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Preparation and Properties of Infrared Transparent Conductive Thin Films

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ABSTRACT

This paper presents results for infrared transparent and conducting thin films based on In_2O_3. The films have been prepared by magnetrons sputtering equipment with different condition. Typical transmittance of 70%-80% with a film sheet resistance of 80-300Ω/□ in the 3.5-5.0μrn region has been achieved.

Optically transparent and electrically conductive semiconductor Oxide films have been extensively studied in recent years. Such films have been prepared by various methods. In general, these films have high visible transmittance, but are opaque in the IR wavelength range of 1-12μm IR transmission. The infrared transparent and electrically conductive thin films are useful in certain important applications. For example, these films can be use as antistatic coatings, and while permitting a reasonable transmission coefficient for IR. Another obvious application is to serve as the conducting electrode for various optical devices where good infrared transmission is important. So, it is important to research indium oxide base infrared (3-5 um) transparent conduction thin films.

It has been developed that preparation condition influence on properties of thin films. Such as the sputtering time, and pressure, and power, and the substrate temperature, had great influence on the crystal structure, optical and electrical properties of In_2O_3-based thin films.

The In_2O_3-based thin films obtained were characterized and analyzed by X-ray Diffractometer (XRD), Atomic Force Microscope (AFM), Vander Pauw Method and Fourier Transform Infrared Spectroscopy (FTIR).

INTRODUCTION

Transparent conductive oxide (TCO) has been applied widely in liquid crystal displays, solar cells, organic light emitted devices, thermal reflection thin film, optical fibre [1-3], and so on since the high transmittance, and conductivity. The first TCO thin film is cadmium oxide (CdO) obtained by thermal oxidation of sputtered cadmium films reported by Badeker in 1907 [4]. Presently, TCO thin films that have been reported include tin-doped indium oxide (ITO), antimony -doped tin oxide (ATO), fluorine-doped tin oxide (FTO), aluminum-doped zinc oxide (AZO), and others metal oxide thin films [5-9].

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Indium trioxide or indium oxide (In_2O_3) thin film is polycrystalline bixbyite structure with band-gap of 3.75eV. In_2O_3 is an n-type material since the oxygen vacancies and indium interstices. The electric characteristics of In_2O_3 thin film can be improved by doping. Tin, zirconium, titanium, molybdenum, tungsten and so on have been used to enhance the performance of In_2O_3 thin film [10-14]. One of the most important characteristics for In_2O_3 thin film is transparent in infrared region, especially in 3-5μm and 8-12μm.

In this paper, transparent conductive In_2O_3 thin film works in 3-5μm is presented. Magnetrons sputtering equipment is used to achieve the In_2O_3 infrared transparent conducting thin films under different experimental conditions such as sputtering time, sputtering power, substrate temperature, and sputtering pressure. The performances of thin film crystal structure, transmittance in infrared region and conductivity are characterized and analyzed by X-ray Diffractometer (XRD), Atomic Force Microscope (AFM), Vander Pauw method and infrared light spectrophotometer respectively. The optimal processing conditions for In_2O_3 transparent conductive thin film in infrared region of 3-5μm, therefore, can be obtained according to above analysis. On the other hand, in order to enhance the conductivity of In_2O_3 thin film, aluminum (Al) is chosen to sputter together with In_2O_3 to achieve the aluminum-doped In_2O_3 thin film.

THEORETICAL PRICIPLE OF AL-DOPED IN$_2$O$_3$

The conductivity of Al-doped In_2O_3 thin film ($In_{2-x}Al_xO_3$) is better than pure In_2O_3 thin film. The reaction equation for Al-doped In_2O_3 thin film can be written as:

$$In_2O_3+Al\rightarrow In_{2-x}Al_xO_3+In_x \tag{1}$$

Similarly, the oxygen vacancy process is described as:

$$In_2O_3\rightarrow In^{3+}{}_{2-x}\,(In^{3+}2e)\,{}_xO^{2-}{}_{3-x}+x/2O_2 \tag{2}$$

The optimal doped concentration is given as:

$$x_{opt}=\frac{\exp(-\frac{\Delta E}{kT})}{Z+1} \tag{3}$$

where Z is the number of adjacent lattices for doped lattice. According to the crystal structure of In_2O_3, magnetrons sputtering process and equation(3), the optimal Al doped concentration for magnetrons sputtered In_2O_3 thin film can be calculated as 9.577% because the average coordination number of indium ions is 16/3.

EXPERIMETNAL

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A radio-frequency (RF) magnetrons sputtering system (JZCK-IVB, Juzhi Inc.) with the RF source under the maximum sputtering power of 500W is used to deposit infrared transparent conductive In_2O_3 or Al-doped In_2O_3 thin film on the sapphire substrate. The source material for In_2O_3 and Al-doped In_2O_3 thin film are 99.99% purity In_2O_3 and Al targets with 51mm diameter respectively. The distance between target and sapphire substrate is set as 6.5cm for In_2O_3 target and 9.5cm for aluminum target. Before sputtering, the vacuum chamber is evacuated down to a basic pressure of 1.0×10^{-3} Pa. High purity of 99.99% argon is introduced through separate mass flow controllers into vacuum chamber. The pre-sputtering is processed for removing the impurity on the surface of target. The experimental conditions are presented in table I.

