Effects of dopant content on optical and electrical properties of In2O3: W transparent conductive films

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Effects of dopant content on optical and electrical properties of In_2O_3: W transparent conductive films

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Abstract

The In_2O_3: W (IWO) films with different W content were deposited on glass substrate using direct current sputtering method. The structure, surface morphology, and optical and electrical properties were investigated. Results showed that both the carrier concentration and carrier mobility were increased with the doping of W. The IWO film with the lowest resistivity of 1.0×10^{-3} Ω·cm, highest carrier mobility of 43.7 $cm^2\cdot V^{-1}\cdot s^{-1}$ and carrier concentration of 1.4×10^{20} cm^{-3} was obtained at the content of 2.8 wt.%. The average optical transmittance from 300 nm to 900 nm reached 87.6%.

Keywords: In_2O_3: W thin film; doping content; DC magnetron sputtering; optical and electrical properties

1 Introduction

Transparent conducting oxide (TCO) films are widely used in various applications, such as flat panel display, light emitting diodes, and photovoltaic cell [1–3] due to its low electrical resistivity and high transparency in the visible range of solar spectrum [4]. However, all commonly used TCO films, such as In_2O_3:Sn (ITO), SnO_2:F, and ZnO:Al (AZO) as transparent window electrodes of solar cells suffer from the free carrier absorption in the near infrared region, limiting the crucial long-wavelength response of solar cells [5].

To date, amorphous ITO films with resistivity lower than 7.0×10^{-4} Ω·cm and high transmittance prepared by using metallic target were rarely reported [6]. Traditionally, much effort is afforded to lower the resistivity of TCO films merely by the increasing of carrier concentration, which, however, reduces the transmittance of TCO films. Meng *et al*. [7–8] reported molybdenum-doped indium oxide (IMO) film with low resistivity and high transmittance, which is to be attributed to the increasing of carrier mobility rather than carrier concentration. Tungsten ion can also exist with W^{+6} like Mo^{+6}. Compared with other kinds of TCO films, the high valence difference between W^{6+} and In^{3+} in IWO films is of great advantage to realize low resistivity and high transparency. Many groups have reported the fabrication of tungsten doped In_2O_3 films using various methods, such as DC magnetron sputtering technique and pulsed laser deposition [9].

In this paper, IWO films were prepared by DC magnetron sputtering. Results demonstrate that the replacement of tungsten with indium in the In_2O_3 lattice structure and the high valence doping of tungsten provide more carrier and then correspondingly decrease the resistivity of IWO without sacrificing the optical properties. The highest transmittance from 300 to 900 nm reaches 92% when the resistivity is 1.0×10^{-3} Ω·cm. The correlations between the electrical and optical characteristics of In_2O_3: W films were also discussed in this paper.

2 Experimental

Common glass was boiled in the mixture of strong sulfuric acid and H_2O_2 and then further cleaned with supersonic wave device before being used as the substrate of IWO thin film. The IWO thin film was deposited on the glass substrate from a metal In-W target (diameter, 64 mm) with a direct current (DC) reactive magnetron sputtering system. The gas in the reactive chamber was a mixture of argon (Ar, 99.99%) and oxygen (O_2, 99.99%). The substrate temperature was 275 °C, and the distance between substrate and target was 78 mm. The working pressure was 1.00 Pa, oxygen partial

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pressure 0.24 Pa, and argon partial pressure 0.76 Pa. The sputtering power was 42 W, and the sputtering time was 10 min. With all parameters above maintained during the sputtering process, the content of W was adjusted at 0, 2.8 wt.%, 5.5 wt.%, 6.4 wt.%, 7.2 wt.%, and 8.0 wt.%, respectively, and accordingly, six groups of samples were obtained.

X-ray diffraction meter (XRD D/max-2200pc) with a Cu-Kα source was used to determine the crystalline structure of the films. The morphologies of the samples were investigated by scanning electron microscope (SEM, HITACHI S4200). The electrical properties were measured using Hall measurement. UV-Vis spectrophotometer (HITACHI UV-3010) was employed to record the transmittance spectra of the films. Through the above measurements and the following analysis and discussion, the effects of W doping content on the optical and electrical properties of the IWO thin films were investigated.

