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Effect of Target Density on Microstructural, Electrical, and Optical Properties of Indium Tin Oxide Thin Films

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In this paper, indium tin oxide (ITO) targets with different densities were used to deposit ITO thin films. The thin films were deposited from these targets at room temperature and annealed at 750°C. Microstructural, electrical, and optical properties of the as-prepared films were studied. It was found that the target density had no effect on the properties or deposition rate of radiofrequency (RF)-sputtered ITO thin films, different from the findings for direct current (DC)-sputtered films. Therefore, when using RF sputtering, the target does not require a high density and may be reused.

Key words: Indium tin oxide, target density, thin film

INTRODUCTION

Indium tin oxide (ITO) thin films have been extensively utilized in the electronic and optoelectronic industries for many applications such as solar cells, flat-panel displays, surface heaters for automobile windows, and transparent heat-reflecting window material for buildings, lamps, and solar collectors, due to their high electrical conductivity combined with high transmission in the visible region.[1–3] There are many deposition techniques for ITO films, such as direct current (DC) or radiofrequency (RF) sputtering, reactive evaporation, sol–gel process, and chemical vapor deposition.[4–6] However, the most frequently used deposition technique is RF magnetron sputtering, which provides high deposition rates, large deposition areas, and less damaged areas. Compared with the DC sputtering method, RF sputtering can be used to deposit thin films with lower surface roughness. It is also applicable to nonconducting targets.[7,8]

The electrical, optical, and microstructural properties of RF-sputtered ITO films are sensitive to sputtering parameters: total sputtering pressure, oxygen content in the sputtering gas, target-to-substrate distance, substrate temperature, deposition rate, postdeposition treatment, and target quality.[6,8,9] It was reported that an increase in target density could lead to a slight decrease in the resistivity of DC-sputtered ITO films. This may have led to the common belief that the target should be as dense as possible for high-quality ITO films.[3,9,10] So, there is an active demand for commercial ITO targets with density above 99% of theoretical density (TD) for DC or RF sputtering processes. Surprisingly, the effect of target density has not been systematically studied for RF-sputtered ITO films. In this paper, the effect of target density on the properties of RF-sputtered ITO films was studied. All the ITO films were grown by RF magnetron sputtering using the same sputtering parameters except for the target density.

EXPERIMENTAL PROCEDURES

Sintering or annealing at high temperature can generate ITO films with low sheet resistance.[7,8] However, in most cases, the substrate material is soda lime silica glass, which often cannot tolerate temperatures above 600°C. In this study, quartz glass, which can endure high annealing temperature over 1100°C, was used as substrate material. All samples were annealed to 750°C to reduce the sheet resistance.

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ITO thin films were deposited by RF sputtering at room temperature, using ITO targets with 55.0% (ρ_0), 65.3% (ρ_1), 90.4% (ρ_2), 98.8% (ρ_3), and 99.7% (ρ_4) of the TD of this material (7.15 g/cm^3).

ITO raw powders with 90 ± 3 nm or 40 ± 3 nm particle size used to prepare the targets were synthesized using a low-pressure urea-based hydrothermal method.[11] The ITO ceramic targets (ρ_1 to ρ_4) with diameter of 65 mm and thickness of 5 mm were sintered at 1200°C to 1350°C using the mixture of the above ITO powders with weight ratio of $w_{90\text{nm}}$:$w_{40\text{nm}}$ = 70:30. The ρ_1, ρ_2, ρ_3, and ρ_4 targets were obtained by sintering at 1200°C, 1250°C, 1300°C, and 1350°C, respectively.[11] The target ρ_0 was a green pellet of the mixed ITO powders formed by a cold isostatic pressing process without sintering.

ITO films with thickness of 300 nm were deposited at room temperature and annealed at 750°C. The ITO target was placed about 5 cm away from the substrate. The base pressure of the vacuum chamber was maintained to be less than 1×10^{-3} Pa by using mechanical and oil diffusion pumps before deposition. The sputtering power was 100 W. Sputtering was carried out in argon atmosphere at pressure of 0.5 Pa.

Various techniques were employed to measure the properties of the ITO films. The crystalline structure and phase were investigated by using x-ray diffraction analysis (XRD, Rigaku Geigerflex D/Max 2200) using Cu K_α radiation. The morphologies of surface and cross-section were observed by scanning electron microscopy (Hitachi S-4100, Japan). The surface morphology was also studied by using atomic force microscopy (AFM, SPA-300 HV). The sheet resistance was measured by using a CMT-ST1000 four-point probe. The Hall mobility and free carrier density were estimated using Hall-effect measurements (HMS-3000, ECOPIA). The spectral transmittance was measured by using a Hitachi U 3000UV spectrophotometer in the visible wavelength range of 300 nm to 800 nm.

