Optical Properties of Titanium Dioxide Thin Films and Their Application in Energy Saving Glass

Nirun Witit, Surasing Chaiyakan

Abstract

Titanium dioxide (TiO\textsubscript{2}) thin films were deposited by reactive DC magnetron sputtering technique. The crystal structure was characterized by XRPD, surface morphology was evaluated by AFM, and optical transmittance was measured by spectrophotometer, respectively. The TiO\textsubscript{2} thin films were mixed phase of anatase and rutile. The film thickness was 134 nm and transparent with high transmittance. The optical properties of the films were determined from transmission spectra. The refractive index (n) in the visible was relatively high (2.42) while the extinction coefficient (k) was low (0.0044). The energy bandgap was found to be 3.2 eV. A heat mirror was fabricated based on the TiO\textsubscript{2}/Ag-alloy/TiO\textsubscript{2}/glass system. This heat mirror was found to be moderate transparent in the visible with an average transmittance of 66\% and low transmittance in the near infrared of 16\%, which shows that it can be used in energy saving glass.

Keywords: TiO\textsubscript{2} films, Anatase, Rutile, optical constant, reactive sputtering

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INTRODUCTION

Titanium dioxide (TiO₂) thin films are extensively used in optical device applications, such as anti-reflection coatings, multilayer coatings (Barge et al., 1991), etc., owing to their good durability, high transmittance in the visible spectral range, and high refractive index (at λ = 550 nm, n = 2.54 for anatase or 2.75 for rutile). The structure of the thin films can be modified by different processing (Meng and Santos, 1993). The optical properties of a thin film include refractive index (n) and extinction coefficient (k). The optical properties of titanium oxide thin films have been extensively studied (Antar et al., 1997; Mardare, 2002; Hwu et al., 2003). There has been a large scatter in the reported values of the optical constants. This scatter could be attributed to several factors including the deposition method and the deposition conditions.

The solar spectrum is roughly split between the visible regions (λ from 400 to 700 nm) and the near-infrared (λ from 700 to 2000 nm) regions. Three-layer coatings of dielectric/metal/dielectric (D/M/D) on glass substrates are used as spectrally selective coatings for various purposes including energy saving mirror, energy efficient windows (Leftheriotis et al., 1997; Granqvist, 1981). By varying materials and thickness of each layer, the optical properties of the D/M/D coating system can be tailored to suit in different applications. In warm climates, for example, it is desirable to design energy saving glass that reflects the infrared part of the solar spectrum, while transmitting visible light, which the D/M/D structure on glass is called a heat mirror. For example, TiO₂/Ag/TiO₂ or ZnO/Ag/ZnO (Ebisawa and Ando, 1998), ZnS/Ag(Al)/ZnS (Leftheriotis et al., 1997). The key factor controlling the reflectance of infrared radiation is the metal layer. The highly reflective metal film, that otherwise transmits very little energy in the visible, such as Ag or Au, is sandwiched between the two dielectric layers, such as TiO₂, ZnS or ZnO, that act as anti-reflective coatings of the D/M/D coating system to enhance the energy transmitted in the visible region (Leftheriotis et al., 1997; Granqvist, 1981).

This work has two main objectives: First, titanium dioxide thin films were deposited by reactive DC sputtering technique. The structural, surface morphology and optical were investigated. Second, titanium dioxide thin films were employed in the three-layer system of TiO₂/Ag-alloy/TiO₂/glass to produce the heat mirror that have high transmission in the visible regions and high reflection in the near-infrared for applied in energy saving glass.

MATERIALS AND METHODS

Titanium dioxide thin film was deposited onto well-cleaned glass substrates and Si-wafer substrates by using home made DC magnetron sputtering system. Pure titanium (99.97%) of 54 mm diameter has been used as sputtering target. High purity argon (99.999%) and oxygen (99.999%) were used as the sputtered and reactive gases respectively. Figure 1 shows a diagram of coating system. The cylindrical chamber of the system with 31 cm in diameter and 37 cm in height was
connected to the vacuum pump system. Rotary and diffusion pump combination was used to get the desired vacuum. After attaining the base pressure, about \(10^{-5}\) mbar, the mixed gas of argon and oxygen in the ratio of 1:4 was let into the vacuum chamber, controlled by mass flow controller. The thin films deposition was carried out at a total pressure of 5.0x10^{-3} mbar. The distance between the target and substrates (\(d_{st}\)) was kept at 12 cm. The thickness of films was controlled by the deposition rate of each sputter target. The films deposition condition was summarized in Table 1.

