In this study, antimony (6 wt %)-doped tin oxide (ATO) films were prepared on a poly(ether sulphone) (PES) flexible substrate by radio frequency (RF) magnetron sputtering at room temperature, with varying deposition parameters such as RF power and working pressure. The RF power was varied from 50 to 150 W in steps of 25 W. The working pressure was varied from 0.67 to 1.2 Pa in steps of 0.27 Pa at room temperature. The thickness of the deposited ATO films was about 200 nm. The (110), (101), (200), and (211) diffraction peaks were observed for the ATO films deposited with two different conditions. All the samples were found to be crystalline with a cassiterite tetragonal (rutile type) structure that has a preferred orientation in the (101) direction, which is structurally stable and exists mainly in nature. The ATO film deposited at a RF power of 125 W with a working pressure of 0.67 Pa showed the lowest resistivity of 6.9 x 10^{-3} Ω cm, and the optical transmittance was 80.1% in the visible wavelength range from 400 to 800 nm. © 2011 The Japan Society of Applied Physics

### Table I. The experimental process parameters used in this study.

<table>
<thead>
<tr>
<th>Target</th>
<th>SnO_2:Sb (94 : 6 wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>PES</td>
</tr>
<tr>
<td>Target–substrate distance (mm)</td>
<td>60</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>RT</td>
</tr>
<tr>
<td>Working pressure (Pa)</td>
<td>0.67, 0.93, 1.2</td>
</tr>
<tr>
<td>RF power (W)</td>
<td>50, 75, 100, 125, 150</td>
</tr>
<tr>
<td>Film thickness (nm)</td>
<td>200 ± 5</td>
</tr>
</tbody>
</table>

1. Introduction

Transparent conducting oxide (TCO) films have been widely used as a transparent conducting thin-film material for application in various fields such as gas sensors, optoelectronic devices, flat panel displays, heat mirrors, and solar cells.\(^1\)\(^-\)\(^3\) The increased utilization of many transparent electrodes has recently accelerated the development of inexpensive TCO materials. Indium-doped tin oxide (ITO) film is a generally preferred TCO material for these applications owing to its excellent electrical and optical properties.\(^3\) However, its high processing cost is a disadvantage. ZnO film is cheaper than ITO, but it shows poor thermal stability. In contrast, SnO\(_2\) film shows the best thermal and chemical stabilities. Also, it is inexpensive to make and has good mechanical durability, but has a high resistivity. SnO\(_2\) is an n-type semiconductor with a wide band gap of approximately 3.7 eV. Pure SnO\(_2\) films are poor electrical conductors that are highly transparent in the visible range. However, their poor electrical conductivity can be improved by controlling the stoichiometry or doping with impurities. Conductive antimony-doped tin oxide (ATO) films are prepared by various methods such as chemical vapor deposition (CVD), spray pyrolysis, sputtering, and evaporation. Sputtering has advantages among these methods, since film deposition can be carried out at low temperatures, whilst yielding the preferred orientation and uniform properties.

In general, glass is the most commonly selected substrate for all TCO films. However, for future development in flexible devices glass is limited by its intrinsic inflexibility, thickness, and weight characteristics.

In this work, ATO films were deposited on a poly(ether sulphone) (PES) flexible substrate at room temperature by RF magnetron sputtering. The optimization process was performed by varying the sputtering parameters such as RF power and working pressure, and the parameter effects on the structural, electrical, and optical properties of the ATO films were investigated.

2. Experimental Procedure

ATO film was prepared on a PES flexible substrate by using RF magnetron sputtering. The sputtered target was a mixture of SnO\(_2\) (99.99%) and Sb\(_2\)O\(_3\) (99.99%), pressed on a copper saucer with a diameter of 4 in. The content of Sb\(_2\)O\(_3\) added to the SnO\(_2\) target was 6 wt %. The sputtering chamber was evacuated to a base pressure of 0.13 mPa using a turbomolecular pump before the generation of plasma activated by RF power at 13.56 MHz. The two electrodes were placed in parallel. The distance between the target and the substrate was 60 mm. Before the deposition of each film, presputtering was carried out by Ar plasma for 5 min to remove the hydrolyzed surface layer of the target. The flow rate of Ar (99.999%) gas was fixed at 100 sccm by a mass flow controller (MFC). The thicknesses of all the ATO films were kept constant at 200 nm.

The samples were prepared in two different groups. One group was synthesized with varying working pressure in the range from 0.67 to 1.2 Pa with the RF power fixed at 125 W. The other group was synthesized with the RF power varying in the range from 50 to 150 W with working pressure fixed at 0.67 Pa. The experimental process parameters used in this study are shown in Table I.

The surface morphologies of the ATO films were measured using a field-emission scanning electron microscope (FESEM; JEOL JSM-6700F). The crystalline structure of the film was characterized by X-ray diffractometry (Bruker AXS D8 Discover) using Kα radiation in the powder diffraction configuration. X-ray diffraction (XRD) spectra were collected in the 20–80° 2θ range with a measurement step of 0.02°. Sheet resistance was measured by the four point probe (CMT-ST 1000) method. The Hall mobility and the carrier concentration were examined by Hall measurement (ECOPIA HMS-3000). The spectral
transmittance of the film was observed using a UV-spectrophotometer (Hitachi U3000) in the visible wavelength range of 400–800 nm.