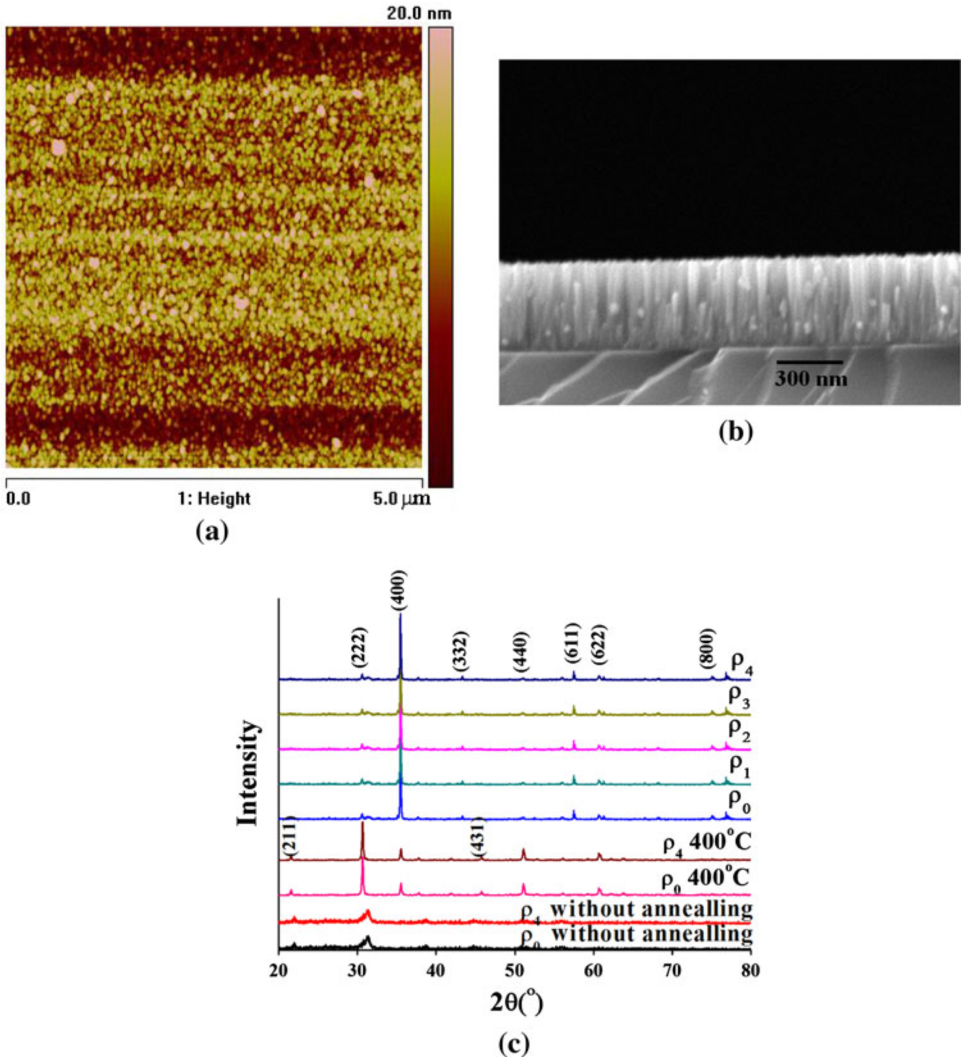
RESULTS AND DISCUSSION

All the sintered targets had grain sizes of 100 nm to 400 nm and average grain size of ~150 nm. All the ITO films prepared from different density targets had the same surface roughness of 4.65 nm. Representative AFM and SEM images are shown in Fig. 1a, b, for a film deposited using the ρ_0 target. Figure 1c shows that the XRD spectra of the as-prepared thin films using different density ITO targets had similar peak positions and widths, corresponding to cubic In_2O_3 (JCPDS 6-0416). As shown in Fig. 1c, there are no characteristic peaks of Sn, SnO or SnO_2, meaning that all tin atoms were incorporated substitutionally into the In_2O_3 lattice. It is therefore concluded that the morphology, surface roughness, and phase of thin films are not affected by the density of the target. Furthermore, the deposition rate estimated from the thickness of the film was also unaffected by the target density.

Figure 2 shows the variation of film resistivity, carrier concentration, and Hall mobility as a function of target density. All the ITO films deposited from different targets had resistivity of 1.56×10^{-4} Ω cm, and their resistivity, mobility, and carrier concentration did not depend on the target density. This result is different from that reported by Utsumi et al.,[9] who prepared ITO films by using the DC magnetron sputtering method. They found that an increase in target density led to a decrease in discharge voltage and thus a slight increase in carrier concentration and then a slight decrease in resistivity.[10] However, DC magnetron sputtering requires a relatively high process voltage to maintain the discharge through secondary electron emission at the cathode. On the other hand, RF magnetron sputtering requires a lower discharge voltage than DC magnetron sputtering because ionization from RF magnetron sputtering is affected mainly by electrons that perform oscillatory motion in the plasma. In the case of the RF sputtering process, the target density has little effect on the discharge voltage, as monitored using the displays of the power supplies. The optical transmittance spectra of ITO films prepared with the different density targets are shown in Fig. 3. It can be seen that their transmittance spectra are similar, with average transmittance of 87% in the visible spectrum.