Table I. Experimental conditions for In_2O_3 and Al-doped In_2O_3 thin film deposition

Thin film	In_2O_3	Al-doped In_2O_3
Target	99.99% purity In_2O_3	99.99% purity Al
Gas	Argon	
Sputtering pressure	0.2Pa-2Pa	
Sputtering power	100-250W	7-15W
Distance from target to substrate	6.5cm	9.5cm
Deposition temperature	Room temperature to 600K	
Sputtering time	15min pre-sputtering, 20-50min sputtering	

The thickness of deposited thin film is measured by a step profiler (XP-2, AMBIOS Technology Inc.), and the thin film sheet resistance is obtained by reformative Van der Pauw method. A Fourier transform infrared (FTIR) spectrophotometer is used to achieve the transmittance of In_2O_3 and Al-doped In_2O_3 thin films in infrared region. Structure, crystal lattice coefficient and grain size of deposited samples are measured by an X-ray diffractometer (D8 ADVANCE, BRUKER AXS Inc.). At the same time, the surface topography is observed by an atomic force microscope (CSPM5000, Benyuan).

RESULTS AND DISCUSSION

Performances and characteristics of deposited thin film are determined by deposit conditions such as sputtering time, sputtering power, substrate temperature and sputtering pressure. Figure 1 present the XRD patterns for pure In_2O_3 thin films under different sputtering time in the case of constant sputtering power, substrate temperature and sputtering pressure. The intensity of (222) peak is increased with sputtering time after 20 minutes sputtering. The full width at half maximum (FWHM) of (222) peak for the case of 30min, 40min and 50min is 0.128, 0.189 and 0.342 respectively, therefore, the grain size can be calculated as 63.63nm, 43.09nm and 23.81nm that reduced with sputtering time. Similarly, figure 2 illustrate the XRD patterns for In_2O_3 under different sputtering power. The intensity of (222) peak is increased obviously with sputtering power above 100W sputtering. The FWHM of (222) peak with 150W, 200W and 250W

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sputtering power is 0.342, 0.223 and 0.188 respectively, at the same time, the grain size is 23.81nm, 36.52nm and 43.32nm that increased with sputtering power. Figure 3 show the XRD patterns for In_2O_3 under different substrate temperature for the case of constant sputtering time, power and pressure. The FWHM of (222) peak under 300K, 400K, 500K and 600K substrate temperature is 0.342, 0.181, 0.180 and 0.201 respectively, as a result, the grain size is 23.81nm, 44.99nm, 45.24nm and 40.52nm that increased from 300K to 500K while decreased at 600K. Moreover, the XRD patterns with different sputtering pressure are illustrated in figure 4. The intensity of (222) peak is reduced with sputtering pressure since the increased scattering of sputtering atoms under more and more pressure. The FWHM of (222) peak in the case of 0.25Pa, 0.6Pa, 1Pa and 2Pa is 0.149, 0.183, 0.342 and 0.151 respectively. Hence the grain sizes are 54.66nm, 44.50nm, 23.81nm and 53.93nm.