3. Results and Discussion

Figure 1 shows a cross-section SEM image of the ATO film deposited at room temperature on a PES flexible substrate at a RF power of 125 W with a working pressure of 0.67 Pa. From the SEM image, the thickness of the deposited ATO film was about 200 nm.

The effects of the working pressure and RF power on the XRD patterns of the ATO films were studied to optimize the growth conditions. Figures 2(a) and 2(b) show the XRD spectra of the ATO films deposited on a PES flexible substrate as a function of the RF power and working pressure, respectively. The (101), (200), and (211) diffraction peaks were observed for the ATO films deposited with two different conditions. All the samples were found to be polycrystalline with a cassiterite tetragonal (rutile type) structure that has a preferred orientation in the (101) direction, regardless of the variation of the RF power or working pressure. The preferred orientation of the (101) direction peak was taken from the Joint Commission for Power Diffraction Standards (JCPDS) data. At different RF powers and at a working pressure of 0.67 Pa, it was observed that the preferred orientation of the (101) direction peak became more intense and sharper with increasing RF power, and the FWHM of the (101) peak decreased [Fig. 2(a)]. This indicates that the crystallinity was improved and the grain size became larger with the increase in the RF power. As shown in Fig. 2(b), at a different working pressure with a RF power of 125 W, the preferred orientation of the (101) direction peak became more intense and sharper with decreasing working pressure, and the FWHM of the (101) peak decreased. This indicates that the crystallinity of the film was improved and the grain size became larger at a lower working pressure. That is, the crystallinity of the ATO films was expected to improve at lower gas pressures by increasing the bombardment of sputtered atoms to the film growing on the substrate. The grain size was estimated from these XRD spectra using the Scherrer equation:

$$D = 0.9 \frac{\lambda}{\beta \cos \theta_B},$$

where $D$ is the grain size, $\lambda$ is the wavelength of the X-rays (1.54178 Å), $\beta$ is the broadening of the diffraction line measured at half its maximum intensity in radians (FWHM), and $\theta$ is the diffractive angle. Figure 3 summarizes the values of the grain size at different RF powers and working pressures.

Figures 3(a) and 3(b) show the grain size of the ATO films deposited on a PES flexible substrate as a function of the RF power and the working pressure, respectively. This supports the XRD spectra results. As the RF power increased from 75 to 150 W, the grain size of the ATO film increased from 15.0 to 22.4 nm. As the working pressure decreased from 1.2 to 0.67 Pa, the grain size of the ATO film increased from 19.4 to 21.9 nm. The surface morphology variation of the films deposited at different RF powers and different working pressures was investigated to confirm the effects of RF power and working pressure on the morphology of the ATO films. Figure 4 shows FESEM images of the ATO films deposited on a PES flexible substrate as a function of the different RF powers with a working pressure of 0.67 Pa and with different working pressures with a RF power of 125 W. From this result, the grain size was observed to increase with the increase in RF power because the increased...
Fig. 3. (Color online) Grain size variation of the ATO films estimated from the Scherrer equation as a function of (a) different RF powers with a working pressure of 0.67 Pa and (b) different working pressures with a RF power of 125 W.

Fig. 4. (Color online) FESEM images of the ATO films deposited on a PES flexible substrate as a function of (a) different RF powers with a working pressure of 0.67 Pa and (b) different working pressures with a RF power of 125 W.

Fig. 5. (Color online) Deposition rate, resistivity, carrier concentration, and Hall mobility of the ATO films deposited on a PES flexible substrate as a function of (a) different RF powers with a working pressure of 0.67 Pa and (b) different working pressures with a RF power of 125 W.
power caused an increase in the energy of the Ar ions when they collided with the target and thus an increase in the surface mobility of the sputtered particles. Also, in the lower working pressure, the mean free paths of the particles in plasma are longer than those at higher working pressures because fewer collisions occur within the plasma.\(^{(3)}\)