3 Results and discussion

3.1 Structure and surface morphology

Figure 1 shows the SEM pictures of IWO thin films with different W-doping contents. Under identical depositing times, the thickness of samples is 200.0, 289.5, 409.5, 305.3, 331.4, and 436.5 nm, respectively. Two trends with the increase of doping content can be observed. First, the grain size increases as the doping content grows, which is in good consistence with the XRD results shown in Fig. 2. Second, with the increasing of W content, the surface roughness also grows. The trends are in accordance with the growing thickness. The XRD patterns of the IWO films are presented in Fig. 2. The diffraction peaks of In_2O_3 and IWO thin films show no difference with those of bixbyite-type In_2O_3, which shows that the doping of tungsten does not change the lattice structure of In_2O_3 thin film. With the increasing of doping content, the highest diffraction peak shifts from (222) to (400), which indicates that the doping of tungsten could result in the variation of the preferred orientation of In_2O_3 films. On the other hand, the growing of the grain size as the doping of tungsten and the preference of (400) direction may be because the ionic radius of tungsten is smaller than that of indium, which leads to the variation of surface energy after the W doping.

Except the sample with W-doping content of 8.0 wt.%, the diffraction angle (2θ) of the (222) peak of the other five samples is 30.14°, 30.48°, 30.46°, 30.38°, and 30.52° (W-doping content from 0 to 7.2%). In comparison with the undoped In_2O_3 thin film, the position of (222) peak of IWO thin films are closer to that of In_2O_3 powder with the 2θ value of 30.577°(JCPDS file No.76-0152). This fact shows that in IWO films, the substitution of W for In results in the changes of the planar distance [10].

According to Scherrer formula, $D_{hkl} = \dfrac{K\lambda}{\beta_{hkl}\cos\theta_{hkl}}$

Where D_{hkl} represents the crystal size(nm), K Scherrer constant equaling 0.89, β_{hkl} the full width at half maximum of diffraction excluding the broadening effect caused by apparatus, θ_{hkl} the diffraction angle, λ the wavelength of X-ray used in XRD test, and λ 0.15406 nm, the crystal sizes of all samples were calculated to be 11.87, 68.61, 73.79, 73.21,

