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3. Optical and Electrical Properties of SiO_2-Overcoated ITO Films for Automotive Windows

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The optical and electrical properties of SiO_2-overcoated ITO films were investigated. These films were deposited on UVverre™ glass by DC magnetron sputtering at room temperature and heat-treated at a temperature of 650 or 690℃ in air. As a result, heat-shielding glass with a high luminous transmittance of 73 % and a low solar energy transmittance of 41 % was obtained. The reason why such a low solar energy transmittance is realized is that the ITO films deposited in an Ar gas have the low mobility and high carrier concentration after heat-treatment.

1. Introduction

From the viewpoints on energy saving and more comfortable driving, heat-shielding glass has been becoming more and more important[(1)~(4)]. Low-emissive (Low-E) and solar-control glasses with sputtered thin films are widely used as heat-shielding glass for architectural windows. These films include at least a transparent oxide layer and a reflecting or absorbing layer such as metal or nitride[(5)], which reflects or absorbs the light of the near-infrared (near-IR) region (0.78-2 μm in wavelength)[(6)]. Generally, Ag or Ag-based alloy is used for the metal film and high melting-point metal nitrides such as titanium nitride are used for the nitride one. However, these films are not sufficient to be applied to automotive windows because of their poor transmission in the visible region (0.38-0.78 μm) and their low thermal, mechanical and chemical durabilities[(7)~(9)]. The development of heat-shielding coatings composed of oxide films with high durability and high transmission in the visible region has been expected.

Indium-tin-oxide (ITO) is one of the most hopeful candidates for the heat-shielding coating materials because of its preferably highly mechanical and chemical durability. However, a single-layered ITO film has a problem of an increase in transmittances in the near-IR region by tempering at temperatures of 650-690°C due to a decrease in free-carriers by oxidation.

The purpose of this study is to develop temperable heat-shielding coatings appropriate for automotive windows. ITO films overcoated with SiO_2 films were evaluated for their potential for achieving the purpose. This paper reports on the optical and electrical properties of the SiO_2/ITO films on glass before and after heat-treatment.

2. Experimental

ITO films were deposited on glass substrates (3.5 mm thick) using ITO targets by DC magnetron sputtering. UVverre™ glass (Asahi Glass), which is greenish-tinted glass widely used as automotive windows, were used as the glass substrates. The composition of the ITO targets was 90 mass % In_2O_3 and 10 mass % SnO_2 (purity: higher than 99.99 %). The deposition of ITO films was carried out at a pressure of 0.4 Pa in an Ar gas or a gas mixture of Ar and O_2 at room temperature. SiO_2 films were consecutively deposited on the ITO films by pulsed-DC magnetron sputtering using Si targets. The deposition of SiO_2 films was carried out at a pressure of 0.4 Pa in a gas mixture of 33 vol. % Ar and 67 vol. % O_2 at room temperature. The thickness of the ITO and SiO_2 films was fixed to be 150 and 80 nm, respectively. The film thickness was

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determined to be low reflective in the visible region.

A belt-conveyor-type furnace (DZ20-4-TA; Denko) was used to heat-treat the samples. The heat-treatment was carried out at a temperature of 650 or 690°C in air for 2 min. These temperatures are equivalent to tempering temperatures.

The resistivity, Hall mobility and carrier concentration of ITO films were measured by Hall-effect measurements in the van der Pauw geometry. In this measurement, in order to ensure the contact between ITO films and the electrodes, a part of SiO_2 films were removed with abrasive paper and ITO films were soldered with an ultra-sonic iron at the four contact points. The optical measurements were made using a spectrophotometer (UV-3100PC; Shimadzu). The performance as heat-shielding glass was estimated using the ratio of T_v to T_e (= T_v/T_e-ratio), where T_v is the luminous transmittance and T_e is the solar energy transmittance (solar factor). These T_v and T_e comply with JIS-R3106 (1998). High T_v/T_e-ratios, i.e. the high luminous transmittance and low solar energy transmittance, are requested for the window application. The crystallinity of ITO films was investigated by X-ray diffraction (XRD) with 30 kV-10 mA Cu-Kα radiations. The film thickness was measured with a stylus profilometer.

3. Results and discussion

Figure 1 shows the T_v/T_e-ratio as a function of oxygen concentration in a sputtering gas. In the as-deposited films, the T_v/T_e-ratio increases with increasing oxygen concentration. The main reason is that the T_v-value increases with increasing oxygen concentration in a sputtering gas. In contrast, in the heat-treated films, the T_v/T_e-ratio increases with decreasing oxygen concentration. The T_v-values of these films are all preferably high. From the results of the optical measurements, the reason why the T_v/T_e-ratio increases with decreasing oxygen concentration is that the T_e-value of the films deposited at low oxygen concentrations decreases with decreasing oxygen concentration. Thus, deposition of ITO films in an Ar gas (oxygen concentration: 0 vol. %) leads to the highest T_v/T_e-ratio after heat-treatment.