Figures 5(a) and 5(b) show the deposition rate, resistivity, carrier concentration, and Hall mobility of the ATO films deposited on a PES flexible substrate as a function of the different RF powers with a working pressure of 0.67 Pa. As shown in Fig. 5(a), as the RF power increased from 50 to 150 W, the deposition rate decreased from 7.14 to 21.2 nm. This is consistent with the previously mentioned results. That is, the number of sputtered SnO molecules at the target surface increases owing to the enhancement of bombardment by Ar ions as the RF power increases and the resulting deposition rate increases. Moreover, the kinetic energy of SnO molecules arriving at the substrate increases with increasing RF power. This can affect the properties of films, such as the surface morphology and crystallinity. As the RF power increased from 50 to 125 W, the resistivity of the ATO films deposited on a PES flexible substrate decreased from 6.9 × 10\(^{-3}\) to 6.9 × 10\(^{-3}\) Ω cm. This result is consistent with the previously mentioned results. That is, the crystallinity was enhanced with higher RF power for film deposition. However, as the RF power increased from 125 to 150 W, the resistivity increased from 6.9 × 10\(^{-3}\) to 14.5 × 10\(^{-3}\) Ω cm. As shown in Fig. 5(b), as the RF power increased from 50 to 125 W, the carrier concentration and Hall mobility were increased from 4.19 × 10\(^{20}\) to 6.62 × 10\(^{20}\) cm\(^{-3}\) and from 0.64 to 1.37 cm\(^2\) V\(^{-1}\) s\(^{-1}\), respectively. The carrier concentration and Hall mobility were increased by the improved crystallinity of the ATO film with increasing RF power, as mentioned previously. Consequently, the resistivity of the films was reduced. This was due to the decrease in carrier scattering attributable to the reduced grain boundaries, so that the mobility was enhanced. As the RF power increased from 125 to 150 W, the change in carrier concentration was not obvious. However, the Hall mobility rapidly decreased from 1.37 to 0.65 cm\(^2\) V\(^{-1}\) s\(^{-1}\). This is supported by the FESEM analysis of the surface morphology of the ATO film deposited on a PES flexible substrate as described below. As shown in Fig. 6, the resistivity of the films increased with increasing RF power above 150 W because of the decrease in the surface mobility due to the surface cracking and fracture of the PES flexible substrate.

Figures 7(a) and 7(b) show the deposition rate, resistivity, carrier concentration, and Hall mobility of the ATO films deposited on a PES flexible substrate at a working pressure of 0.67 Pa with a RF power of 125 W. In Fig. 7(a), as the working pressure decreased from 1.2 to 0.67 Pa, the deposition rate of the ATO film increased from 14.7 to 16.6 nm. That is, the decrease in the deposition rate at higher pressures is due to the increased number of collisions between the sputtered particles and the Ar atoms. Therefore, the deposition rate decreased, since the number of sputtered particles reaching the substrate was reduced.\(^{(1)}\) As the working pressure decreased from 1.2 to 0.67 Pa, the resistivity of the ATO films deposited on the glass substrate decreased from 9.7 × 10\(^{-3}\) to 6.9 × 10\(^{-3}\) Ω cm. Moreover, in Fig. 7(b), as the working pressure decreased from 1.2 to 0.67 Pa, the carrier concentration and Hall mobility increased from 5.47 to 6.62 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and from 1.18 × 10\(^{20}\) to 1.37 × 10\(^{20}\) cm\(^{-3}\), respectively. The change in FWHM reflects the change in the grain size of crystallites, that is, the decrease in FWHM corresponds to the increase in grain size. Therefore, the increment of Hall mobility with decreasing working pressure can be ascribed to the increase in grain size, namely, the decrease in the grain boundary.\(^{(17)}\)
This causes a decrease in scattering centers for the carriers, giving a low electrical resistivity. Note that the resistivity ($6.9 \times 10^{-3} \Omega \text{cm}$) for the ATO film deposited at room temperature in this work stands in comparison with that of ITO films\(^{[18]}\) and is better than that of ATO films from other groups\(^{[16,19]}\) deposited at room temperature by RF sputtering.

Figures 8(a) and 8(b) show the optical transmittance in the visible wavelength range from 400 to 800 nm of the ATO films deposited on a PES flexible substrate as a function of the RF power and working pressure, respectively. As shown in Fig. 8(a), the maximum average optical transmittance of the ATO films deposited on a PES flexible substrate with a RF power of 125 W and a working pressure of 0.67 Pa can reach up to 80.1% in the visible wavelength range. This implies that the transmittance in the visible wavelength range of the film is closely related to the film structure. Moreover, the surface morphology also affects the film transmittance. When the grain size increases, light is less scattered by decreasing grain boundaries.

4. Conclusions

In this study, antimony-doped tin oxide (SnO\(_2\):Sb, ATO) films were deposited on a poly(ether sulfone) (PES) flexible substrate by RF magnetron sputtering utilizing a commercial ceramic target with a mixture of SnO\(_2\) and Sb (6 wt%). The optimization process was performed by varying the sputtering parameters, such as RF power and working pressure, and the parameter effects on the structural, electrical, and optical properties of the ATO films were investigated. Crystallinity improved with an increase in the RF power and a decrease in the working pressure. The change in FWHM reflects the change in the grain size of crystallites. That is, a decrease in FWHM corresponds to an increase in grain size. Moreover, the higher RF power improves the structural properties of the film and leads to an improvement in Hall mobility by increasing the crystallinity of the film. The increment of mobility with decreasing working pressure can be ascribed to the increase in grain size, namely, the decrease in the grain boundary. Consequently, the resistivity of the films was reduced owing to the decrease in carrier scattering attributable to the reduced grain boundaries, and therefore the mobility was enhanced. At a RF power of 125 W and a working pressure of 0.67 Pa, an ATO film deposited on a PES flexible substrate with an electrical resistivity of $6.9 \times 10^{-3} \Omega \text{cm}$ and an average optical transmittance of 80.1% in the visible wavelength range was obtained.

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