Although the target density has little effect on the above properties of the RF-sputtered ITO thin films, increase of the target density is beneficial for decreasing target nodules. After an ITO target is sputtered for a long period of time, many black spots, called nodules, are formed at the target surface near the center of the erosion racetrack.[12] As nodules grow and the nodule density increases, the sputtering system must be shut down to clean or replace the ITO target. If the target is prepared by sintering of powder (such as for targets ρ_1 to ρ_4), the waste ITO target has to be redissolved to prepare ITO powders. However, if the target is prepared by compressing powder (such as for target ρ_0), the waste ITO target can be easily cleaned away the nodules, which can then be used to remake a target by adding some ITO powder without affecting the film properties.

It should be noted that all the as-deposited ITO thin films in this work have (400) preferred orientation. For comparison, films deposited using the ρ_0 and ρ_4 targets were also annealed at 400°C. The films without annealing and the films annealed at 400°C had (222) preferred orientation, in agreement with previous studies.[6–8] This difference in orientation can be related to the stress of the ITO films affected by the thermal energy.[7,8] The annealing process seems to reduce the stress of the as-deposited films, and a higher temperature can lead to the orientation in the (400) direction. It has been reported that the (400) peak intensity is related to



(a)

(b)

(c)

Fig. 1. Properties of the as-sputtered and annealed ITO thin films: (a) AFM, (b) cross-section SEM, and (c) XRD.

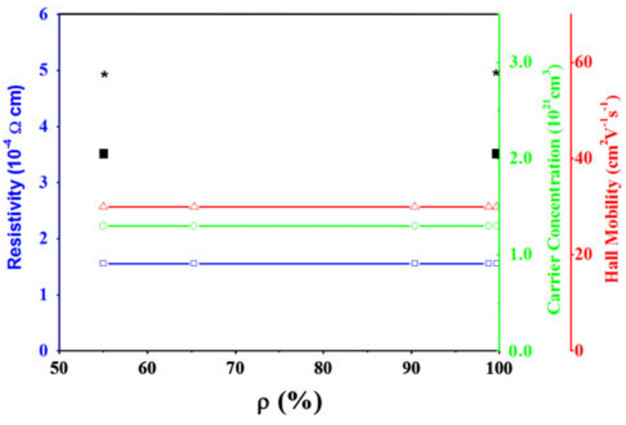


Fig. 2. Electrical properties of the ITO films as a function of target density (□, resistivity; ○, carrier concentration; △, Hall mobility; ■, resistivity at 400°C; *, resistivity of film without annealing).

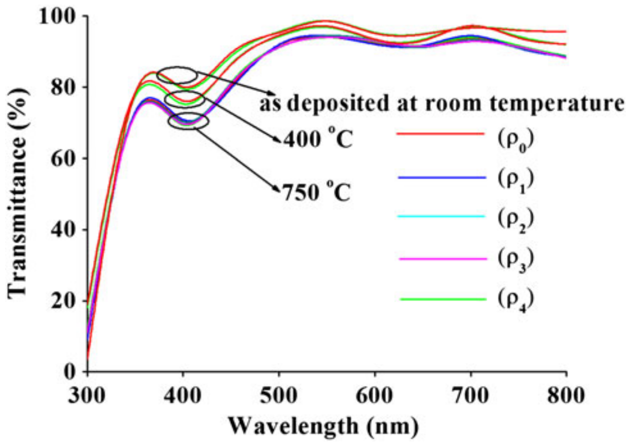


Fig. 3. Transmittance spectra of as-prepared and annealed ITO films from different density targets.

the number of oxygen deficiencies in the ITO films, and a strong (400) peak is good for the electrical properties but not for the optical properties of ITO films due to the greater number of vacancies and higher carrier concentration.[7] Therefore, the as-prepared ITO films annealed at 750°C had lower resistivity than those annealed at 400°C and those without annealing (Fig. 2). However, the transmittance of the as-prepared ITO films annealed at 750°C was found to decrease slightly, as compared with the film annealed at 400°C and those without annealing (Fig. 3). Thus, our results suggest that the electrical and optical properties of as-prepared ITO thin films are not affected by the target density, but strongly affected by the postannealing process and annealing temperature.

CONCLUSIONS

The properties of ITO thin films deposited from targets with different densities were systematically studied. It was found that the target density has no effect on the deposition rate or microstructural, electrical, and optical properties of the ITO thin films prepared by the RF sputtering method, although it has an effect on target nodule formation. Moreover, a correlation between the properties and the annealing temperature was observed. Increasing the annealed temperature could decrease both the resistivity and the transmittance.

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