Near Infrared Reflecting Properties of TiO$_2$/Ag/TiO$_2$
Multilayers Prepared by DC/RF Magnetron Sputtering

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Abstract: The near-infrared (NIR) reflecting properties of TiO$_2$/Ag/TiO$_2$ (TAT) multilayers deposited using DC/RF magnetron sputtering were investigated. For high transmittance and reflectance in the visible and NIR ranges, respectively, the thickness of each layer was theoretically optimized by the index matching method. As the Ag layer thickness increased, the reflectance of the TAT multilayers in the NIR range increased significantly because of surface plasmon resonance (SPR). It was confirmed that the TAT multilayer with a 12 nm-thick Ag layer showed both good transmittance and reflectance. After irradiation with an IR lamp for 10 min, the temperature of the bare glass increased from 27 to 41 °C, while that of the TAT films increased by only 6 °C. This is because of the enhancement of the SPR effect with the increase in carrier density and mobility. The TAT multilayers were found to be suitable for NIR reflecting windows.

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I. INTRODUCTION

In recent years, concerns for environmental pollution, fuel depletion, and energy waste has steadily increased. As a result, research is being focused on developing methods to construct
buildings with pleasant interiors while saving energy. Also, the energy consumed by the fabricated buildings materials accounts for nearly 30% of the total energy consumption. Hence, developing materials to save energy in buildings is essential. In particular, the use of window materials in modern buildings is increasing. As a result, energy losses through windows is also increasing [1].

In order to address this problem, many studies have focussed on developing energy saving near-infrared reflective (NIR) window coatings, since they decrease the inner or outer energy losses. Oxide semiconductors such as indium-tin-oxide are typically used as NIR reflecting coatings because they reflect NIR light, due to surface plasmon resonance (SPR) [2,3]. However, because of the toxic properties and high cost of indium, indium-free materials like ZnO have recently been studied for NIR reflecting coatings [4].

ZnO-based materials are usually used in transparent electrodes because of their electrical properties and transparency in the visible range. Many studies have focussed on developing NIR reflecting coatings by doping ZnO with Al [5,6] and Ga [7,8]. Because they provide high transmittance in the visible range as well as high reflectance (due to index matching) in the NIR range, oxide-metal-oxide (OMO) multilayers have become attractive alternatives to semiconductor oxide-based NIR reflecting coatings [9].

Titanium oxide (TiO₂) has good optical properties, high refractive index, low absorption, and high transmittance and high adhesion to glass and plastic substrates [10]. In addition, it has both good stability and non-toxic properties, which are important characteristics for window materials. TiO₂ can be used for optical coatings on large area substrates for architectural, automotive, and display applications, and for protective layers for very large-scale integrated circuits.
In this work, the high refractive index of TiO$_2$ and the low refractive index and good electrical properties of Ag were combined to fabricate TiO$_2$/Ag/TiO$_2$ (TAT) multilayers. The optical and electrical properties of these TAT multilayers were investigated, to evaluate their performance as NIR reflecting coatings. The multilayers were deposited on glass substrates by RF/DC magnetron sputtering at room temperature. The performance of these multilayers was then evaluated at elevated temperatures after IR lamp heating.

II. EXPERIMENTAL PROCEDURE

The optical properties of the multilayers were analysed using the Essential Macleod program for determining the optimum transmittance and reflectance.

The TAT multilayers were deposited using a dual cathode magnetron sputtering system equipped with two cathodes on 50 mm x 50 mm Corning glass (E-2000) without substrate heating. As shown in Fig. 1, a TiO$_2$-sintered ceramic disk (99.99% purity, 3 inch φ) and an Ag metal target (99.99% purity, 3 inch φ) were used. The base pressure and working pressure were ~ 10$^{-5}$ Torr and 7.5 X 10$^{-3}$ Torr, respectively. The sputtering powers for the TiO$_2$ and Ag cathodes were RF 200 W and DC 50 W, respectively.
Fig. 1. Schematic diagram of the dual target magnetron sputtering

The thickness of the TAT multilayer films was determined by optical ellipsometry (J. A. Woollam, Alpha-SE). The surface morphology of the Ag layers grown on the bottom TiO$_2$ layers was evaluated by SEM (Hitachi, S-5000) at an operating voltage of 20 kV. The electrical properties of the films were determined by Hall effect measurements (Ecopia, HMS-3000). The transmittance and reflectance of the TAT multilayers were measured using a UV-Vis-NIR spectrometer (Shimadzu, UV-2000) for air reference.

