Effects of mixing Al₂O₃ particles with tin-doped indium oxide particles on the properties of aerosol-deposited thin films

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Tin-doped indium oxide (ITO) thin films are a key material for optical devices due to their high electrical conductivity and high optical transparency. Thin films were formed on glass and polyvinylchloride substrates by aerosol deposition (AD) using aerosol mixtures of ITO and Al₂O₃ (AO) particles; X-ray diffraction measurements indicated that the composite thin films comprised AO and ITO. The thickness of the film increased with increasing AO volume and reached the maximum value at approximately 50 vol %, giving a film thickness that was approximately 10 times that of a thin film deposited using only ITO particles. This study revealed that the amount of ITO particles required to generate ITO films using AD is about 20 times less than that required to fabricate ITO films of the same thickness and resistivity using conventional approaches. The resistivities of films deposited using an aerosol with 33.3 vol % ITO or more were similar to that of ITO thin films. The absorption coefficients in the visible region for ITO thin films deposited by AD were approximately 40% smaller than that of commercially available ITO thin films.

Key-words : Aerosol deposition, Tin-doped indium oxide, Al₂O₃, Composite, Thin film, Percolation

1. Introduction

Transparent conductive films have recently become key components in various devices such as flat-panel displays and solar battery electrodes. Tin-doped indium oxide (ITO) is commonly used as the film material due to its low resistivity and high optical transparency. ITO films are typically formed using sputter deposition. Aerosol-assisted chemical transport (AACT) deposition of ITO thin films has also been reported, but unlike sputter deposition, AACT is not a dry process. Sputter deposition is suitable for various types of ceramic substrates due to strong adhesion to the substrate, the ability to modify films while maintaining the composition ratio of the target, and the ease with which the film thickness can be controlled. However, sputter deposition is not suitable for the fabrication of thick films due to the low deposition rate. Furthermore, sputter deposition requires heating of the substrate to obtain an ITO thin film with low resistivity, and thus ITO thin films cannot be fabricated using this method on substrates with a low melting point, such as resins.

In contrast, aerosol deposition (AD) is a novel technique that can be used to fabricate ceramic films at room temperature. This technique is different from AACT because the source particles are directly deposited through a mechanism called room-temperature impact consolidation, which is a dry process. We previously reported that AD can be used to deposit thin films of aluminum oxide (alpha alumina, α-Al₂O₃, AO) or anatase titanium dioxide (TiO₂) onto substrates such as ceramics and resins, and that the film thickness can be easily controlled by adjusting the gas flow rate and deposition time. The films exhibited high densities, good adhesion to a variety of substrates, and could be deposited over a large area under a low vacuum of several Pa. Composite films could be also be fabricated using a powder mixture of TiO₂ and aluminum nitride. The fabricated films maintained the same crystal structure as that of the source materials. Furthermore, we evaluated the properties of ITO thin films formed on glass or single-crystal sapphire (c-axis) substrates using AD. On glass substrates, the ITO thin films had a resistivity of approximately 3.0 × 10⁻⁶ Ω·cm. In addition, a film 0.24 μm thick exhibited a high optical transmittance of approximately 90% in the visible region, which is higher than that for commercially available ITO thin films. However, ITO is an expensive material. According to percolation theory, electrically conductive spherical particles condense in a medium of insulator particles above a specific concentration (percolation threshold value), resulting in the formation of clusters of conductive particles to form a composite system exhibiting conductive properties. If the particles assume a simple cubic lattice arrangement, the percolation threshold value of the volume concentration for the conductive particles is 31.17 vol % and conductive percolation is observed at higher volume ratios. Therefore, it is expected that fabricating films using aerosols of a powder mixture of the insulator and conductive particles by AD might require fewer conductive particles. In this study we attempted to fabricate composite thin films of ITO and AO particles by AD in order to determine the amount of ITO required and to evaluate the properties of the thin films produced.

