The Effect of Geometric Structure on Photoluminescence Characteristics of 1-D TiO₂ Nanotubes and 2-D TiO₂ Films Fabricated by Atomic Layer Deposition

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Due to their unique physical and chemical properties, nanostructured materials have attracted considerable number of interests in recent years. Among them, TiO₂ nanostructures have become one of the most promising materials for the application of optoelectronic devices due to the following characteristics: variety of growing methods, a high melting point of 1855°C, high thermal and chemical stability at high temperatures, a wide and indirect band-gap semiconductor, high photo-conversion efficiency and photo-stability. Because of these excellent optical properties, TiO₂ has been utilized in many applications including field emitters, dye sensitized solar cells, photodetectors, and gas sensors. In 1972, Fujishima and Honda reported that water can be decomposed directly by irradiating TiO₂ surface with the incident light of wavelengths shorter than 190 nm. In 1991, M. Grätzel et al. fabricated dye sensitized solar cells (DSSCs) using nanocrystalline porous TiO₂ as the electrode to convert solar light to electron-hole pairs. Furthermore, in order to enhance the optical absorption characteristic at 325 nm wavelength for TiO₂ thin film, a continuous beam of He-Cd laser of 325 nm wavelength as the excitation source.

Experimental

To fabricate an AAO template, an Al film of 1 μm in thickness was deposited on P-type (100) silicon or quartz substrate by a thermal evaporation coater. After the fabrication procedure described in an earlier report was performed, we obtained an AAO template possessing an average diameter of about 70 nm, a pore distance of about 95 nm, a height of about 750 nm, and nanopores with an aspect ratio of 10.7. ALD technique was then employed to deposit TiO₂ onto AAO nanopores. Under the operating environment of 1.6×10⁻¹³ Torr and 400°C, Titanium tetrachloride (TiCl₄) and deionized (DI) water were used as the precursors for TiO₂ deposition. Pure Ar gas (99.999%) was used to carrier gas and purge gas, and the reaction is shown as the following:

\[ \text{TiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{HCl} \] (1)

The precursors were kept separately in a canister at 30 ± 1°C and 25 ± 1°C, and TiO₂ was deposited onto Si or quartz substrates with or without AAO template in a quartz tube reactor. Each deposition cycle consisted of eight steps, which included TiCl₄ reactant entry, pump-down, Ar purge, pump-down, H₂O reactant entry, pump-down, Ar purge, and pump-down. Typical pulse time for the introduction of TiCl₄ and H₂O precursors was 1 second. Ar purge time was also 1 second. In order to remove the residual reactants and by-products efficiently, 1s pump-down step was added after each step. The deposition cycles of 50, 100, 200, 300 and 700 cycles were chosen to produce TiO₂ thin films with different thicknesses or nanotubes with different wall thicknesses. After the deposition of TiO₂ nanotube arrays on AAO nanopores was completed, TiO₂ film on the top surface of the AAO was removed with mechanical polishing as shown in Figure 2. Then the AAO template was selectively removed by a 0.4 wt% sodium hydroxide (NaOH(aq)) solution. Finally, the self-aligned, equal height and almost equal spaced TiO₂ nanotubes were successfully fabricated.

The nanostructures of the TiO₂ arrays and thin films were examined by a field-emission scanning electron microscope (FESEM, JSM-6500F) and a transmission electron microscope (TEM, JEM-2100F). UV-vis spectrometer (U-3500, Hitachi) was used to measure the light absorption characteristic at 325 nm wavelength for TiO₂ thin film and nanotubes on quartz substrate. Photoluminescence (PL) of TiO₂ nanostructures and thin films on silicon substrate was measured at room temperature, using a continuous beam of He-Cd laser of 325 nm wavelength as the excitation source.