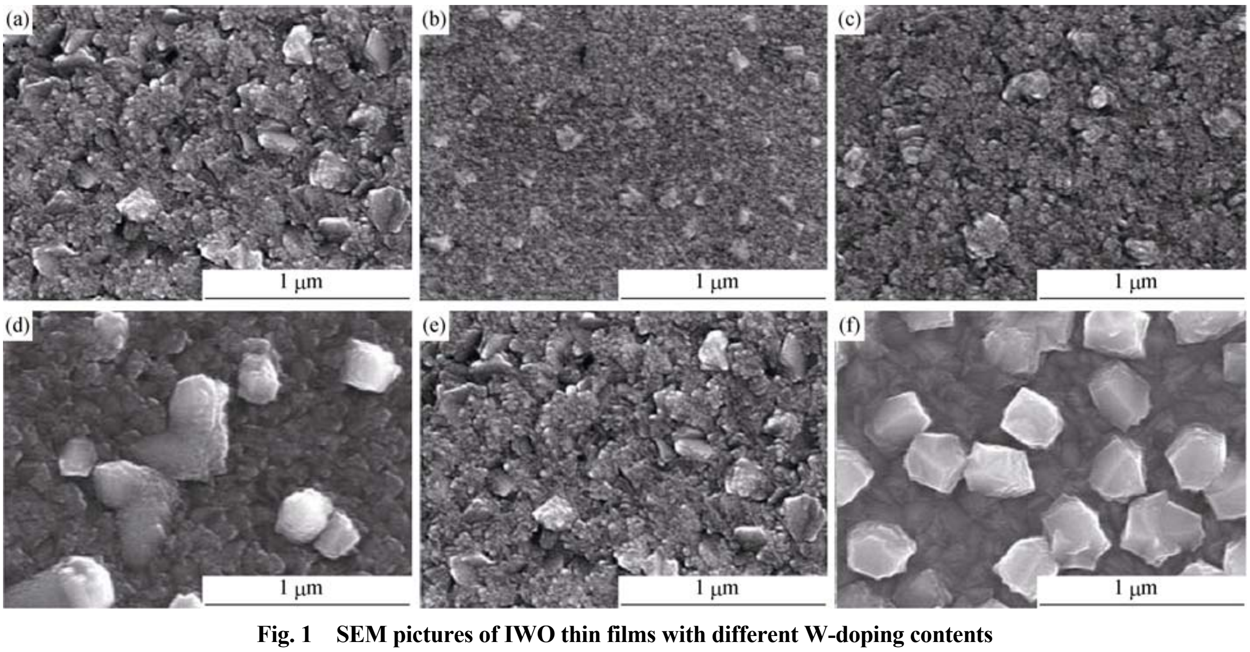

Fig. 1 SEM pictures of IWO thin films with different W-doping contents
(a) 0; (b) 2.8 wt.%; (c) 5.5 wt.%; (d) 6.4 wt.%; (e) 7.2 wt.%; (f) 8.0 wt.%

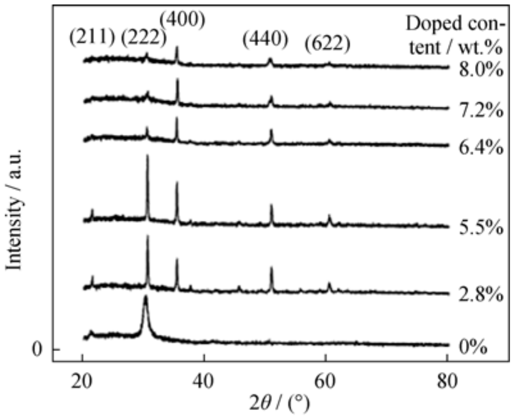

Fig. 2 XRD patterns of IWO thin films with different W-doping contents

74.09, and 48.46 nm when W-doping content is 0, 2.8%, 5.5%, 6.4%, 7.2%, and 8.0%, respectively. In our experiment, the value of β_{hkl} is measured without eliminating the inaccuracy caused by instrument, so the value of D_{hkl} is only sketchy result. It can still present the trend that the crystallinity turns better with the increasing of W-doping content.

3.2 Electrical properties

Figure 3 shows that the carrier concentration increases with the growing of W content but drops sharply when W content reaches 8.0 wt.%. The resistivity of undoped In_2O_3 films is 1.4 Ω·cm with the carrier mobility of 6.1 $cm^2 \cdot V^{-1} \cdot s^{-1}$ and carrier concentration of 1.2×10^{18} cm^{-3}. The data suggest the carrier concentration of IWO films is much higher than that of undoped In_2O_3 films and is also growing initially with the increasing of W-doping content but decreases with further increasing of W-doping content. The initial growing of carrier concentration of IWO films is due to the increasing of donor electrons proportional to the tungsten. In this case, the free carriers are provided not only by oxygen vacancies but also by doped ions with valences different from the substituted ions in host matrix oxides. Theoretically, W can exist in IWO films with the valence of +6; however, on the average, the amount of electron every W atom provides is less than 0.75 [11].

