Influence of post-annealing on the properties of Ta-doped In$_2$O$_3$ transparent conductive films

XU Lei$^{1,2}$, WANG Rui$^{1,2,*}$, LIU Yong$^1$, ZHANG Dan$^1$ & XIAO Qi$^1$

$^1$Key Laboratory of Composite Materials, Tianjin Polytechnic University, Tianjin 300160, China; $^2$School of Textiles, Tianjin Polytechnic University, Tianjin 300160, China

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Ta-doped In$_2$O$_3$ transparent conductive oxide films were deposited on glass substrates using radio-frequency (RF) sputtering at 300°C. The influence of post-annealing on the structural, morphologic, electrical and optical properties of the films was investigated using X-ray diffraction, field emission scanning electron microscopy, Hall measurements and optical transmission spectroscopy. The obtained films were polycrystalline with a cubic structure and were preferentially oriented in the (222) crystallographic direction. The lowest resistivity, $5.1 \times 10^{-4} \Omega \text{cm}$, was obtained in the film annealed at 500°C, which is half of that of the un-annealed film ($9.9 \times 10^{-4} \Omega \text{cm}$). The average optical transmittance of the films was over 90%. The optical bandgap was found to decrease with increasing annealing temperature.

Transparent conductive films, transparent semiconductors, Hall measurement, optical bandgap, radio-frequency sputtering

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exceptionally large deposition area, and allows for uniform in film morphology, thickness and compaction. Moreover, it works with an especially diversified range of material compositions [16]. In this paper, we prepare Ta-doped In$_2$O$_3$ films on glass substrates using RF sputtering at 300°C, and then post-treat them at various annealing temperatures. Through this process, we explore the effect of post-annealing on TCO film properties and the effects of metal additives on the electric performance. The dependence of the structural, morphologic, electrical and optical properties of the Ta-doped In$_2$O$_3$ films on this post-annealing was then characterized.

1 Experimental

Ta-doped In$_2$O$_3$ films were deposited on conventional glass substrates (7105) using an RF sputtering system (JZCK-IVB, Shenyang, China) at 300°C. A commercially available, sintered ceramic 4 wt% Ta$_2$O$_5$-doped In$_2$O$_3$ target of 99.999% purity and 54 mm in diameter was employed as the source material. The target-to-substrate distance was kept at 6 cm. Before sputtering, the vacuum chamber was evacuated 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 target was pre-sputtered in an Ar+O$_2$ atmosphere for 20 min to remove any impurities on the surface of the target. The deposition power was fixed at 150 W at a frequency of 13.56 MHz. The total pressure during sputtering was maintained at 1.0 Pa, and the Ar/O$_2$ ratio was 12:1. The substrate temperature was held at 300°C. About 20 min after deposition, the glass substrates with Ta-doped In$_2$O$_3$ films were post-annealed in the temperature range, 400–600°C, for 30 min in a N$_2$ (99.99%).

X-ray diffraction (XRD) analysis was conducted using a Rigaku D/max-2500 X-ray diffractometer with Cu K$_\alpha$ radiation ($\lambda$=1.5418 Å, Tokyo, Japan). Field emission scanning electron microscopy (FE-SEM) images were taken on a JEOL JEM-6700F microscope (Tokyo, Japan) equipped with energy dispersive X-ray (EDX) spectroscopy. The film thickness was measured using a step profiler (AMBIOS Technology INC XP-2, Santa Cruz, CA, USA). Hall-effect measurements were performed in the Van der Pauw configuration with indium ohmic electrodes using a Bio-Rad Microscience HL5500 Hall System (Hercules, CA, USA) at room temperature (25°C). The optical transmission measurements were measured using a spectrophotometer (UV-1700, Shimadzu, Kyoto, Japan).

2 Results and discussion

Using EDX, we determined that the Ta content in the films is about 5.28 wt%, which is higher than that in the target. The film thickness was measured to be about 300 nm. Figure 1 shows the XRD patterns for Ta-doped In$_2$O$_3$ films before and after annealing at different temperatures. All of the diffraction peaks could be indexed to cubic In$_2$O$_3$ with a lattice constant of $a=1.011$ nm (JCPDS card no. 06-0416) [3]. No peaks corresponding to Ta$_2$O$_5$ are observed, which suggests that the tantalum may have been incorporated into the In$_2$O$_3$ lattice. The radius of In$^{3+}$ and Ta$^{5+}$ are 0.081 and 0.073 nm, respectively. Thus, the doped tantalum ions can replace the indium atoms in the lattice. Note that the (222) peak becomes more intense and narrower with increasing annealing temperature, which indicates enhancing film quality.