Results and Discussion

Figure 1 shows the TEM cross section of TiO₂ thin film with 50 to 700 deposition cycles. Based on the growth rate of 0.058 nm/cycle, the thickness was 6.6 nm, 8.1 nm, 12 nm, 18.2 nm and 41.1 nm with 50, 100, 200, 300 and 700 deposition cycles, respectively. Figure 1f is the high resolution TEM picture of Figure 1b after 100 deposition cycles, and from the picture, we observed a clear layer of crystalline TiO₂ grown on the top of the native oxide. Furthermore, the lattice spacing was 3.52 Å, which is the distance between (101) planes of the crystalline TiO₂.
Figure 1. TEM cross section of TiO$_2$ thin films with deposition cycles of (a) 50, (b) 100, (c) 200, (d) 300 and (e) 700 at 400 °C. (f) is the high resolution TEM picture of the dotted circle shown in (b). After 100 deposition cycles at 400 °C, a layer of crystalline TiO$_2$ was clearly observed on the top of the native oxide.

Figure 2a–2e shows that FESEM cross section of TiO$_2$ nanotube arrays on AAO templates after deposition cycles of 50, 100, 200, 300 and 700. As the deposition cycle was increased, the nanotube wall thickness was increased and the inner diameter of the nanopores was reduced. In addition, the inner diameter of nanotubes seemed to be consistent from the top to the bottom of the nanotubes. It was 21.9 nm at the top and 22.1 nm at the bottom of the nanotubes with 100 deposition cycles, presenting just a minor difference. Figure 2f and the inset in the figure show the cross-sectional and plan-view SEM images of the TiO$_2$ nanotube arrays deposited at 200 cycles after the AAO removal. The nanotubes are vertical to the Si substrate, and no residual AAO template was observed. The average diameter of the nanotube is about 75 nm, the wall thickness is about 8.8 nm, and the height of TiO$_2$ nanotube array is about 550 nm. Because the mechanical strength for the tubular structure at cycles less than 100 is not strong enough to support the tubular structures after the removal of the AAO, the PL tests for the tubular structures can be performed only in 700-300- and 200-cycle conditions. The result confirms the excellent capability for ALD to fill a hole with high aspect ratio because it can precisely control the wall-thickness of TiO$_2$ nanotube by cycle numbers due to its self-limiting reaction caused by the saturated surface adsorption of reactants. As a result, ALD can produce thin films with high uniformity and provides excellent step coverage. Based on the TEM pictures not shown here, with the growth rate of 0.05 nm/cycle, the wall thicknesses of TiO$_2$ nanotube arrays were 3.0 nm, 5.3 nm, 8.9 nm, 15.2 nm and 30.7 nm for deposition cycles of 50, 100, 200, 300 and 700, respectively.

In the study of PL characteristic, there are two factors contributing to the intensity of the TiO$_2$ spectrum. One is called excitation emission, contributed from the transitions of electrons from the conduction band to the valence band, and possesses the wavelength of 388 nm located in the ultraviolet light region. The other is contributed from the defects inside the material, and it is the transitions of electrons from the defect energy level to the valence band, possessing the wavelength between 400~600 nm located in the visible light region. According to the literature, the possible defects that can contribute to PL characteristic are oxygen vacancies, titanium interstitials, impurities or defects in the crystal. Among them, the existence of oxygen vacancies is the most accepted source of emission for TiO$_2$. The two kinds of oxygen vacancies that can contribute to the PL characteristic in TiO$_2$ include F centers and F$^+$ centers. F center represents neutral oxygen vacancy whereas F$^+$ center represents oxygen vacancy losing one electrons. The sub-bands contributed from the two kinds of oxygen vacancies, as shown in Figure 3, are located at 465 nm and 525 nm in the PL spectrum, respectively.
Figure 4 shows the PL spectra of TiO₂ thin films with 50, 100, 200, 300 and 700 deposition cycles. The sub-band of 488 nm contributed from the excitation emission was not observed because anatase TiO₂ is an indirect bandgap material, and most PL observed is attributed from the transitions of defects in TiO₂. From the PL spectra, we also notice that PL intensity increases with film thickness. In other words, film thickness has a direct relationship with the PL intensity, even though the relationship between the two is not entirely linear as shown in Figure 5. Nevertheless, Figure 5 shows that when the film thickness was increased, light absorption was also increased. Because more electron-hole pairs were generated by the light absorption of the thicker film, the probability of electrons transitioned from the defect energy levels to the valence band also increased, producing a higher PL intensity.