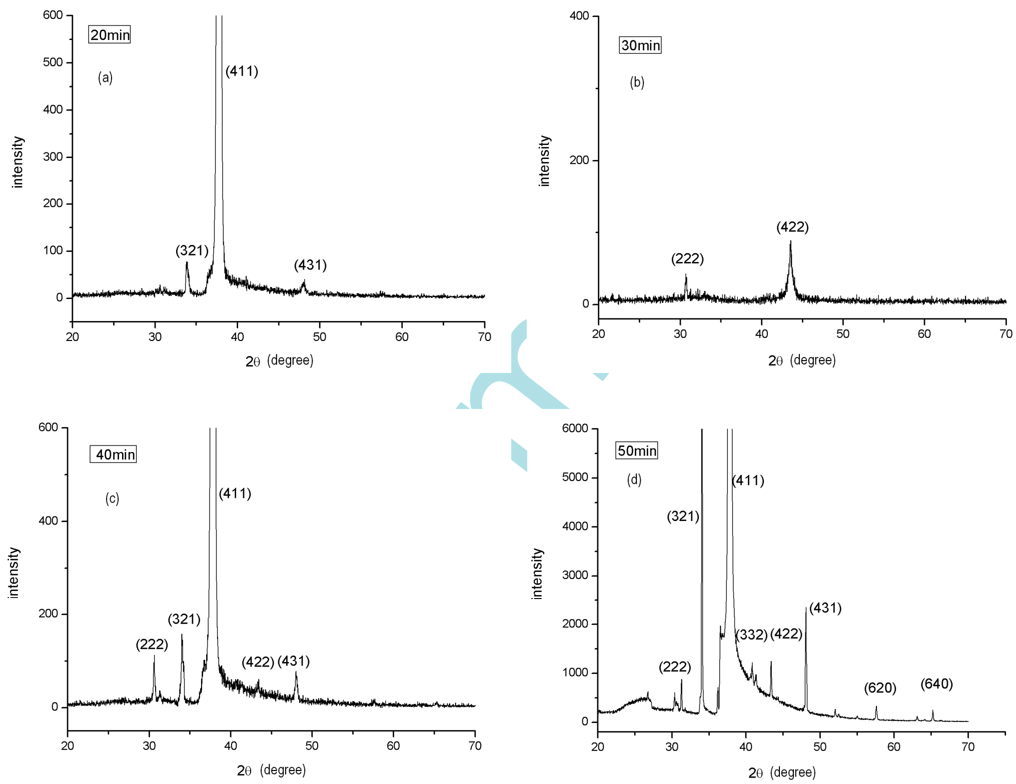


Figure 1. XRD patterns with sputtering time, (a) 20min, (b) 30min, (c) 40min, and (d) 50min.

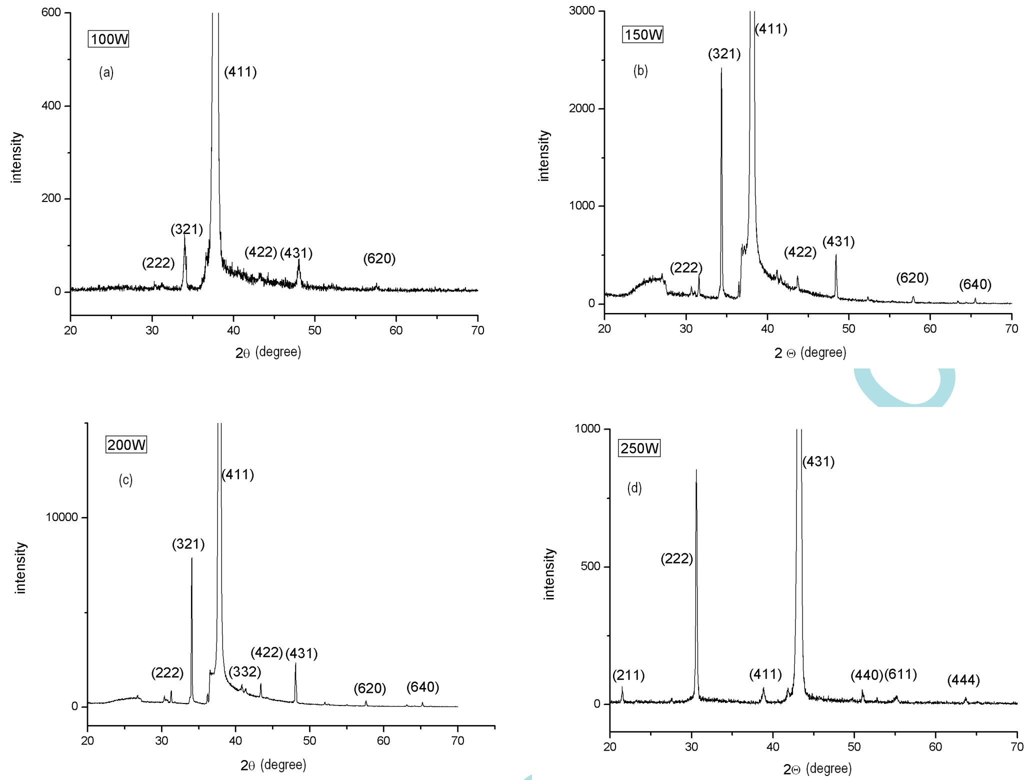


Figure 2. XRD patterns with sputtering power, (a) 100W, (b) 150W, (c) 200W, and (d) 250W.