The silicon substrates were analyzed by XRD (Rigaku RINT2000) to determine the crystallographic phase. The XRD patterns were measured at a glancing angle of 3° and using Cu Kα radiation (\(\lambda = 1.54059\) Å) at 40 kV and 40 mA with a pattern recorded from 2\(^\circ\) 20° to 60° at a scan rate of 0.02° 2\(^\circ\)/min. The evolution of the surface morphology and thickness of the samples has been investigated by AFM (Nanoscope IV, Veeco Instrument Inc.). The UVAAS transmission spectroscopy of the films was measured with the UVAAS-NIR spectrophotometer system (Shimadzu MPC-3100) in the range of 200 nm to 2100 nm. Swanepoel’s envelope method was employed to evaluate the optical constants, the refractive index (\(n\)) and the extinction coefficient (\(k\)), from transmittance spectra (Swanepoel, 1983).

The heat mirror, from the three-layer system in this work was fabricated on glass slides based on the TiO\(_2\)/Ag alloy/TiO\(_2\)/glass system. The TiO\(_2\) films were deposited as mentioned above with a thickness of 30 nm. The Ag alloy film was sputter from Ag alloy target (97.25%Ag7.5%Cu) with the thickness of 30 nm. The normal incidence transmittance and reflectance of the three-layer system were measured with spectrophotometer.
Figure 1. Schematic diagram of the DC magnetron sputtering system.
Table 1. The thin films deposition condition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Thin film</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition technique</td>
<td>DC sputtering</td>
<td>reactive DC sputtering</td>
</tr>
<tr>
<td>Sputter target</td>
<td>Ag alloy (92.5%Ag-7.5%Cu)</td>
<td>Ti (99.97%)</td>
</tr>
<tr>
<td>Substrate Temp</td>
<td>Room temperature</td>
<td></td>
</tr>
<tr>
<td>d₁₁</td>
<td>12 cm</td>
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<tr>
<td>Base pressure</td>
<td>3.0x10⁻⁵ mbar</td>
<td></td>
</tr>
<tr>
<td>Working pressure</td>
<td>3.5x10⁻³ mbar</td>
<td>5.0x10⁻³ mbar</td>
</tr>
<tr>
<td>Power</td>
<td>135 W</td>
<td>220 W</td>
</tr>
<tr>
<td>Flow rate: Ar</td>
<td>2 sccm</td>
<td>1 sccm</td>
</tr>
<tr>
<td>Flow rate: O₂</td>
<td>-</td>
<td>4 sccm</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>0.6 nm/sec</td>
<td>0.7 nm/sec</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Structural and surface morphology of TiO₂ thin film

The deposited films were transparent with the thickness of 134 nm result from AFM. In order to get crystalline TiO₂ films using sputtering methods, the deposition parameters should be well controlled. High sputtering power, long sputtering time and short target-substrate distance are always demanded (Okimura et al., 1995). Due to the plasma heating effect, the substrate temperature is gradually increased from room temperature to a relatively high temperature, which equals to carry out substrate heating and will affect the crystallinity, structure and properties of the films deposited.

Figure 2 shows the XRD patterns of TiO₂ film. The results show that as-deposited film possesses characteristic peaks mixed of anatase and rutile structure. The diffraction angles 2θ of the sample is 25.3°, 27.5° and 36.2° which are attributed to anatase (101), rutile (110) and rutile (101) respectively.

Figure 2 XRD patterns of TiO₂ films deposited on Si wafer
Figure 3 shows the AFM images, 2D and 3D, of the TiO$_2$ films grown on Si-wafers. The surfaces show spherical nodules spread over the surface with some high granules. From the 3D image the nodules aggregate together and leave some of valleys between these aggregates and seem to be less coalescent. The roughness ($R_{\text{rms}}$) was about 3.3 nm. It was suggested that the film roughness correlated with the adatom mobility, which was governed by the energy of the impinging particles (Meng and Santos, 1993; Kim et al., 2002).