2. Experimental

Figure 1 shows a schematic diagram of the AD apparatus, which consists of a deposition chamber and an aerosol chamber connected by a transportation tube. The deposition chamber is used for depositing ceramic films. It has a fixed narrow slit nozzle (5 mm × 0.3 mm), a substrate holder mounted on a motorized XY translation stage, and a heating system for the substrate. Before film formation, both the deposition and aerosol chambers are evacuated to approximately 2 Pa by a mechanical booster pump and an oil-sealed rotary pump. Both the ITO particles (average diameter ~700 nm) and the AO particles (AL-160SG-3, Showa Denko, average diameter ~520 nm) were dried by heating at 200°C for 2 h under vacuum to prevent agglomeration.
The dried ITO and AO particles were mixed with soda-lime glass beads (average diameter 1 μm) and supplied into the aerosol chamber. The glass beads were used to ease the dispersion of the ITO and Al₂O₃ particles in the aerosol chamber. The mixture of dried ITO and AO particles and glass beads was mixed with nitrogen carrier gas (N₂) to generate a colloidal aerosol in the aerosol chamber. In addition, the aerosol chamber was continuously vibrated to create a fine colloidal aerosol. The carrier gas flow was controlled with a mass flow controller. Only the ITO and AO aerosol was transported by the carrier gas from the aerosol chamber to the deposition chamber using the pressure difference between the two chambers, while the glass beads remained in the aerosol chamber. The ITO and AO particles were accelerated to the speed of sound through the nozzle and ejected toward the substrate. The distance from the nozzle to the substrate was fixed at 10 mm. Both the ITO and AO particles were pulverized by collisions with the substrate and the already deposited film. A film deposited with an AO volume ratio of X vol % is henceforth referred to as an AO X vol % thin film.

A glass or transparent polyvinylchloride (PVC) resin plate was used as the substrate. The substrate was placed on an XY stage and the stage was scanned at 100 μm/s to deposit a film of uniform thickness. The substrate temperature was fixed at room temperature. The surface of the film was observed using scanning electron microscopy (SEM; JSM75000F, JEOL) and the thickness of each film was measured using a profilometer (DEKTAK150, Veeco). The elemental compositions of the deposited film were analyzed using an X-ray diffraction (XRD) instrument (CuKa, MULTIFLEX; Rigaku Corporation). Resistivity was measured using the four-probe method at room temperature. The surface of the thin film was observed using X-ray reflective topography using an X-ray diffractometer (U-3900, Hitachi).

3. Results and discussion

The thin film did not separate from the substrate, even under ultrasonication in water, indicating that it is strongly adhered to the substrate. Figure 2(a) shows XRD patterns for the source ITO and AO particles, and for the films deposited on the glass substrate using mixtures of ITO and AO particles with AO volume fractions between 0 and 100 vol %, while maintaining a carrier gas flow rate of 4 L/min and a scan number of 10. AO 100 vol % thin film could be deposited and the thickness was approximately 0.5 μm. Figure 2(b) shows the XRD patterns of glass substrate, and AO 100 and 80 vol % thin films. The crystal structure of ITO is very similar to that of cubic In₂O₃. In₂O₃ has three crystalline phases, the two most common being the cubic (I23) and hexagonal (R3) phases. In Fig. 2, the diffraction peaks for AO 30–80 vol % thin films are almost the same as those for the ITO particles. This confirms that the films contain ITO, and have the same crystal structure as the source ITO particles. Diffraction peaks associated with AO are absent in the XRD spectra of the AO 30–80 vol % thin films, except for diffraction peaks at 2θ ≈ 35.14–35.5°, which are the diffraction peaks for the (400) plane (ITO, 2θ ≈ 35.5°) and (104) plane (AO, 2θ ≈ 35.14°), as shown in Fig. 2(a). However, diffraction peaks associated with AO are present in the pattern for the AO 100 vol % thin film, as shown in Fig. 2(b), although their intensity is very weak because the deposition rate was low. The results of X-ray diffraction measurements indicated that ITO was the only crystalline phase present in the films.

