Spectroscopic ellipsometry study of the optoelectrical properties of $\text{In}_2\text{O}_3\text{:Sn-ZnO:Al}$ thin films deposited through alternating sputtering

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In this study, indium tin oxide (ITO) and indium zinc oxide (IZO) films were deposited on quartz glass through alternating sputtering. The optical and electrical properties of these films were characterized through spectroscopic ellipsometry (SE). The optical constants of ITO and IZO films were accurately estimated using a model that combined the Tauc-Lorentz, Gauss, and Drude models. However, the estimated resistivity was close to the Hall measurements only when the film thickness was higher than 250 nm. Anisotropy caused by the preferential orientation of crystallites increased the difficulty of the SE fitting process. Furthermore, a k -factor defined on the basis of the estimated optical constants was used to examine the Zn content of the IZO films. Variation in the k -factor was consistent with the band gap of the IZO films.

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1. Introduction

Indium tin oxide (ITO) films are the most functional transparent conductive oxide (TCO) films and are widely used in flat display panels and other optoelectronic devices because of their high transmittance and conductivity and ease of etching.^{1),2)} However, additional studies are necessary for developing TCO films with outstanding optical properties without sacrificing their electrical properties. Multicomponent oxides have received much attention because of their adjustable compositions and structures.³⁾ The electrical properties of amorphous indium zinc oxide (IZO) films are similar to those of ITO films.⁴⁾ Their transmittance is higher in the visible and near-infrared (NIR) region, allowing the use of thicker films and thus reducing sheet resistance. In addition, IZO films have high chemical stability, making them ideal transparent electrodes in thin-film solar cells.^{5),6)} Perkins et al. developed a low-temperature deposition process to fabricate high-mobility IZO films. They demonstrated that adding ZnO enhances the humidity resistance and ameliorates the water-induced degradation of ITO films.⁵⁾ Moreover, Perkins et al. developed a radio frequency (RF)-direct current sputtering method to overcome the problem of color change, and IZO films were successfully applied in copper-indium-gallium-selenide (CIGS), silicon heterojunction, and organic solar cells.⁶⁾

Synowicki⁷⁾ reported that ITO films have complex or gradient microstructures with varying absorption properties and that their optical properties are easily affected by the sputtering and annealing conditions. Therefore, the refractive index and film

thickness of ITO films should be modeled using the Lorentz model and gradient model. Jung⁸⁾ used the Drude and Lorentz models to estimate the optical constant of ITO films sputtered in different conditions and with a two-layer structure to simulate the gradient properties of ITO films. The results showed that the more evident the preferential orientation, the higher the refractive index. However, the extinction coefficient was affected by the crystallinity and carrier concentration. El Rhaleb et al.⁹⁾ analyzed the optical properties of IZO films by using the Drude and Lorentz models and found that the complex refractive index varied significantly as a function of the Zn content. However, spectroscopic ellipsometry (SE) measurements in their study were not performed in the UV region. Talagrand et al.¹⁰⁾ used the Tauc-Lorentz (TL), Drude, and Lorentz models to analyze the influence of RF-sputtering parameters on the optoelectrical properties of amorphous indium-gallium-zinc oxide films. They reported that a basic model, such as the Cauchy model, was adequate for determining film thickness; however, a more precise optical model was necessary to obtain the refractive index, n , and extinction coefficient, k .¹⁰⁾

The fabrication techniques for ITO and IZO films have been well established over the recent decades. Furthermore, SE has been successfully applied to various semiconductor manufacturing processes. However, because of the complexity of TCO materials and the “inverse” problem associated with SE, numerous problems must still be overcome before applying SE to the evaluation of TCO film properties. In this study, the TL model was used to describe the optical properties of amorphous materials, the Gauss model was applied to obtain the optical constant of TCO materials with band gaps, and the Drude model was used to simulate the behaviors of electron gas in the TCO materials. A model combining the TL, Gauss, and Drude models was used to analyze the optical constants of various ITO films for the first time, thereby establishing a robust set of fitting parameters.