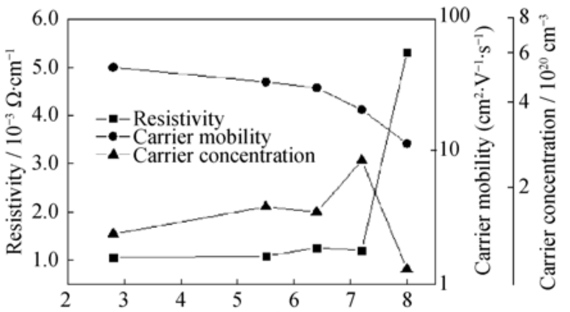

Fig. 3 Electrical properties of IWO thin films with different W-doping content

The carrier mobility of TCO films is influenced by the interplay between electron and phonon (the lattice vibration), neutral impurity scattering, and crystal boundary scattering [12–13]. As analyzed above, the carrier concentration of IWO films is much higher than that of undoped In_2O_3 film. However, the carrier mobility higher than 30.0 $cm^2 \cdot V^{-1} \cdot s^{-1}$ of IWO films is still much greater than 6.1 $cm^2 \cdot V^{-1} \cdot s^{-1}$ of undoped In_2O_3 film. According to the XRD results, the grain size grows with the increasing of W-content, which results in the decreasing of crystal boundary scattering, and the carrier mobility increases accordingly [10–11, 14]. However, when the W-doping content is higher than 4.0 wt.%, the over doped tungsten forms scattering center, which contributes to the abnormal decreasing of carrier mobility.

3.3 Optical properties

Figure 4 shows the optical transmittance of IWO films with different W content both in ultraviolet and visible range. The average optical transmittance in the region from 300 to 900 nm was calculated using curve fitting. The result is 87.6%, 76.2%, 63.5%, 68.8%, and 70.0% when the W-doping content is 2.8%, 5.5%, 6.4%, 7.2%, and 8.0%, respectively. The variation trend of carrier concentration is presented in Fig.3, and the calculated average transmittances show that the increasing of carrier concentration reduces the optical transmittance both in visible and ultraviolet range. The data shows that when W content is 2.8%, the highest average optical transmittance of IWO is 87.6%, and the lowest resistivity 1.0×10^{-3} Ω·cm appears simultaneously. Figure 5 shows detailed enlarged scale, which indicates that the transmittance spectrum blue shifts with the increase of W-doping content. This can be explained with the theory of Burstein-Moss shift. With the increasing of carrier concentration, the band gap is broadened; the lowest conduction band is occupied by electron, so the lowest energy level of empty conduction band shifts higher. Therefore, electrons need more energy to jump from a valence band to a conduction band that is not occupied [15].

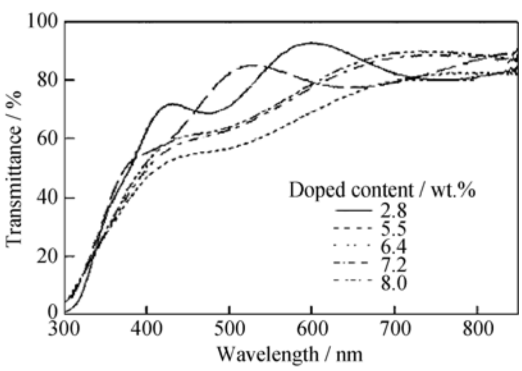

Fig. 4 Transmittance spectra of IWO films with different W content

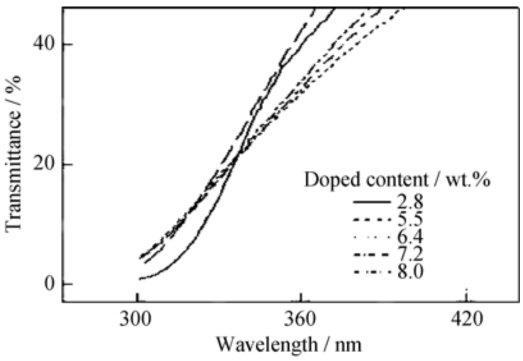

Fig. 5 Transmittance spectra in ultraviolet range of IWO films with different W content (detail with enlarged scale)

4 Conclusion

In summary, transparent conductive oxide thin films of tungsten-doped In_2O_3 were deposited on the conventional glass substrates by DC magnetron sputtering. The lowest resistivity of 1.0×10^{-3} Ω·cm was obtained at a tungsten-doped content of 2.8 wt.% when the carrier concentration is 1.4×10^{20} cm^{-3} and carrier mobility reached the maximum value of 43.7 $cm^2\cdot V^{-1}\cdot s^{-1}$. The average transmittance between 300 and 900 nm reaches 87.6%. Compared with that of ITO thin films, the low resistivity of IWO films is obtained through the increasing of carrier mobility but not merely carrier concentration. Therefore, IWO film is of great advantage to keep high optical transmittance when resistivity is relatively low.

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