To evaluate the heat reflective performance of the TAT multilayers, we used an instrument developed in house. This instrument can monitor the temperature changes of the sample, which was kept in a heat insulating box, as shown in Fig. 2. The light source used in this instrument was a Philips BR125, which emitted light with wavelengths in the range of 900–2000 nm under a source power of 250 W. To prevent heat loss from the box, a heat insulating layer was constructed of Styrofoam. The sample was located at the centre of the box and at a distance of 20 cm from the NIR source.

In order to concentrate the NIR light, we made 15 cm length, 50 mm x 50 mm rectangular channels using Al plates because of their emissivity. The base temperature of the box (without
heating) was 27 °C. The temperature changes in the box were monitored by a thermometer at intervals of 1 min for 10 min.

**Fig. 2. Schematic of the heat reflecting measurement system.**

### III. RESULTS AND DISCUSSION

To design the NIR reflecting coating, we used the Essential Macleod optical simulating program. The thickness of each layer was determined to obtain the desired optical transmittance and reflectance for the multilayer films. Durrani et al. [11] suggested that the thickness of the first and third layers in O/M/O structures be equal. A multilayer provides maximum transmittance. With this assumption, the thickness of the TiO₂ layer was fixed at 40 nm, while that of the Ag layer was varied to obtain the best optical properties.
Fig. 3. (a) Calculated and (b) measured transmittance and reflectance of TiO₂/Ag/TiO₂ as functions of the Ag layer thickness.

The optical properties of the TAT multilayers with a 40 nm-thick TiO₂ layer and varying thicknesses of the Ag layer are shown in Fig. 3 (a). All of the multilayers showed a transmittance greater than 90% and a reflectance of less than 5% in the visible range. On the other hand, the reflectance of the TAT multilayers in the NIR range increased significantly with increasing Ag layer thickness. The reflectance of the TAT multilayers increased from 40 to 78% as the Ag layer thickness increased from 8 to 14 nm at 1500 nm. Therefore, on the basis of the transmittance and reflectance values obtained, the TiO₂(40)/Ag(12)/TiO₂(40) film can be expected to be suitable for NIR reflecting coatings.

Figure 3 (b) shows the measured transmittance and reflectance of the TAT multilayers for different Ag layer thicknesses. The transmittance decreased from 75 to 58% at 550 nm as the Ag layer thickness increased from 10 to 14 nm. This indicates that the measured optical transmittance of the TAT multilayers in the visible range was lower than the calculated values. This is because in the simulation process, the surfaces of the Ag and TiO₂ layers were considered to be smooth. However, in practice, the Ag and TiO₂ layers have rough surfaces. Therefore,
difference was observed between the measured and calculated transmittance values of the TAT multilayers because of light scattering and reflection.

The reflectance of the TAT multilayers increased from 18 to 86% at 1500 nm when the Ag layer thickness increased from 8 to 14 nm. The measured reflectance of the TAT multilayers exhibited a small difference compared with the calculated values. The reflectance was low at low Ag layer thicknesses (8, 10, 12 nm), while it was high at high Ag layer thicknesses. This is expected to affect the surface morphology of the TAT films and SPR.

Morphology is also an important factor affecting the reflecting performance of NIR coatings. Figure 4 shows SEM images of the Ag films (with various Ag layer thicknesses) deposited on the TiO₂ surface.

Fig. 4. SEM images of the Ag films with various Ag layer thicknesses (a) 10 nm, (b) 12 nm, (c) 14 nm deposited on the TiO₂ bottom layer.

From this figure, a clear grain growth can be observed with an increase in the Ag layer thickness. It was confirmed that the microstructure of the Ag films changed in three steps as the film thickness was increased. In the first step, an island structure was observed (at an Ag layer thickness of 10 nm). In the second step, the coalescence of the islands occurred (at an Ag layer thickness of 12 nm), and finally, a continuous layer was formed (at an Ag layer thickness of 14
nm). The islands showed a gradual coalescence as the Ag layer thickness reached a critical value and finally formed a continuous layer at an Ag layer thickness of 14 nm.

