin deposited films using 200–600 coating cycles. PL emission studies showed two peaks in the NBE region, and the emission activity was shown to increase with the growth temperature.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matchemphys.2018.12.067.

References


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