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Ta-doped In_2O_3 transparent conductive films with high transmittance and low resistance

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Ta-doped In_2O_3 transparent conductive oxide (TCO) thin films are deposited on glass substrates by radio-frequency (RF) sputtering at room-temperature. The influence of sputtering power on the structural, morphologic, electrical, and optical properties of the films is investigated by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), Hall measurement, and optical transmission spectroscopy. The obtained films are polycrystalline with a cubic structure and preferentially oriented in the (222) crystallographic direction. The minimum resistivity of 2.8×10^{-4} Ωcm is obtained from the film deposited at the sputtering power of 170 W. The average optical transmittance of the films is over 90%.

Keywords: sputtering, In_2O_3, transparent conductive oxide, thin films.

1. Introduction

Transparent conductive oxide (TCO) thin films have received much attention because of their wide applications in the fields of thin-film solar cells, flat panel displays, and defrosters [1–5]. With the development of these optoelectronic devices, pursuing of novel TCO materials with improved electrical and optical properties which may contribute to better device performances is continuing [6–10]. Many different methods, such as radio frequency (RF) sputtering, direct current (DC) sputtering, magnetron sputtering, spray pyrolysis, chemical-vapor deposition (CVD), pulsed laser ablation (PLA), sol–gel, reactive thermal evaporation, and ion plating, have been used for the preparation of TCO films [11–15]. Among these, RF sputtering has gained special focus owing to the good product quality and high yield. Extensive scientific and technological efforts have been made in this technique, aiming at improving the transmittance and conductance of the films. In_2O_3 is a widely used metal oxide for TCO films, and doping metals in In_2O_3 target (which is used in RF sputtering) can

effectively increase the conductivity of these films. Among many doping metals, Ta seems to be a promising one because the radius of Ta^{5+} is closer to, as well as being smaller than that of In^{3+} in comparison to other impurities, and only small In_2O_3 lattice deformations are caused even if high concentrations of Ta are introduced. Up to now, only the magnetron sputtering has been used to prepare Ta-doped In_2O_3 films [16, 17]. No reports on preparation and characteristic of Ta-doped In_2O_3 by RF sputtering have been exposed.

In this paper, Ta-doped In_2O_3 films have been deposited on glass substrates by using the RF sputtering, and their crystalline structure and surface morphology have been studied. The Ta-doped In_2O_3 films exhibit low resistance and high transmission in our optoelectronic investigations, indicating their potential applications in TCO thin films.

2. Experiment

Ta-doped In_2O_3 films were deposited on the conventional glass substrates by a RF sputtering system at room temperature. The high purity Ta_2O_5/In_2O_3 (99.99%) target was used in our experiments. The percentage of Ta_2O_5 in the target was 4 wt%. The target-to-substrate distance was kept as 6 cm. Before sputtering, the vacuum chamber was evacuated down to a base pressure of 1.0×10^{-3} Pa. High purity (99.999%) Ar and (99.999%) O_2 were introduced through separate mass flow controllers. The total pressure during sputtering was maintained at 0.9 Pa, and the Ar/O_2 ratio was 15:1. Before deposition, the target was pre-sputtered in Ar + O_2 atmosphere for 20 min to remove any impurity on the surface of the target. The sputtering power was varied from 100 to 210 W.

X-ray diffraction (XRD) analysis was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Field emission scanning electron microscopy (FE-SEM) images were performed on a JEOL JEM-6700F microscope equipped with energy dispersive X-ray (EDX) spectroscopy. The film thickness was measured by a step profiler (AMBIOS Technology INC XP-2). Hall effect measurements were carried out in the Van der Pauw configuration with indium ohmic electrodes by Bio-Rad Microscience HL5500 Hall System at 25 °C. The optical transmission measurements were measured with a spectrophotometer (UV-1700, SHIMADZU).

3. Results and discussion

The Ta content in the films is about 4.7 wt%, as determined by EDX, which is higher than that in the target. The film thickness is measured to be about 300 nm. Figure 1 shows the XRD patterns of Ta-doped In_2O_3 films deposited at different sputtering powers, in which peaks corresponding to the cubic phase of bixbyite-type In_2O_3 can be easily identified and no other impurity phases are observed. The radii of In^{3+} and Ta^{5+} are 0.081 and 0.073 nm, respectively, thus the doped tantalum ion can substitute

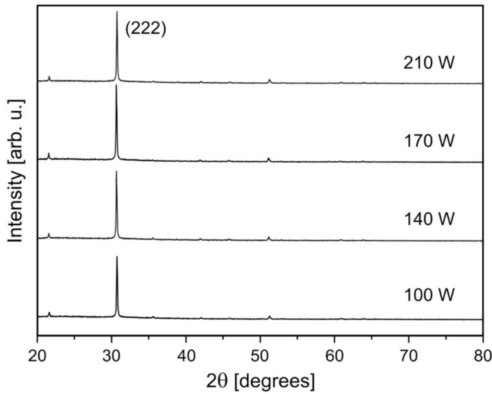

Fig. 1. XRD patterns of Ta-doped In_2O_3 films deposited at different sputtering powers.