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Furthermore, this SE model was applied to estimate the optical constant and resistivity of IZO films. Finally, the Zn content of the IZO films was evaluated using a k -factor defined on the basis of the obtained optical constants.

2. Preparation and characterization

In the first experiment, ITO films were deposited on quartz glass in different conditions (working pressure 5 and 8 mTorr; sputtering power 50, 70, 90, and 110 W; deposition time 200, 400, and 600 s). A 4-inch ITO (In_2O_3 with 10 wt % SnO_2) target was used for RF sputtering. The target and the glass substrate were 5 cm apart. In the second experiment, 4-inch ITO and AZO (ZnO with 2 wt % Al_2O_3) targets were alternatively used during RF sputtering to obtain IZO films of thickness approximately 120 nm on quartz glass. Five cycles of sputtering were conducted for all IZO films. In each cycle, one ITO layer and one AZO layer were sputtered. The composition of the IZO films was controlled by varying the deposition time and power. The targets and the glass substrate were 8.5 cm apart, and the working pressure was 8 mTorr. In both experiments, the substrate temperature was set at room temperature and the flow rate of the Ar gas was set at 40 sccm.

Considering the complex structure of TCO films, Gauss, Drude, and TL models were used to describe the optical behaviors of these materials. The Drude model considers charges as an electron gas in the NIR region and is useful for analyzing the conductivity of degenerate semiconductors such as TCO films. The dielectric function is as follows:¹¹⁾

$$\varepsilon_D(E) = \varepsilon_\infty - \frac{i4\pi\hbar^2}{\rho \left(\frac{\hbar}{E} + i\frac{\tau}{E^2} \right)} \quad (1)$$

where ρ is the electrical resistivity and τ is the mean scattering time. The Gauss model is similar to the Lorentz model but has a shorter working range and is suitable for obtaining the optical constant of semiconductors and TCOs, especially those with band gaps. The imaginary component $\varepsilon_{2,G}(E)$ of this model is given by¹¹⁾

$$\varepsilon_{2,G}(E) = A_G e^{-\left(\frac{E-E_{n,G}}{B_G}\right)^2} + A_G e^{-\left(\frac{E+E_{n,G}}{B_G}\right)^2} \quad (2)$$

where A_G , B_G , and $E_{n,G}$ are the fitting parameters. The Gauss model reduced the mean squared error (MSE) in this study. Furthermore, the TL model was used for describing the optical properties of amorphous materials. The imaginary component $\varepsilon_{2,TL}(E)$ of this dielectric function is described as¹²⁾

$$\varepsilon_{2,TL}(E) = \begin{cases} \frac{A_{TL}E_{0,TL}C_{TL}(E - E_{g,TL})^2}{(E^2 - E_{g,TL}^2)^2 + C_{TL}^2E^2} \cdot \frac{1}{E} & E > E_{g,TL}, \\ 0 & E \leq E_{g,TL}. \end{cases} \quad (3)$$

where A_{TL} , $E_{0,TL}$, $E_{g,TL}$, and C_{TL} represent amplitude, peak positions, band gap, and broadening, respectively. $\varepsilon_{1,G}$ and $\varepsilon_{1,TL}$ can be calculated using the Kramers–Kronig equation. Finally, the dielectric function of the combined model for the fitting process is

$$\varepsilon(E) = \varepsilon_D(E) + \varepsilon_G(E) + \varepsilon_{TL}(E) \quad (4)$$

Experimental data (Ψ and Δ) were measured using a variable angle spectroscopic ellipsometer (M-2000U, Woollam). All SE measurements were conducted in the 245–1000 nm wavelength range at three incident angles (65, 70, and 75°). A least squares fitting method was employed, and MSE was used to evaluate the

Table 1. Thickness and Zn content of IZO films; film thickness was evaluated through SE

Sample	A	B	C	D	E	F	G	H	I
Zn/(In + Zn) [%]	0.0	10.7	11.8	15.5	26.1	59.4	67.0	77.9	100
Thickness [nm]	121.8	127.5	118.5	126.0	127.0	121.2	120.1	119.8	126.7

Fig. 1. Optical band gap $E_{g,opt}$ (triangles), center energy $E_{0,TL}$, and band gaps $E_{g,TL}$ of ITO films versus film thickness. Solid and hollow symbols represent working pressures of 8 and 5 mTorr, respectively; stars, diamonds, circles, and squares represent sputtering at 50, 70, 90, and 110 W, respectively.

fitting quality. All data were analyzed using the CompleteEASE® software package.