Figure 2 shows the transmission spectra of the as-deposited (deposited in Ar) and heat-treated (690°C) films (including substrates) as well as that of the UVverre™ glass substrate. The transmittance of the as-deposited film is low in the visible region and high in the near-IR region, nevertheless, it becomes high in the visible region and low in the near-IR region after heat-treatment. As the best performance in this study, a high luminous transmittance of 73 % and a low solar energy transmittance of 41 % were obtained after heat-treatment. The optical and electrical properties of the sample shown in **Fig. 2** are listed as **Table 1**. The heat-treated coatings have not only high heat-shielding properties but also some practical features such as a neutral color tone and a low luminous reflectance.

Figures 3 to **5** show the resistivity, Hall mobility and carrier concentration of ITO films as a function of oxygen concentration in a sputtering gas, respectively. In the heat-treated films, the resistivity reached its lowest level of 1.55×10^{-4} Ω·cm at an oxygen concentration of 1 vol. %. The mobility reached its highest level of 29.6 $cm^2/V\cdot s$ at an oxygen concentration of 1 vol. %. It decreases with decreasing oxygen concentration in less than 1 vol.

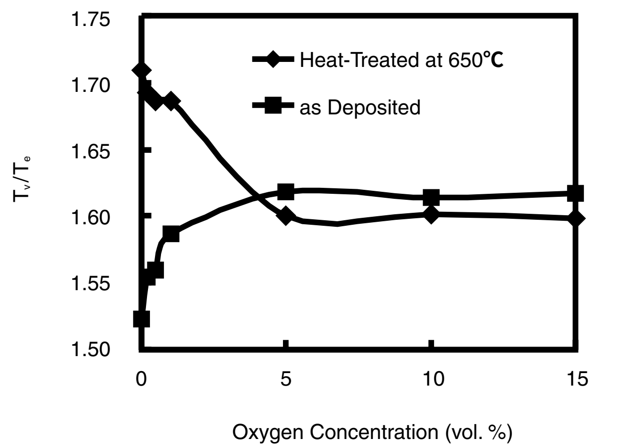

Fig. 1 The T_v/T_e ratio as a function of oxygen concentration in a sputtering gas.

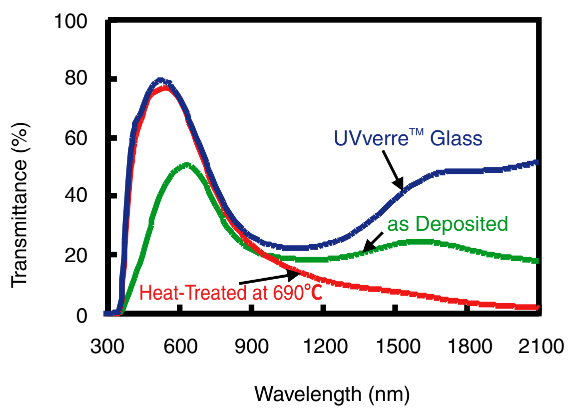

Fig. 2 The transmission spectra of the as-deposited and heat-treated (690℃) films and a UVverre™ glass substrate. The films were deposited in an Ar gas.

Table 1 List of the Optical and Electrical Properties of the Sample Shown in Fig. 2.

Item	as Deposited	Heat-Treated (690℃)
Solar Energy Transmittance: T_e (%)	30.7	41.3
Luminous Transmittance: T_v (%)	44.6	73.1
x Chromaticity Coordinate (Transmission): x	0.370	0.309
y Chromaticity Coordinate (Transmission): y	0.391	0.330
Solar Energy Reflectance on the Film Side: R_{ef} (%)	4.45	9.65
Luminous Reflectance on the Film Side: R_{vf} (%)	3.48	4.46
x Chromaticity Coordinate (Reflection on the Film Side): x	0.423	0.295
y Chromaticity Coordinate (Reflection on the Film Side): y	0.454	0.374
Solar Energy Reflectance on the Glass Side: R_{eg} (%)	5.36	6.23
Luminous Reflectance on the Glass Side: R_{vg} (%)	7.03	5.36
x Chromaticity Coordinate (Reflection on the Glass Side): x	0.310	0.299
y Chromaticity Coordinate (Reflection on the Glass Side): y	0.338	0.337
Skin Healing Factor[2]: SHF	Not Measured	44
Sheet Resistance (Ω/sq.)	140	9.3
Resistivity (Ω・cm)	2.61×10^{-3}	2.08×10^{-4}
Mobility (cm^2/V・s)	5.36	15.3
Carrier Concentration (cm^{-3})	4.47×10^{20}	1.97×10^{21}