To quantitatively assess the film quality, the full-width at half-maximum (FWHM) values of the (222) peak and the crystallite dimension were estimated according to Scherrer’s formula [17], $t = 0.9\lambda/\beta \cos \theta$, where $\lambda$ is the X-ray wavelength, $\beta$ is the full-width at half-maximum of the (222) diffraction line, and $\theta$ is the diffraction angle of the XRD spectra (Figure 2). The FWHM values are 0.261°, 0.253°, 0.219° and 0.21° for the Ta-doped In$_2$O$_3$ films before and after annealing at 400°C, 500°C and 600°C, respectively.

Figure 1 XRD patterns for the Ta-doped In$_2$O$_3$ films before and after annealing at different temperatures.

Figure 2 FWHM of the (222) XRD peak and the grain size of Ta-doped In$_2$O$_3$ films before and after annealing at various temperatures.
The corresponding crystallite dimensions are about 31.4, 32.6, 37.1 and 40.8 nm, respectively.

Figure 3 shows the surface morphologies of the Ta-doped In$_2$O$_3$ films before and after annealing at 400°C, 500°C and 600°C. The obtained grains were continuous and dense. The crystallite sizes were found to increase with increasing annealing temperature, which agrees with the XRD results. This is because the ions or ion clusters have more energy at high annealing temperature, which increases their mobility allowing the adjustment of their bond direction and length [18]. This allows the grain size to increase and improve the film crystallinity.

Figure 4 shows the variation in resistivity, carrier concentration and Hall mobility as a function of the annealing temperature for the Ta-doped In$_2$O$_3$ films. The results showed that all the films were degenerate doped n-type semiconductors. Compared with original film, the annealed films exhibit increased conductivity. The lowest resistivity, $5.1 \times 10^{-4}$ Ω cm, was measured in the film that was post-annealed at 500°C. This is half of the value of that of the un-annealed film ($9.9 \times 10^{-4}$ Ω cm). The effect of post-annealing on film resistivity can be explained by considering both the total change in the carrier concentration and mobility. The mobility increases with increasing annealing temperature. This finding is in accordance with the measured improvement in the film crystallinity [19]. However, the carrier concentration was found to decrease. This is because there was more un-oxidized In in the film, which can be transformed to In$_2$O$_3$ at high annealing temperatures. Moreover, the corresponding increase in O concentration is favorable for the formation of Ta$_2$O$_5$, which contributes to the decrease in carrier concentration [19].

Figure 5 shows the transmittance of the Ta-doped In$_2$O$_3$ films before and annealing at various temperatures. All of the films have a high optical transmittance with average of 85% over a significant portion of the visible wavelength spectrum (500–800 nm) for the films and the glass substrates. This corresponds to over 90% for the Ta-doped In$_2$O$_3$ films when 90% average glass substrate transmission is accounted for. As the annealing temperature increases, the absorption edge shifts to longer wavelengths, which is known as the Burstein-Moss shift [20].

The optical bandgap ($E_g$) of the films can be obtained by plotting $\alpha^2$-hv (α is the absorption coefficient and hv is the photon energy). Then, we extend plot to the energy axis through extrapolation of its linear component of this plot [11]. The optical bandgaps were 3.91, 3.86, 3.85 and 3.82 eV for Ta-doped In$_2$O$_3$ films before annealing and after annealing at 400, 500 and 600°C, respectively (Figure 6). The obtained optical bandgaps for these films were larger than that of undoped In$_2$O$_3$ (3.75 eV) because of the Burstein-Moss effect [20]. The variation in the optical bandgap is closely related to the carrier concentration.

3 Conclusions

In conclusion, Ta-doped In$_2$O$_3$ films were deposited on
glass substrates at 300°C by RF sputtering. The effects of post-annealing on the structural, morphologic, electrical and optical properties of the films were investigated. The deposited films were polycrystalline with a bixbyite cubic phase and a preferential orientation of [222] with respect to their substrates. The lowest resistivity, $5.1 \times 10^{-4}$ Ω cm, was measured in the film post-annealed at 500°C. This is half of the value of that of the un-annealed film ($9.9 \times 10^{-4}$ Ω cm). The average optical transmittance of the films was over 90% over the range between 500–800 nm. The optical bandgap was found to decrease with increasing annealing temperature. The results revealed that post-annealing can be used to improve the properties of In$_2$O$_3$-based TCO films. We also demonstrated the potential application of Ta-doped In$_2$O$_3$ films for fabricating high performance TCO films.

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