Figure 6 shows the Gauss fitting of PL spectra contributed from oxygen vacancies for TiO₂ thin films with 200, 300 and 700 deposition cycles. The two sub-bands are located at 465 nm and 525 nm in the PL spectrum as mentioned earlier. The intensities of sub-bands decrease with the intensity of the PL spectrum. The detail summary of the PL intensity for the two sub-bands, calculated by the area under the spectra of TiO₂ thin films, is shown in Table I. As observed from Table I, the intensity representing F center was decreasing at a very fast rate with decreasing deposition cycles. The intensity representing F⁺ center also had a similar trend, but was decreasing at a much slower rate. The ratio of the intensity for F center was 7.1:4.0:1.0 for 700, 300 and 200 deposition cycles whereas the ratio of the intensity for F⁺ center was 3.9:3.2:1.0 for 700, 300, and 200 deposition cycles. The intensity of F center decreased more rapidly than F⁺ center was due to the reason that the depletion region on the surface of thin films only contained F⁺ center. When the thickness of the TiO₂ thin film was decreased, the number of F⁺ center on the surface was only reduced by a small amount. The number of F⁺ center and F center inside the bulk TiO₂, however, was highly affected by the volume of thin films. This is because when the thickness of the film was reduced, the ratio of surface area to volume was increased. In other words, the value of F⁺/F became higher and the surface area factor became more important.

Table I. The summary of the PL intensity for sub-bands of F center and F⁺ center oxygen vacancies calculated by the area under the spectra of TiO₂ thin film.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>465 nm (F) PL area</th>
<th>525 nm (F⁺) PL area</th>
<th>F⁺/F</th>
<th>Surface area Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>6161</td>
<td>11336</td>
<td>1.84</td>
<td>0.024</td>
</tr>
<tr>
<td>300</td>
<td>3735</td>
<td>9240</td>
<td>2.47</td>
<td>0.055</td>
</tr>
<tr>
<td>200</td>
<td>867</td>
<td>2879</td>
<td>3.32</td>
<td>0.083</td>
</tr>
</tbody>
</table>

Figure 7 shows the PL spectrum of TiO₂ nanotube arrays with 200, 300 and 700 deposition cycles at 400°C. Again, because anatase TiO₂ has an indirect bandgap, the intensity was only contributed from defect levels of oxygen vacancies. As shown in the spectra, TiO₂ nanotubes with 200 cycles seemed to have better PL performance. However, when we compare the absorption spectrum with the PL spectrum, we see that two spectrums had opposite trend. The absorbability of the nanotubes increased but PL intensity decreased with tube wall
Figure 7. PL spectra of TiO$_2$ nanotube arrays with 200, 300 and 700 deposition cycles at 400°C.

thickness. As observed in Figure 8, TiO$_2$ nanotube arrays with 700 deposition cycles showed higher absorbability but lower PL intensity, whereas TiO$_2$ nanotube arrays with 200 deposition cycles had lower absorbability but higher PL intensity. According to the investigation of Wu et al.\textsuperscript{35} on the PL spectra of ZnO nanorods and nanotubes, the tubular structure is advantageous to the optical characteristic because of the higher porosity and larger surface area. Therefore, even though both volume and surface area affect the performance of PL, when the trend of these two factors contradicts with each other, surface area dominates the performance of PL. The reason most likely stems from the fact that the surface area represents a discontinuity of atomic arrangement. Larger surface has higher number of surface defects thus higher number of oxygen vacancies\textsuperscript{30–33,35,36} that can contribute to higher intensity for the PL spectrum.