It is well known that Ag films grown on an amorphous TiO$_2$ surface follow the island growth mechanism of the Volmer-Weber model [12]. At Ag layer thicknesses of 8–12 nm, no continuous Ag layers were observed, and the surface roughness was not comparable to that of continuous layers. Therefore, in this range, an increase in Ag layer thickness seemed to reduce reflectance, since no continuous layers were formed in this range. At an Ag layer thickness of 14 nm, there was a small increase in the measured reflectance as compared to the calculated value, which might be explained by SPR. This result indicates that the electrical conductivity of the multilayer was affected by the thickness of Ag layer [13], which also affected reflectance due to SPR.

SPR is another important factor affecting NIR reflecting performance. The phenomenon is generated by the high concentration of electrons in the materials. The infrared reflective property of transparent conductive thin films initiates the SPR phenomenon [14]. The cut off frequency ($\omega_c$) and plasma frequency ($\omega_p$) of the films can be determined using Eq. (1)

$$\omega_c = \omega_p \left(\frac{\varepsilon_{\infty}}{\varepsilon_0} - 1\right)^{1/2} \quad (1)$$

The $\omega_p$ value depends on the electron concentration ($n_e$), effective electron mass ($m_e^*$), electron mobility ($\mu$), and collision frequency ($\gamma$). The relation is as follows:

$$\omega_p^2 = n_e e^2 / [\varepsilon_0 m_e^* (\varepsilon_{\infty} - 1)] - \gamma^2 \quad (2)$$

$$\gamma = e / (m_e^* \mu) \quad (3)$$

Here, $m_e^* = 0.38 m_e$, $\varepsilon_0$ is the permittivity of free space, and $\varepsilon_{\infty} = 3.85$ is a constant at very high frequencies. The plasma wavelength $\lambda_p$ is expressed as

$$\lambda_p = \frac{2\pi c_0}{\omega_p} \quad (4)$$
Therefore, when $n_e$ and $\mu$ increase, the reflectance spectra peaks shift to lower wavelengths. This means that the reflectance in the NIR range is improved with an increase in the $n_e$ and $\mu$ values. In order to achieve a highly NIR reflecting coating, both $n_e$ and $\mu$ should be high.

![Graph](image)

**Fig. 5. Electrical properties of the TAT multilayers as a function of the Ag layer thickness.**

Figure 5 shows the electrical properties of the TAT multilayers as a function of the Ag layer thickness. This plot indicates that the carrier concentration depends strongly on the Ag layer thickness. The resistivity of the TAT multilayers decreased from $1.3 \times 10^{-4}$ to $3.6 \times 10^{-5}$ $\Omega$·cm with an increase in the Ag layer thickness. On the other hand, the $n_e$ and $\mu$ of the TAT multilayers increased from $7.08 \times 10^{21}$ to $1.12 \times 10^{22}$ and from $7.9$ cm$^2$/V·s to $19.8$ cm$^2$/V·s, respectively, as the Ag layer thickness increased from 8 to 14 nm.

This result suggests that the electrical properties of the TAT multilayers are dominated by the Ag layer thickness. Accordingly, when an Ag film with a thickness of 8 nm was deposited between the TiO$_2$ layers, the TAT multilayer had a resistivity of $1.3 \times 10^{-5}$ $\Omega$·cm, which then decreased to $3.6 \times 10^{-6}$ $\Omega$·cm when the Ag layer thickness was increased to 14 nm. These results suggest that the change in electron mobility due to the transition from the island structure to a continuous layer with the increasing thickness of the Ag layer significantly affected the electrical properties.
properties of the multilayer. Like reflectance, $n_e$ also showed an increasing trend with the increasing thickness of the Ag layer.

It was found that the reflectance of the films was dominated by $n_e$ rather than $\mu$ because of the SPR phenomenon. Figure 3 (b) shows that a lower wavelength shift was observed in the reflectance spectra with an increase in the Ag layer thickness. This observation is in good agreement with the SPR relation.

To design the NIR coating, we considered both the reflectance and transmittance. With TAT multilayers, there is an apparent trade-off between reflectance and transmittance. Considering the reflectance values, the TAT multilayer with the 14 nm-thick Ag layer was found to be most suitable for NIR reflecting coatings. However, it showed low transmittance in the visible range, which is not suitable for NIR reflecting coatings. Likewise, the TAT multilayer with the 10 nm-thick Ag layer showed good transmittance, but it was not appropriate for NIR reflecting coating due to its low reflectance. Considering both transmittance and reflectance for the NIR coating, it was determined that the TiO$_2$(40)/Ag(12)/TiO$_2$(40) multilayer was the most appropriate for NIR reflecting coatings.