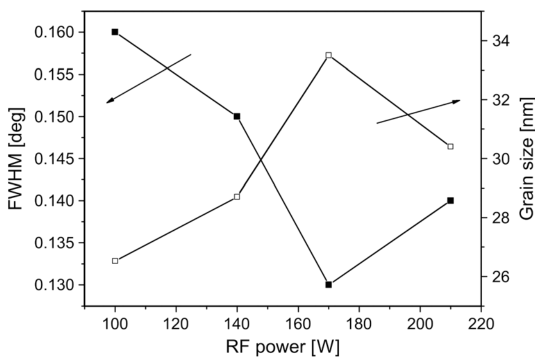

Fig. 2. FWHM of (222) XRD peak and the grain size of Ta-doped In_2O_3 films deposited at different powers.

indium site in the lattice of In_2O_3. No peaks corresponding to Ta_2O_5 are observed, indicating that tantalum gets incorporated into the In_2O_3 lattice. The maximal diffraction intensity of the (002) peak is obtained from the film deposited at the sputtering power of 170 W.

To assess the quality of the Ta-doped In_2O_3 thin films, the full-width at half--maximum (FWHM) values of (002) peak and the crystallite dimension are estimated according to Scherrer formula (Fig. 2) [18]

$$t = \frac{0.9\lambda}{\beta \cos \theta}$$

where λ is the X-ray wavelength, β is the full-width at half-maximum of the (222) diffraction line, and θ is the diffraction angle of the XRD spectra. With the power increasing, the FWHM first decreases and then increases and reaches its minimum value of 0.25° at the power of 170 W. The grain size along the *c*-axis is about 26.5, 28.7, 33.5, and 30.4 nm for the samples deposited at the power of 100, 140, 170, and 210 W, respectively.

The FE-SEM images of Ta-doped In_2O_3 film deposited at different sputtering powers are shown in Fig. 3. The morphology of In_2O_3 grains is found to be continuous and dense. The crystallite size increases by elevating the sputtering power from 100

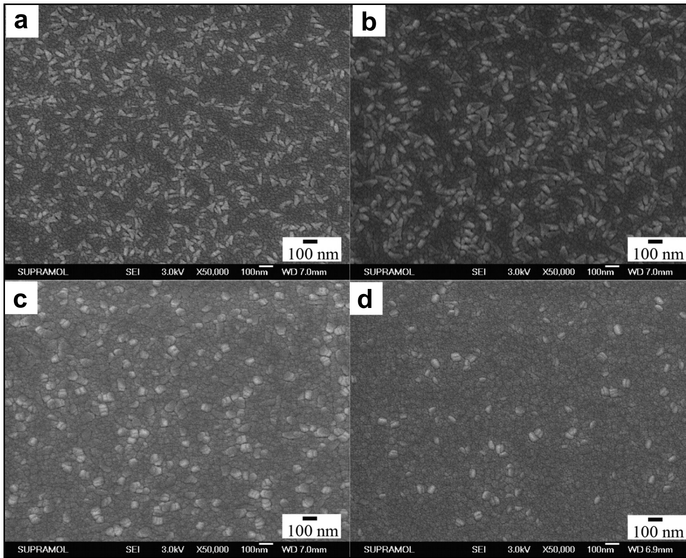

Fig. 3. FE-SEM image of Ta-doped In_2O_3 film deposited at 100 W (**a**), 140 W (**b**), 170 W (**c**), and 210 W (**d**).

to 170 W (Figs. 3**a**–3**c**). This is because the ions or ion clusters can obtain more energy prior to collision with the substrates [19]. The ions or ion clusters with higher energy can easily adjust their own bond direction and length so that they obtain optimum bonding to the adjacent atoms, and this helps them to nucleate and grow up. Some aggregation growths can be found when the power is relatively low (Figs. 3**a** and 3**b**), which is because the ions or ion clusters cannot obtain enough energy to separate. When the sputtering power increases too much (Fig. 3**d**), the grain size of the Ta-doped In_2O_3 film decreases. It is speculated that with high sputtering power, the atoms have more opportunities to reach the substrates and increase the probability of forming nuclei [20]. More nuclei existing on the substrate implies more sites for grain growth. It means that a large number of small grains can grow simultaneously and finally result in small grain structure. All these results are consistent with the XRD observations.