**Optical property of TiO$_2$ thin film**

A normal-incidence transmittance spectrum of the TiO$_2$ thin film is shown in Fig. 4. The films were transparent down to a wavelength of 300 nm. The most obvious indication of the presence of a small inhomogeneity in a thin film is usually seen in the change that occurs in the transmittance extrema (Tikhonravov et al., 1997). If the nonabsorbing films were homogeneous, the maximum transmittance value ($T_{\text{max}}$) would correspond to the transmittance of the uncoated substrate ($T_s$). On the other hand, for nonabsorbing inhomogeneous thin films, $T_{\text{max}} > T_s$ has been observed (Tikhonravov et al., 1997). In our case, the films were homogeneous since the maximum in the transmittance ($T_{\text{max}}$) was almost equal to the transmittance of the uncoated substrate ($T_s$).

The optical constants, the refractive index ($n$) and the extinction coefficient ($k$) were evaluated using the "envelope method", which calculate by using the envelope curve for $T_{\text{max}}$ and $T_{\text{min}}$ in the transmission spectra (Swane, 1983). Figure 5 and Figure 6 show the refractive index ($n$) and the extinction coefficient ($k$) of the as-deposited film at wavelength of 550 nm. The result was 2.42 and 0.0044 respectively, which agrees with the values reported in the literature (Amor et al., 1997).
Due to the fundamental absorption in the vicinity of band gap, the transmission decreases sharply as the wavelength reaches the ultraviolet radiation. The optical band gap $E_g$ can be determined from the absorption coefficient $\alpha$ calculated as a function of incident photon energy $E(h\nu)$. Near the absorption edge, $\alpha$ can be expressed as $\alpha = -\ln(T)/d$, where $d$ is the film thickness. The optical band gap $E_g$ can be derived from the expression as follows: $\alpha \propto (h\nu - E_g)^m$. Where $m = 2$ for indirect allowed transition. The $E_g$ value can be obtained by extrapolating the linear portion to the photon energy axis, as shown in Figure 7. In this result, we found that TiO$_2$ has a mixture phase of anatase and rutile and the band gap was 3.2 eV.
Fabrication of the TiO$_2$ thin film based heat mirror

There are many theoretical models which optimize the properties of the D/M/D system for operation as a heat mirror which show that (Durrani et al., 2004): First, the two dielectric layers should have the same thickness. Second, the dielectric needs to have a high refractive index. Third, the metal layer should have high transparency in the visible region. Fourth, as the metal layer thickness increases, the average transmittance in the visible decreases, while the average reflectance in the infrared increases. Therefore, the thickness of the metal layer should be minimized. However, metal films thinner than 15 nm tend to be inhomogeneous and granular. More realistic values of the metal layer thickness are considered to be in the range 16-24 nm (Leftheriotis et al., 1997).

The optical properties of TiO$_2$ thin films, in this work, indicate that these films are suitable for using as dielectrics in energy efficient applications, such as heat mirrors. They meet the requirement of transparency over the entire solar spectrum. Moreover, they are dense with a high refractive index. Their mechanical, thermal and chemical stability make them durable and environmentally stable.

Figure 8 and Figure 9 show the experimental values of the transmittance and reflectance of this heat mirror with the three layer system of TiO$_2$/Ag-alloy/TiO$_2$/glass. The average transmittance in the visible region ($T_{avg, VIS}$) is given by $<T_{avg, VIS}> = \frac{\int T \, d\lambda}{\int d\lambda}$, for $\lambda = 400$–700 nm, while the value of ($T_{avg, VIS}$) was 66%. The average reflectance in the near infrared region ($R_{avg,NIR}$) is given by $<R_{avg,NIR}> = \frac{\int R \, d\lambda}{\int d\lambda}$, for $\lambda = 700$–2000 nm, and the value of ($R_{avg,NIR}$) was 16%.

**CONCLUSIONS**

The as-deposited TiO$_2$ thin films were a mixture phase of anatase and rutile with the thickness of 134 nm. The TiO$_2$ thin films had a relatively high refractive index, dense and transparent down to a wavelength of 300 nm. These properties coupled with the mechanical, thermal and chemical stability make this material a potential candidate for energy saving applications. In addition, the heat mirror was fabricated which found to be moderate transparent in the visible with an average transmittance of 66% and low transmittance in the near infrared of 16%.