The temperature variations inside the box are shown in Fig. 6. For the bare glass, a large increase was observed in the temperature with an increase in the heating time. A remarkable improvement was observed in the heat reflecting performance of the TAT multilayers as the Ag layer thickness increased. The temperature decreased from 72 to 47 °C when the Ag layer thickness was increased from bare glass to 14 nm. The same trend was observed in the case of reflectance (Figure. 4). A small difference was observed in the reflectance of the bare glass and the multilayer with an 8 nm-thick Ag layer. However, the difference became more pronounced as the Ag layer thickness increased to 10–12 nm. This is because of SPR, and the change in the
morphology of the Ag layers from island structure to a continuous layer. As the heating time increased, the temperature inside the box increased slowly. The insulating box seemed to be saturated with heat.

![Heat reflecting properties of the TAT multilayers as a function of the Ag layer thickness.](image)

Fig. 6. Heat reflecting properties of the TAT multilayers as a function of the Ag layer thickness.

This can be explained by the energy heating the air in the box, using the following basic relation.

\[ Q = c \cdot m \cdot \Delta T \]  \hspace{1cm} (5)

where \( c \) is the specific heat of air (0.72 J/g K), \( m \) is the mass of the air in the box (16.125 g), and \( \Delta T \) is the difference in the temperature before and after heating. Using this relation, the heat energy supplied to the bare glass and the multilayers with an Ag layer thickness of 8–12 nm were found to be 516.7, 441.2, 316.9, 264.7, and 241.5 J, respectively. It was found that the heat energy saving performance of the multilayers was better than that of the bare glass. Therefore, these multilayers are potential candidates for NIR reflecting coatings.
Fig. 7. The temperature changes inside the insulated box over a duration of 10 min captured by IR camera. (a) base condition without heating, (b) bare glass, (c) TAT multilayer with 12 nm-thick Ag layer, (d) TAT multilayer with 14 nm-thick Ag layer.

To determine the precise temperature inside the box, bare glass was placed on the box and connected to a surface-temperature IR camera (NIKON) for 10 min placed at the back of the box. Figure 7 (a) shows the interior of the box in the absence of the NIR light. Figures 7 (b)–(d) show the temperature changing inside the box from 43 (for the bare glass) to 33 °C (for a 14 nm-thick Ag layer). The temperature rises in the case of the multilayer with a 12 nm-thick Ag layer (35 °C) was about half of that observed for the bare glass (43 °C). This result is consistent with the values reported in previous studies. No remarkable temperature difference (35 to 33 °C) was observed [Figures. 7 (c), (d)]. Considering the optical properties, the TiO$_2$(40)/Ag(12)/TiO$_2$(40) multilayer was found to be the most appropriate for NIR reflecting coatings.

V. CONCLUSION

The NIR reflecting properties of TiO$_2$/Ag/TiO$_2$ multilayers were investigated. In order to achieve high transmittance in the visible range and high reflectance in the NIR range, the optimal thickness of each layer was calculated according to multilayer theory. The measured transmittance of the TAT multilayers was found to be much lower than the calculated values. This difference was due to an increase in reflectance produced by SPR, and changes in the
surface morphology of the TAT multilayer materials. The measured reflectance of the TAT multilayers (with Ag layer thicknesses of 8, 10, and 12 nm) was lower than the calculated values. However, for the multilayer with the 14 nm-thick Ag layer, the measured reflectance was higher than the calculated one. This is because of the change in the surface structure from an island structure to a continuous layer with increasing Ag layer thickness. The $n_e$ and $\mu$ values increased with an increase in the Ag layer thickness. The $n_e$ and $\mu$ values showed a trend similar to that observed for the reflectance with respect to the Ag layer thickness.

${\text{TiO}}_2(40)/\text{Ag}(12)/{\text{TiO}}_2(40)$ was found to be suitable for NIR reflecting coatings. It was found that, compared to the bare glass, about half of the supplied energy was saved in the case of the ${\text{TiO}}_2(40)/\text{Ag}(12)/{\text{TiO}}_2(40)$ multilayers. We also observed a remarkable change in temperature (with the help of an IR camera) when the Ag layer thickness was increased.

These results indicate that ${\text{TiO}}_2(40)/\text{Ag}(12)/{\text{TiO}}_2(40)$ is suitable for preparing energy saving NIR reflecting coatings by the DC/RF sputtering process. This TAT multilayer is expected to create a high performance NIR reflecting window for buildings, vehicles, and optical equipment.

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