Figure 8. The absorbance vs. area of PL intensity for TiO$_2$ nanotubes with different wall thicknesses. PL was measured at room temperature, using a continuous beam of He-Cd laser of 325 nm wavelength as the excitation source. Absorbance was measured at 325 nm wavelength.

![Figure 8](image.png)

Figure 8. The absorbance vs. area of PL intensity for TiO$_2$ nanotubes with different wall thicknesses. PL was measured at room temperature, using a continuous beam of He-Cd laser of 325 nm wavelength as the excitation source. Absorbance was measured at 325 nm wavelength.

The detail summary of the PL intensity for the two oxygen sub-bands, calculated by the area under the spectra of TiO$_2$ nanotube arrays, is shown in Table II. The symbol $S$ is the surface area ratio compared with 700 deposition cycles, and the symbol $V$ is the volume ratio compared with 200 deposition cycles. Besides, based on the dimensions measured from the TEM and SEM images, the surface area and volume in various conditions were calculated. When the deposition

![Figure 9](image.png)

Figure 9. Gauss fitting of PL spectra for TiO$_2$ nanotube arrays with (a) 700, (b) 300, and (c) 200 deposition cycles.

![Table II](image.png)

Table II. The summary of the PL intensity for sub-bands of F center and F$^+$ center oxygen vacancies calculated by the area under the spectra of TiO$_2$ nanotube arrays.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>S</th>
<th>V</th>
<th>465 nm (F) PL area</th>
<th>525 nm (F$^+$) PL area</th>
<th>F$^+$ PL area</th>
<th>Surface area ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>1</td>
<td>1.67</td>
<td>6004</td>
<td>17818</td>
<td>2.97</td>
<td>0.095</td>
</tr>
<tr>
<td>300</td>
<td>1.34</td>
<td>1.61</td>
<td>1161</td>
<td>22378</td>
<td>193.4</td>
<td>0.133</td>
</tr>
<tr>
<td>200</td>
<td>1.49</td>
<td>1</td>
<td>0</td>
<td>31407</td>
<td>$\infty$</td>
<td>0.237</td>
</tr>
</tbody>
</table>
cycles were decreased, or when the wall thickness was reduced, the ratio of surface area to volume was increased. The surface area then became a more important factor and resulted in higher value of $F+/F$.

Figure 10 shows the PL spectra of TiO$_2$ nanotube arrays vs. TiO$_2$ thin film with 200 deposition cycles. TiO$_2$ nanotube arrays had a much higher PL intensity than the TiO$_2$ thin film, and the difference was as large as 53 times. If we perform the analysis between the surface areas and the volumes, the surface area of nanotube arrays vs. thin film was 28.1 whereas the volume ratio of nanotubes vs. thin film was 9.9. We can therefore conclude that nanotube arrays have better PL performance than thin films.

Conclusions

In summary, TiO$_2$ thin films and self-aligned TiO$_2$ nanotubes were fabricated using ALD technique and AAO templates on Si and quartz substrates. Growth rate of TiO$_2$ thin film was 0.058 nm/cycle and that of TiO$_2$ nanotube wall was 0.050 nm/cycle. In particular, by controlling the amount of deposition cycles, the thickness of the film and the wall thickness of the nanotubes can be controlled precisely. For TiO$_2$ thin film, better PL performance was observed as we increased the deposition cycles and thicknesses. On the contrary, for TiO$_2$ nanotube arrays, better PL performance was observed for lower deposition cycles and thinner nanotube walls. Both volume and surface area affected the intensity of PL spectrum. However, when the two factors contradicted with each other, surface area became the dominant factor because oxygen vacancies on the surface were the main contribution to the PL characteristic. Therefore, when the amount of materials was decreased, the ratio of surface area to volume was also increased, and the surface factor becomes a more important characteristic to a material’s optical properties.

Acknowledgment

The authors thank the National Science Council of the Republic of China, Taiwan, for the financial support in this research under Contract No. NSC-96-2628-E-009-010-MY3.

References