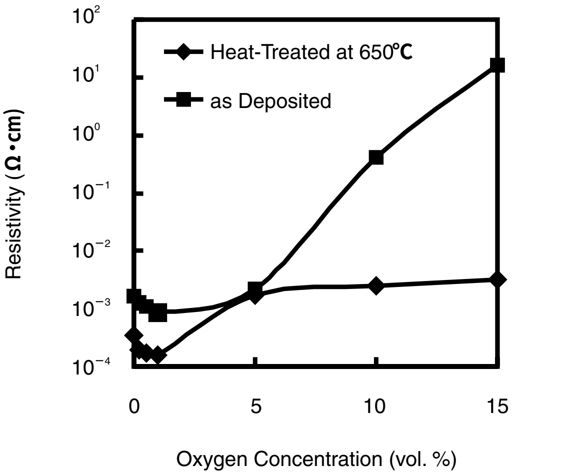

Fig. 3 The resistivity of ITO films as a function of oxygen concentration in a sputtering gas.

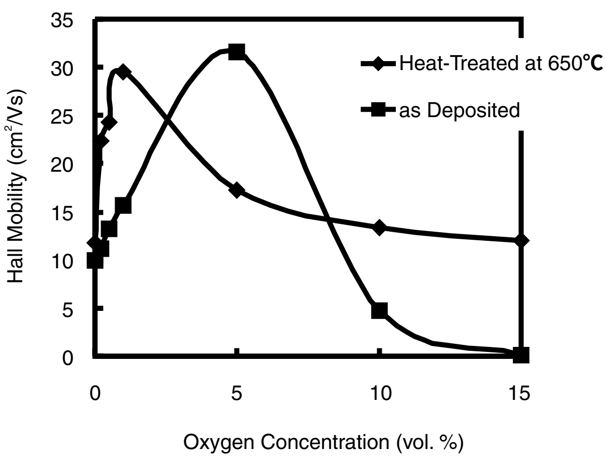

Fig. 4 The Hall mobility of ITO films as a function of oxygen concentration in a sputtering gas.

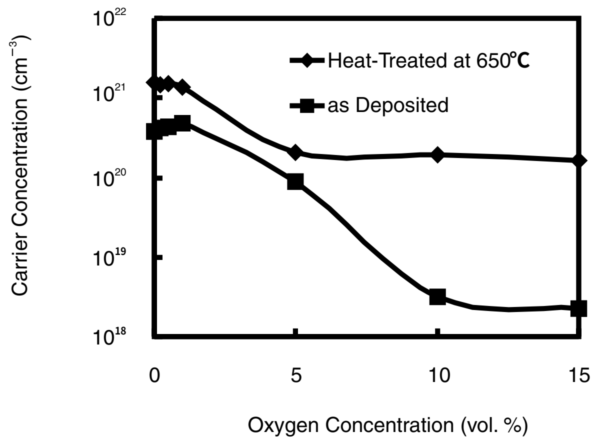

Fig. 5 The carrier concentration of ITO films as a function of oxygen concentration in a sputtering gas.

%. The carrier concentration exceeded 1×10^{21} cm^{-3} at oxygen concentrations of less than 1 vol. %. The carrier concentration reached its highest level of 1.55×10^{21} cm^{-3} at an oxygen concentration of 0 vol. %. This carrier concentration is comparable with that of the single-crystal-like ITO films (resistivity: 0.77-1.0 $\times 10^{-4}$ Ω・cm, carrier concentration: 1.5-1.9 $\times 10^{21}$ cm^{-3}) grown on yttria-stabilized zirconia (YSZ) single-crystals at a temperature of 900°C[10],[11]. This indicates that the process in this paper is an excellent method to manufacture the ITO films with very high carrier concentrations on glass.

Figures 6 and **7** show the XRD patterns of the as-deposited and heat-treated (650°C) films, respectively. Only ITO was detected as the crystal phase in both of the as-deposited and heat-treated films.

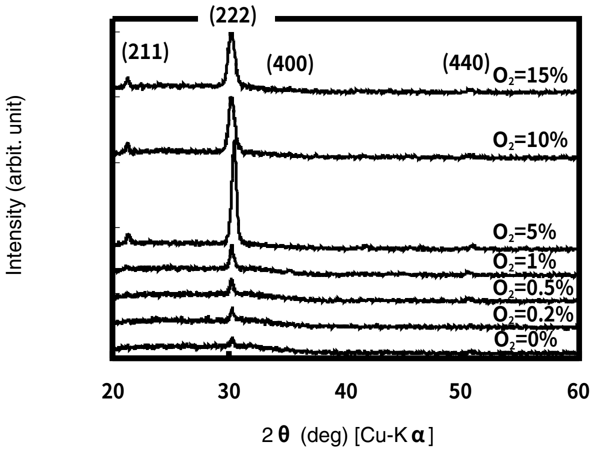

Fig. 6 The XRD patterns of the as-deposited films.