The crystal structure of the ITO and IZO films were studied through thin-film X-ray diffractometry (Rigaku D/MAX 2500). Their electrical properties, optical properties, and Zn content were measured using a Hall measurement system (Ecopia HMS-3000), a UV–Vis–NIR spectrophotometer (Jacos V-670), and an energy dispersive spectrometer, respectively (Table 1).

3. Results and discussion

3.1 Basic properties

The XRD patterns (data not shown) of the samples indicated that the crystallinity of all films except the pure AZO sample was low. Crystallinity slightly increased with sputtering power and deposition time and decreased with increase in the working pressure. The crystal structures of the ITO and In-rich IZO films were similar to the cubic structure of In_2O_3 . The crystal structures of other samples were close to the wurtzite structure of zinc oxide. Transmittance of all films exceeded 80% in the visible range; the main differences in the transmittance spectra were in the NIR region. These films exhibited low transmittance in regions with high carrier concentrations. The optical band gaps ($E_{g,opt}$) of the ITO films were located between 3.60 and 3.95 eV (Fig. 1) and increased with conductivity, whereas the $E_{g,opt}$ of the IZO films were located in the 3.30–3.80 eV range and decreased with increasing Zn content (Fig. 3).

3.2 Electrical properties

The electrical resistivity of the majority of ITO films (except for the samples sputtered at 50 W) was $3.0\text{--}4.6 \times 10^{-4} \Omega \text{ cm}$. Similarly, their carrier density and mobility were $4.0\text{--}7.0 \times 10^{20} \text{ cm}^{-3}$ and $29\text{--}35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. In general, conductivity and carrier density increased with film thickness. Resistivity and carrier density was constant beyond 250 nm.

Fig. 2. Resistivity of ITO films obtained through Hall and SE measurements. The triangles indicate Hall measurements. The other symbols are as explained in Fig. 1.

Fig. 3. Optical band gap $E_{g,opt}$ (triangles), center energy $E_{0,TL}$ (circles), band gaps $E_{g,TL}$ (squares), and k -factor (inverted triangles) of IZO films versus Zn content. The variation in k -factor agrees well with that of $E_{g,opt}$.

The electrical resistivity of the IZO films depended on the Zn content and varied from 3.5 to $18.0 \times 10^{-4} \Omega\text{cm}$ as the Zn content increased from 0.0 to 15.5% . When the resistivity exceeded $4.0 \times 10^{-3} \Omega\text{cm}$, the Hall measurement failed occasionally.

3.3 SE analysis

Several assumptions were made before SE fitting: the poles in the UV and IR region and the high-frequency dielectric constant ϵ_∞ were fixed; these poles described the dispersion induced by the absorptions that occur outside the measured spectral range.¹¹⁾

3.3.1 Indium tin oxides

In general, the experimental data (Ψ and Δ) agreed well with the modeled curves. The MSE values of the ITO samples were lower than 6 except for samples deposited at 110 W and 5 mTorr. The preferential orientation of crystallites increased the difficulty of the SE fitting process.^{7),8)} Furthermore, although the positions of refractive index (n_{max}) varied slightly, the extinction coefficient curves were similar. In Fig. 1, the $E_{g,opt}$ of the ITO films are compared with the center energy $E_{0,TL}$ and band gaps $E_{g,TL}$. $E_{0,TL}$ and $E_{g,TL}$ are the fitting parameters of the SE model. $E_{g,TL}$ describes the onset position of the absorption of amorphous materials and was therefore much smaller than $E_{g,opt}$, which represents the direct band gap. On the contrary, $E_{0,TL}$ corresponds to the position of maximum absorption of the amorphous materials. Both $E_{0,TL}$ and its variation were similar to those of $E_{g,opt}$. However, $E_{0,TL}$ variation was more apparent because of the high sensitivity of SE.