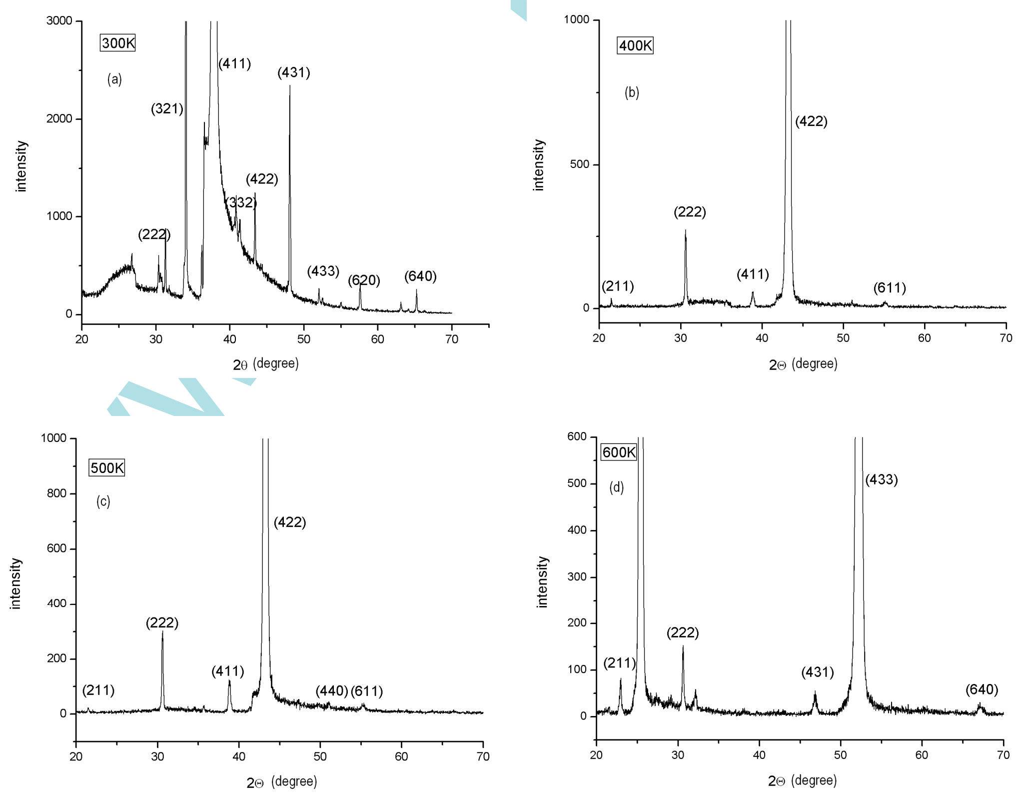


Figure 3. XRD patterns with different substrate temperature, (a) 300K, (b) 400K, (c) 500K, and (d) 600K.

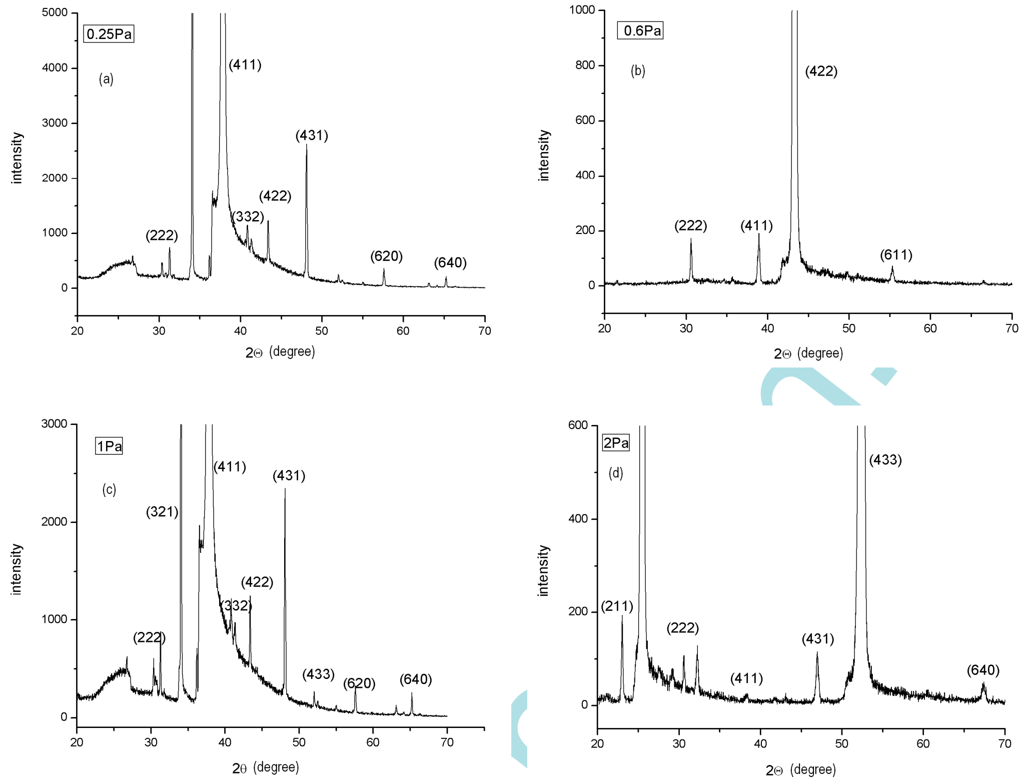


Figure 4. XRD patterns with different sputtering pressure, (a) 0.25Pa, (b) 0.6Pa, (c) 1Pa, and (d) 2Pa.