The smaller ITO grain size in the deposited films gives rise to diffraction peaks that are broader and less intense than those for the source particles, as shown in Fig. 3. Using the Scherrer equation and the full width at half maximum (FWHM) of the ITO (222) plane diffraction peak, the grain size in ITO films deposited on either glass or PVC substrates was estimated to be approximately 20 nm. However, the actual grain size is expected...
to be larger because the Scherrer equation generally provides an underestimation. The actual grain size was unclear from the SEM image shown in Fig. 4(b), possibly due to the presence of condensed primary particles. No preferred ITO grain orientation was found for all thin films deposited at room temperature [see Fig. 2(a)]. In addition, the FWHM of the ITO (222) plane diffraction peak was essentially the same for all the AO 0–80 vol % thin films, indicating that the AO particles do not assist in pulverization of the ITO particles. Figure 5 shows the results of EDS analysis of the composite thin films conducted to confirm the presence of ITO and AO. No Al was present in the glass substrate and its primary components were sodium silicate and silicon oxide, as shown in Fig. 5(a). Both In and Sn were observed in AO 0 vol % thin film, as shown in Fig. 5(b), and the observed Si likely originates from the glass substrate. Furthermore, Al was observed in AO 30 and 50 vol % thin films, as shown in Figs. 5(c) and 5(d). The Al-to-In count ratio increased as the amount of AO to ITO increased. The composition of the AO 50 vol % thin film measured using EDS was \( \approx 28 \text{ mol} \% \text{ Al,} \ \approx 67 \text{ mol} \% \text{ In, and} \ \approx 6 \text{ mol} \% \text{ Sn} \), and the Al-to-In volume ratio was roughly 5:18. It was found that the Al-to-In volume ratio becomes small by the difference in the deposit efficiency by AD as compared with the ratio of source particles. X-ray diffraction measurements indicated that ITO was the only crystalline phase present in the films, despite the films containing AO; the only exception was the AO 100 vol % thin film [see Fig. 2(b)].

The distribution of ITO and AO particles in the AO 50 vol % thin film was investigated next. Figure 6 shows an SEM image and elemental mapping for Al and In in the AO 50 vol % thin film. AO and ITO particles were pulverized and distributed over the whole film. However, larger AO particles were observed in areas of charge-up and appear white in Fig. 6(a). It is therefore very strange that no AO diffraction peaks are observed in AO 30–80 vol % thin films (see Fig. 2).

Figure 7 shows the dependence of film thickness on the volume fraction of AO particles for a carrier gas flow rate of 4 L/min and a scan number of 10. The thickness increased with increasing AO volume fraction, up to approximately 50 vol %, and then decreased to approximately 0.5 \( \mu \text{m} \) for the AO 100 vol % thin film. This decrease may be due to a reduction in the ITO volume fraction.
fraction in the aerosol, given the absence of AO in the film. The maximum film thickness is about 10 times that of the AO 0 vol% thin film (only ITO).

We next investigated why the film thickness increases when AO is mixed with ITO. Formation of a thin film requires that the source particle be first pulverized into finer particles on the substrate, resulting in the substrate being simultaneously cleaned and activated by the particle collisions. The crushed particulates are reconstructed into larger particulates at a given condensation energy and a thin film is formed. It was recently reported that fracto-electrons might be emitted from the fractured surfaces of particles generated when a source particle collides with the substrate, with simultaneous activation of the particle surface. The emitted fracto-electrons may form a plasma near the pulverized particles. The pulverized particles again condense due to the combined action of the plasma energy and the particles’ activated state, resulting in the formation of a thin film. When both ITO and AO particles are present in a mixture, both are pulverized simultaneously on the substrate. We speculate that a change in the amount of generated fracto-electrons and/or differences in the plasma state caused by the pulverization of AO particles might enhance particle condensation as compared to when only ITO is present, but this will require further investigation.