The resistivities of the ITO films obtained through Hall and SE measurements are presented in Fig. 2. The majority of the

Fig. 4. Refractive index curves of IZO films derived from the optical model. The position of the maximum refractive index n_{max} of the IZO film moves to the right as In content increases.

Fig. 5. Peak positions of extinction coefficient k move toward the high-energy area with increasing In content. Two positions k_{In} and k_{Zn} were used to define k -factor as k_{In}/k_{Zn} .

samples exhibit similar Hall conductivity, but the resistivities obtained by the two methods differ slightly; these differences are negligible for samples with thickness >250 nm. Given the SE measurement range of 245 – 1000 nm, the low carrier concentration resulted in the failure of the Drude model. Consequently, the measured resistivity was imprecise.

3.3.2 Indium zinc oxides

The experimental data (Ψ and Δ) agreed well with the modeled data. The MSE values for IZO samples were lower than 3. Surface roughness increased from approximately 2.5 to 5.0 nm with increasing Zn content, which is attributable to the occurrence of crystallites in the IZO films. In Fig. 3, the optical band gaps $E_{g,opt}$ of the IZO films are plotted along with the center energy $E_{0,TL}$ and band gaps $E_{g,TL}$. Similar to the ITO films, $E_{g,TL}$ was generally lower than $E_{g,opt}$. However, $E_{0,TL}$ and its variation was similar to $E_{g,opt}$. Moreover, the variation in $E_{0,TL}$ was evident.

The refractive index and extinction coefficient curves of the IZO films are displayed in Figs. 4 and 5. The positions of the maximum refractive index n_{max} of the IZO films are in two groups, as shown in Fig. 4; n_{max} of the Zn-rich samples were located at approximately 3.5 eV and that of the In-rich samples were located at nearly 4.0 eV. With decreasing Zn content, n_{max} shifted toward the high-energy area. Consequently, the peak position of extinction coefficient k also moved toward the high-energy area (Fig. 5). Therefore, two lines, noted as k_{In} and k_{Zn} , are drawn at these two positions of the maximum extinction coefficient k for the ITO film and the AZO film. Then, the two lines intersect with the extinction coefficient curves of the IZO films. In this way, an index factor is defined as $k\text{-factor} = k_{In}/k_{Zn}$.

Fig. 6. Resistivity of IZO films obtained through Hall and SE measurements.

As shown in Fig. 3, k -factor and $E_{g,opt}$ exhibit similar variation trends because the physical phenomena causing these variations are the same; the k -factor can be easily obtained through SE.

The resistivities of the IZO films obtained through Hall and SE measurements are presented in Fig. 6. The resistivities obtained through these two measurements were similar for some In-rich samples, but the differences were obvious for the remaining samples, primarily because of the low conductivity of especially Zn-rich samples, which caused the failure of the Drude model. In addition, variation in the deposition conditions caused changes in the microstructure of the IZO films, thus causing large variations in the SE results.

4. Conclusion

ITO and IZO films were deposited on quartz glass through alternating sputtering of ZnO:Al and In_2O_3 :Sn targets at room temperature. The optoelectrical properties of various ITO films obtained using TL, Gauss, and Drude models were consistent with the measured results. In addition, the optical constants of the IZO films were effectively estimated using the SE model. Moreover, k -factor, an index defined on the basis of the estimated

extinction coefficient curves, was used to examine the Zn content of the IZO films. Variation in the k -factor was consistent with the band gap of the IZO films. In addition, resistivities obtained using SE and Hall measurements were similar for samples with high conductivity, whereas the Drude model for samples with low carrier concentrations failed. An extension of the measured spectrum to the IR region is expected to improve the fitting results.

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