On the other hand, the surface topography of pure In_2O_3 thin film is characterized by atomic force microscope (AFM). The grain size, height$_{Peak\text{-}Peak}$ and roughness varying with sputtering time, sputtering power, substrate temperature and sputtering pressure obtained from AFM are presented in figures 5-7. It can be seen from figure 5 to figure 7 that the optimal sputtering conditions can be achieved as 40min sputtering time, 250W sputtering power, 400K substrate temperature and 1Pa sputtering pressure for grain size; 40min sputtering time, 250W sputtering power, 600K substrate temperature and 2Pa sputtering pressure for height$_{P\text{-}P}$, 40min sputtering time, 100W sputtering power, 600K substrate temperature and 2Pa sputtering pressure for roughness. However, the optimal experimental conditions for an efficient transparent conductive In_2O_3 thin film should be compromised basing on the XRD patterns and AFM results along with the optical and electrical properties will be discussed hereinafter.

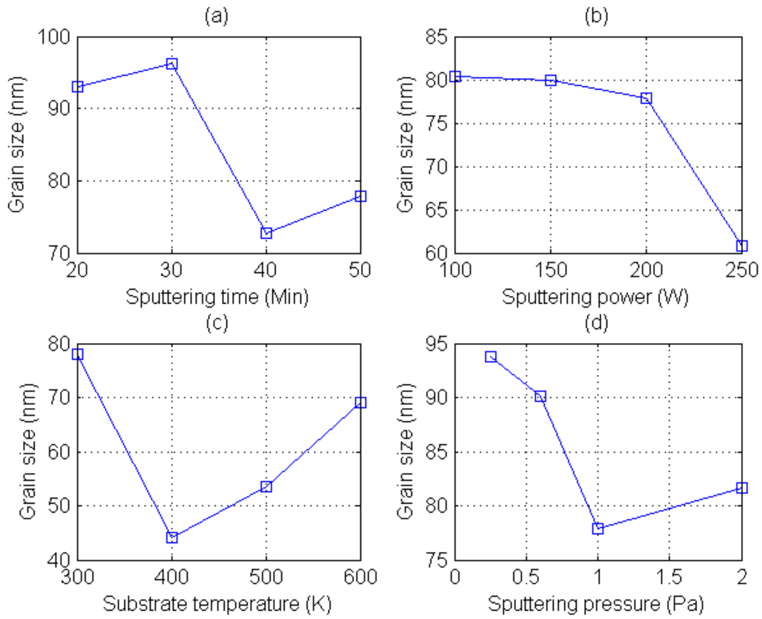


Figure 5. Grain size of pure In_2O_3 thin film under different sputtering conditions, (a) sputtering time, (b) sputtering power, (c) substrate temperature, and (d) sputtering pressure.

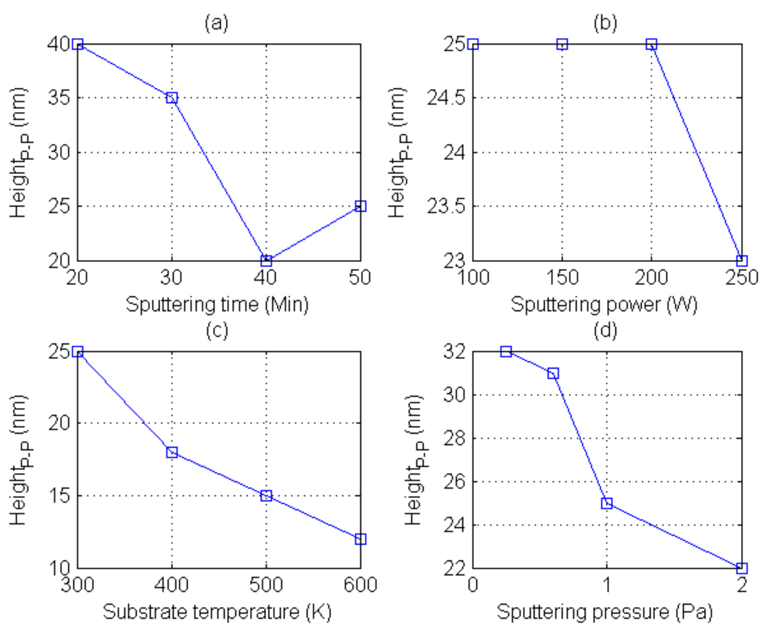


Figure 6. $Height_{P-P}$ of pure In_2O_3 thin film with sputtering conditions, (a) sputtering time, (b) sputtering power, (c) substrate temperature, and (d) sputtering pressure.