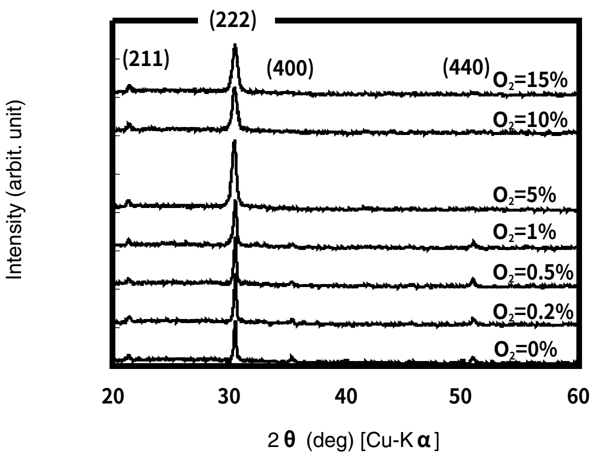

Fig. 7 The XRD patterns of the films heat-treated at 650℃.

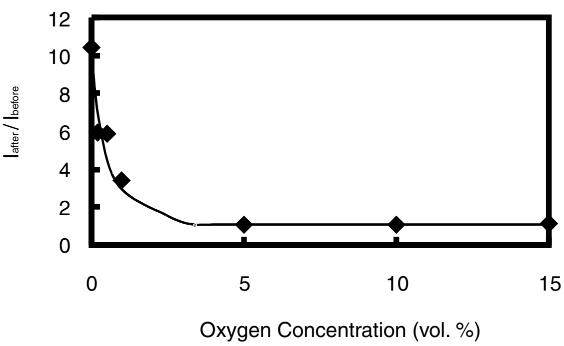

Fig. 8 The ratio of XRD intensities of the (222) plane after to before heat-treatment.

Figure 8 shows the ratio of XRD intensities of the (222) plane after to before heat-treatment as a function of oxygen concentration in a sputtering gas. The ratio shows a constant value of about 1.1 at oxygen concentrations of more than 5 vol. % and drastically increases with decreasing oxygen concentration at oxygen concentrations of less than 1 vol. %. This indicates that the crystallinity of the ITO films deposited at low oxygen concentrations increases much during heat-treatment. However, it is still smaller than that of the ITO films deposited at high oxygen concentrations of more than 5 vol. %.

Now, although the reflection in the visible and near-IR region by plasma resonance of free-carriers is well known[12], the free-carrier absorption is more important than the free-carrier reflection in the range of 0.8-1.3 μm (a part of the near-IR region) in this study. The transmittance in this range strongly affects the solar energy transmittance because of its high weighting factors. The optical phenomena in the near-IR region can be satisfactorily explained on the basis of classical Drude theory. The photon loss due to free-carrier absorption is given by[13]

$$A_{\text{free carrier}} = \frac{\lambda^2 e^3 N t}{4\pi^2 \varepsilon_0 c^3 n m^{*2} \mu} \tag{1}$$

where λ is the wavelength, N is the carrier concentration, m* is the electron effective mass and μ is the mobility. According to the above equation, the photo loss ($A_{\text{free carrier}}$) increases with increasing carrier concentration and/or decreasing mobility. This indicates that a set of the low mobility and the high carrier concentration leads to the low solar energy transmittance. This agrees with the experimental results in this study as shown in **Figs. 4** and **5** In other words, the reason why the ITO films deposited in an Ar gas (oxygen concentration: 0 %) exhibit the highest T_v/T_e-ratio after heat-treatment is that they have the lowest mobility and highest carrier concentration in the heat-treated ITO films. These low mobility and high carrier concentration are probably due to the scattering caused by ionized oxygen defects and the generation of free-carriers during heat-treatment, respectively. It is likely that this free-carrier generation is promoted by the activated mass transfer involved in the crystal growth of ITO during heat-treatment.

4. Conclusion

The optical and electrical properties of SiO_2-overcoated ITO films were investigated. As the best performance in this study, a high luminous transmittance of 73 % and a low solar energy transmittance of 41 % were obtained in the heat-treated films. The reason why such a low solar energy transmittance is realized is that the ITO films deposited in an Ar gas have the low mobility and high carrier concentration after heat-treatment at tempering temperatures. We conclude that the films and process developed in this study are suitable for tempered heat-shielding glass for automotive windows.

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