The variation of electrical resistivity ρ, carrier concentration n, and Hall mobility μ as a function of RF power is shown in Fig. 4. The results show that all the films are degenerate doped n-type semiconductors. The resistivity is found to decrease with increasing the RF power from 100 to 170 W. The lowest resistivity of 2.8×10^{-4} Ωcm is obtained for the film deposited at 170 W. When the sputtering power is higher than 170 W, Hall mobility and carrier concentration begin to decrease, and thus the resistivity increases accordingly. These behaviors can be explained as follows [21] – the sputtered species has low surface mobility on the substrate at low sputtering power, which results in degraded crystallinity and few Ta substitutions, thus the film has low Hall mobility and carrier concentration. With the sputtering power increasing, the species kinetic energy increases, which improves the film crystallinity

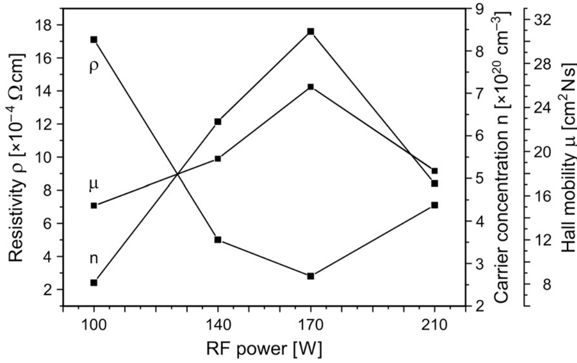

Fig. 4. Resistivities ρ, carrier concentrations n, and Hall mobility μ as a function of sputtering power.

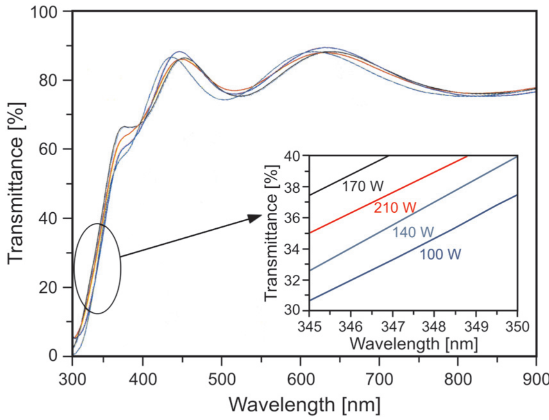

Fig. 5. Transmittance spectra for Ta-doped In_2O_3 films deposited at different sputtering powers.

and Ta substitution. At 170 W, the Hall mobility and carrier concentration reach the maximum value. As the sputtering power further increases, due to large mobile energies of the sputtered species, some species will be rebounded when colliding with the substrate, leading to the degradation of the film crystallinity, so Hall mobility and carrier concentration decrease, finally resulting in the decrease in resistivity of the Ta-doped In_2O_3 films.

A comparison of the transmittance of films prepared at different sputtering powers is shown in Fig. 5. The average optical transmittance of these films is over 90%, and no significant optical differences can be observed among them. The optical gap E_g of the films can be obtained by plotting $\alpha^2 \sim hv$ (α is the absorption coefficient and hv is the photon energy) and extrapolating the straight line portion of this plot to the energy axis. The obtained optical gap for these samples is about 3.83, 3.87, 3.91, and 3.85 eV for the films deposited at 100, 140, 170, and 210 W, respectively. These results are larger than that of undoped In_2O_3 (~ 3.75 eV), which is due to the Burstein–Moss effect [22]. The optical bandgap is closely related to the carrier concentration.

4. Conclusions

In summary, TCO thin films of Ta-doped In_2O_3 are deposited on conventional glass substrates at room temperature by RF sputtering. The influence of sputtering power on the structural, morphologic, electrical, and optical properties of the films is investigated. The as-deposited films are polycrystalline with the cubic phase of bixbyite and have a preferential orientation of (222) to the substrates. The XRD and SEM results suggest that the crystallite size of our films is found to increase by elevating the sputtering power from 100 to 170 W, and then decreasing from 170 to 210 W. The minimum resistivity of 2.8×10^{-4} Ωcm is obtained at 170 W, and the average optical transmittance between 500–800 nm is over 90%. These results suggest that Ta-doped In_2O_3 films are good candidates to fabricate high performance TCO films in practice.

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