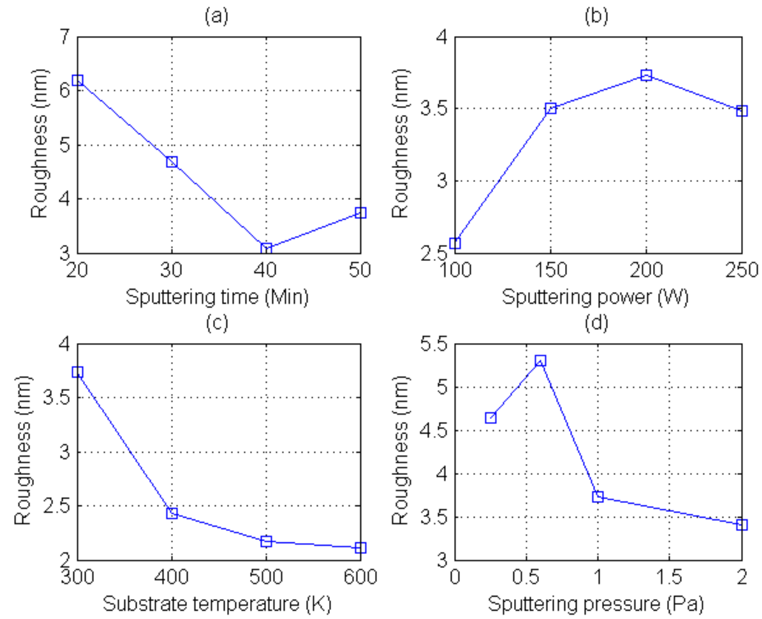
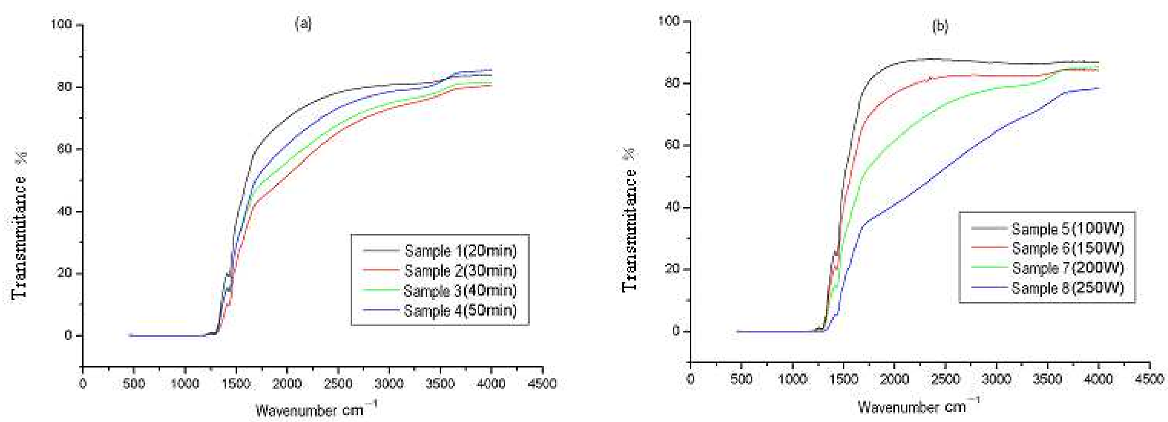


Figure 7. Roughness of pure In_2O_3 thin film under different sputtering conditions, (a) sputtering time, (b) sputtering power, (c) substrate temperature, and (d) sputtering pressure.

Figure 8 illustrates the transparent property of pure In_2O_3 thin films in infrared region under different sputtering conditions. The transmittance is determined by the thickness of thin film that thicker film has weaker transmittance. It can be seen from figure 8 that most transmittances in the region of 3-5μm (2000-3300 cm^{-1} wavenumber) are above 50%. Better transmittance can be achieved through adjusting the sputtering conditions basing on figure 8.



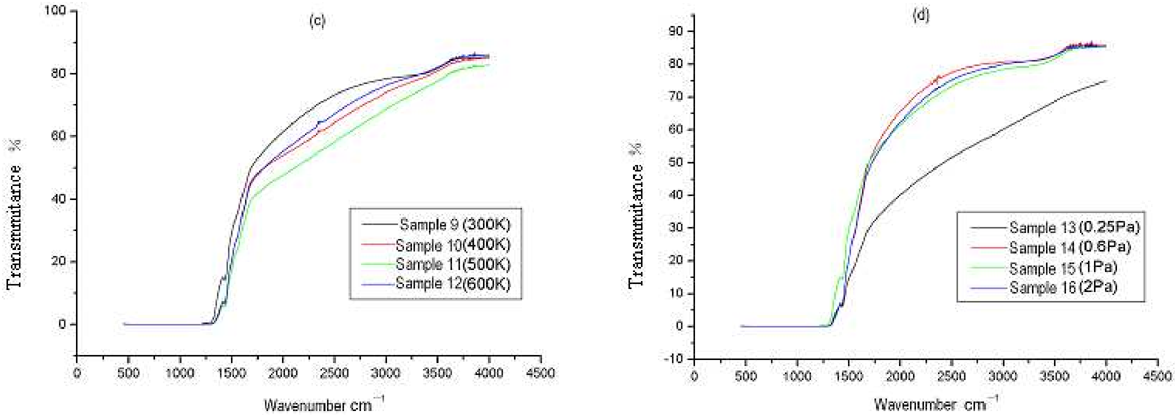
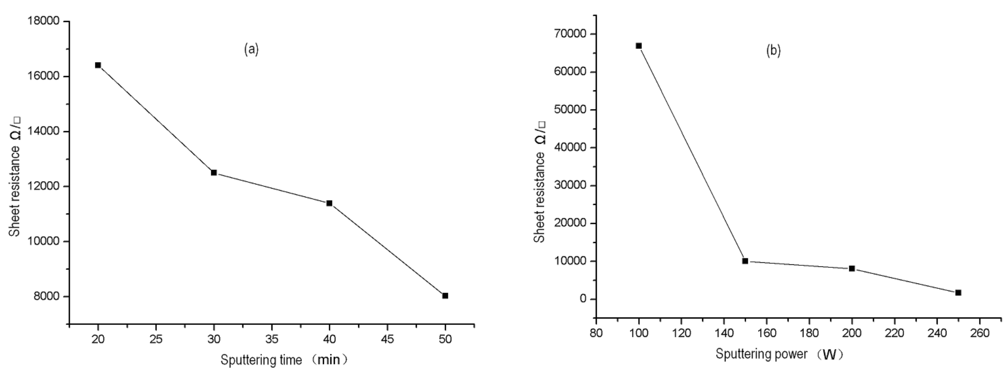