**Figure 8** shows the dependence of film resistivity on the volume fraction of ITO for a carrier gas flow rate of 8 L/min and a scan number of 10. The resistivities of the AO 20 and 30 vol% thin films were approximately 2.0 × 10⁻² and 7.7 × 10⁻³ Ω·cm, respectively, while those of the AO 33.3–70 vol% thin films were in the range 3.0–4.4 × 10⁻⁴ Ω·cm. These values are similar to that of the AO 0 vol% thin film. This indicates that in the presence of AO, 1/20th the amount of ITO particles is required to produce a film of the same thickness and resistivity. The resistivity abruptly changes at an ITO volume ratio of 33.3 vol% (AO 66.6 vol% thin film), which is close to the percolation threshold value of 31.17%. However, presently the cause of this abrupt change cannot be attributed to the percolation threshold because the volume ratio of Al to In in the film deviated from that of source material, judging from the EDS results shown in Figs. 5 and 6. **Figure 9** shows photographs of pure AO 0 vol% and AO 30 vol% thin films deposited on PVC with a carrier gas flow rate of 8 L/min and a scan number of 10. The thickness of the AO 0 vol% thin film could not be measured as it was considerably thinner than the AO 30 vol% film (approximately 0.3 μm). Similar to the deposition of thin films on a glass substrate, AO particles assist in the deposition of ITO particles onto PVC. The resistivity of AO 30 vol% thin film deposited on PVC with a carrier gas flow rate of 8 L/min and a scan number of 10 was approximately 1.2 Ω·cm, which is much larger than that for the same film deposited on glass substrate.

**Figure 10(a)** shows the wavelength dependence of the optical transmittance for the AO 66.6 vol% thin film with a thickness of 2.9 μm and of ITO films with thicknesses of 1.0–4.7 μm deposited on glass substrates. The transmittance of a commercially available ITO thin film is also shown. The transmittance of the AO 66.6 vol% thin film is almost the same as that for ITO films with thicknesses of 1.5 and 3.4 μm. The transmittance of the ITO film with a thickness of 0.24 μm is very similar to that of commercially available ITO thin film with a thickness of 0.23 μm. The transmittance was quantified using Lambert’s law:

\[ T = \exp(-\alpha d), \]

where \( \alpha \) is the absorption coefficient and \( d \) is the film thickness. **Figure 9(b)** shows the relationship between \( \alpha \) and wavelength \( \lambda \):

\[ \alpha = A \exp(-\beta / \lambda), \]

where \( A \) and \( \beta \) are constants. The \( \alpha \) value for the film depends on \( \lambda \) and exponentially decreases with increasing \( \lambda \). The \( \alpha \) value for the ITO thin films deposited by AD was approximately 40%
smaller than that for the commercially available ITO thin film, which means that the transmittance of the ITO thin film deposited by AD was higher. This higher transmittance arises from the small Rayleigh scattering coefficient in the visible region for AD-deposited composite thin film due to pulverization of both the AO and ITO source particles to diameters of several tens of nanometers. Although it is generally believed that transparency is affected by the addition of AO particles, given previous reports that thin films deposited using only AO particles have high transparency, we here speculate that AO particles have little effect on the transparency of a composite thin film.

4. Summary

Composite thin films comprising AO and ITO were formed on glass and PVC substrates by AD using aerosol mixtures of ITO and AO particles. The thickness of the film increased with increasing AO volume fraction and reached the maximum value at approximately 50 vol% AO. This maximum value is approximately 10 times higher than that for a pure ITO film. This investigation revealed that approximately 1/20th the amount of ITO particles is required to deposit ITO films using AD compared to conventional methods. The resistivity of the AO 33.3 vol% film was approximately 3.0–4.4 × 10⁻³ Ω·cm, which is similar to that of AO 0 vol% thin film. The absorption coefficient in the visible region of composite films deposited by AD was about 40% smaller than that for commercially available ITO film.

References