Figure 8. Pure In_2O_3 thin film transparent property in infrared region with different sputtering conditions, (a) different sputtering time under 1Pa sputtering pressure, 200W sputtering power, and 300K substrate temperature, (b) sputtering power with 1Pa sputtering pressure, 300K substrate temperature and 50min sputtering time, (c) substrate temperature with 150W sputtering power, 1Pa sputtering pressure and 50min sputtering time, (d) sputtering pressure under 600K substrate temperature, 50min sputtering time and 150W sputtering power.

The sheet resistance is an important parameter for conductive thin film that also determined by the thickness of thin film that smaller sheet resistance can be obtained in the case of thicker thin film. The sheet resistances of pure In_2O_3 thin film for the case of different sputtering conditions are illustrated in figure 9. The thickness of thin film is dependent on the sputtering time primarily. On the other hand, the sputtering ions power can be increased with the sputtering power; the crystal defect is reduced consequently. Moreover, the oxygen vacancy is increased for high substrate temperature since the enhancive surface desorption, while is decreased with sputtering pressure.



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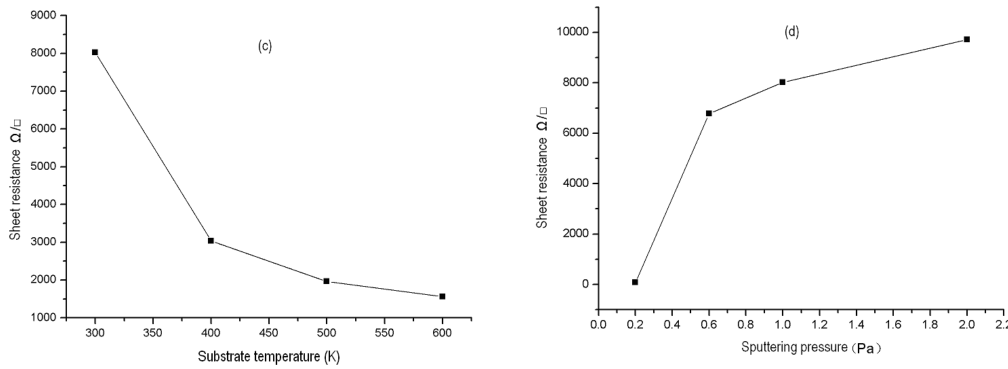

Figure 9. Sheet resistance of In_2O_3 thin film with different sputtering conditions, (a) sputtering time, (b) sputtering power, (c) substrate temperature, and (d) sputtering pressure.

Basing on the previous results, the thickness, diffractive surface and the intensity of diffractive peak of the thin film are all increased with the rising sputtering time; however, the grain size is decreased. That is to say, the quality of thin film is better with the increased sputtering time. Consequently, the transmittance in near infrared region and the sheet resistance is better for the case of 50min sputtering time. The energy of Ar ions arrived on the surface of target material is increased with the sputtering power that is helpful for absorption and diffusion of the sputtered ions. The grown quality of thin film, therefore, is enhanced with the sputtering power. Consequently, the sheet resistance and the transmittance are increased with power. However, the thick film can impede the transmission of infrared light, 150W, therefore, is the best sputtering power for highest transmittance. The mobility of ions on substrate surface is affected by the substrate temperature. Higher temperature is in favor of better quality thin film since the higher surface mobility. However, the bond of In and O can be broken for the temperature over 600K. Therefore, the highest transmittance and lowest sheet resistance can be obtained at 600K substrate temperature. The best transmittance for different sputtering pressure is achieved at 0.6Pa since the slow deposition speed caused by plenty collisions between sputtered atoms and low deposition energy at high sputtering pressure. Moreover, the sheet resistance is depressed with reduced sputtering pressure since the increased oxygen vacancies concentration.

The optimal experimental parameters for In_2O_3 thin film can be obtained as 20 standard-state cubic centimeter per minute (sccm) of Ar flow rate, 20min pre-sputtering, 50min sputtering time, 150W sputtering power, 300K or 600K substrate temperature, and 0.45Pa sputtering pressure. However, the sheet resistant of In_2O_3 is not excellent enough for several applications. Al-doped In_2O_3 thin film, therefore, is deposited in order to achieve high conductivity. Figure 10 present the transmittance and sheet resistance of Al-doped In_2O_3 in the case of DC sputtering power of 7W, 10W, 15W and 20W on Al target. The transmittance and sheet resistance are both reduced with increased sputtering power because too many Al ions produced for high power, at the same time the oxygen vacancies and crystal defects are enhancive that helps for increasing carrier concentration and scatters the infrared light

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respectively. The transmittance of Al-doped In_2O_3 thin film is much higher than pure In_2O_3 thin film and the sheet resistance is lower than pure In_2O_3 thin film can be obtained from figure 10.

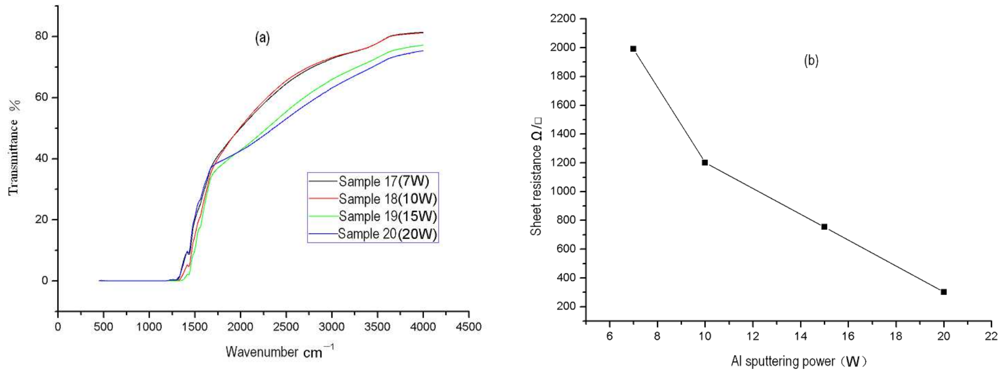

Figure 10. Transmittance and conductivity of Al-doped In_2O_3 thin film with different DC sputtering power on Al target, (a) transmittance, (b) conductivity.

Figure 11 illustrates the XRD pattern of Al-doped In_2O_3 thin film. Only (222) and (422) peaks can be observed in figure 11 with the diffraction angle of 30.58° and 43.78° respectively. A good agreement between XRD pattern shown in figure 11 and standard diffraction peak of In_2O_3 crystal with bixbyite structure can be obtained. That is to say, the In_2O_3 lattice maintains the original structure and does not produce new lattice after Al-doped into In_2O_3 thin film since Al substitutes for In^{3+}. The FWHM of the two diffraction peaks are 0.147 and 0.390, and the grain sizes are 55.0nm and 21.71nm calculated according to Scherrer equation.

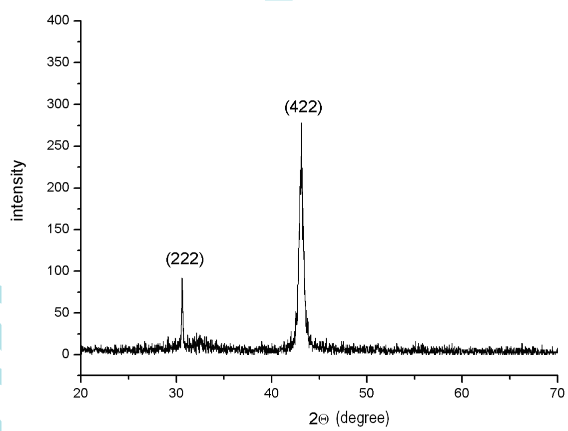

Figure 11. XRD pattern for Al-doped In_2O_3 thin film.

CONCLUSION

The transparent conductive indium oxide thin film deposited on sapphire substrate by RF magnetrons sputtering and characterized by XRD, AFM, Vander Pauw method, FTIR and so on is presented in this paper. The best sputtering conditions for indium oxide thin film is 20 standard-state cubic centimeter per minute (sccm) of Ar flow rate, 20min pre-sputtering, 50min sputtering time, 150W sputtering power, 300K or 600K substrate temperature, and 0.45Pa sputtering pressure. Nevertheless, the Al-doped In_2O_3 thin film is deposited on sapphire substrate by DC sputtering in order to achieve high conductivity. For the case of enhanced Al sputtering power, the oxygen vacancy in the thin film is increased, and more defects exist. At the same time, the light scattering can be enhanced by defects with increased Al sputtering power. As a result, the transmittance of Al-doped In_2O_3 thin film in infrared region is reduced. However, the oxygen vacancy can increase current carrier density. The sheet resistance of Al-doped In_2O_3 thin film, therefore, is decreased with the rising Al sputtering power.

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