INFLUENCE OF SUBSTRATE TEMPERATURE ON STRUCTURAL, ELECTRICAL AND OPTICAL PROPERTIES OF ZnO:Al THIN FILMS

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ABSTRACT

INFLUENCE OF SUBSTRATE TEMPERATURE ON STRUCTURAL, ELECTRICAL AND OPTICAL PROPERTIES OF ZnO:Al THIN FILMS. Transparent and conductive aluminium-doped zinc oxide thin films have been prepared by dc magnetron sputtering technique using targets composed of ZnO and aluminium. Polycrystalline ZnO:Al films were deposited onto a heated glass substrate. Surface morphology and crystalline structure as well as optical and electrical properties of the deposited films were found to depend directly on substrate temperature. From optical and electrical analysis it was observed that optical transmittance and conductivity of the ZnO:Al transparent conductive oxide films increased when the deposition temperature was raised from 200 to 400 ^{o}C. Films grown on substrates heated at 300 ^{o}C showed a high conductivity value of 0.2 x 10^{2} $\Omega^{-1}cm^{-1}$ and a visible transmission of about 80%. The growth of ZnO:Al thin films on the surface of glass substrate at temperatures of 300 ^{o}C and aluminium doping levels of 0.9 at.% were the best to attain ZnO:Al films with optical and structural qualities as required for solar cell applications, as a window material in antireflection coatings or optical filters.

Keywords : polycrystalline, morphology, conductivity, transmittance.

INTRODUCTION

With the rapid growing world population and the increasing environmental and social problems of the nowadays common fossil energy production, the need for clean and sustainable energy sources has become evident. Nuclear energy and also solar energy conversion, such as done in photovoltaic systems, can play a major role for electricity production in the urgent needed energy transition. Zinc oxide (ZnO), a semiconducting, photoconducting, piezoelectric and optical waveguide material, shows a wide range of scientific and technological applications. Due to their optical and electrical properties ZnO thin films have received considerably much attention in recent years. ZnO has also gained much attention due to the many advantages over other oxide thin films such as tin-doped In_2O_3 (ITO) and SnO_2 films. These advantages include cheaper and easier to etch than ITO,

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non-toxicity and much more resistant to hydrogen plasma reduction and can be grown at lower temperatures [1,2].

ZnO is a n-type semiconductor of wurtzite structure with a direct energy wide-band gap of about 3.37 eV and a large exciton binding energy of about 60 meV at room temperature. It can be used as a transparent electrode in solar cells and flat panel displays as well as for the fabrication of gratings in optoelectronic devices, as a window material in antireflection coatings and in optical filters [3,4,5,6]. Furthermore, ZnO is used as a semiconducting gas sensor, due to its conductivity changes when exposed to oxidizing gases such as ozone. ZnO nano-structures with excellent optoelectronic properties are used for light emitting diode and laser diodes [7,8], detectors for blue and ultraviolet range of spectrum [9].

In recent years, aluminium-doped zinc oxide (ZnO:Al) films prepared by rf or dc magnetron sputtering have emerged as a material for transparent conductive oxide (TCO) used as front contact material and play a crucial role in obtaining high efficiencies with a-Si:H and μc-Si:H based solar cells. Besides combining a low series resistance with high transparency, it also has to provide an adequate surface texture for optimized light scattering. Compared with undoped ZnO, Al-doped ZnO films have lower resistivity and better stability. Several techniques have been used to prepare Al-doped ZnO films, such as dc magnetron sputtering, chemical vapor deposition, sol-gel and spray pyrolysis [6,10,11]. Among these methods, the dc magnetron sputtering process is used most often, due to high deposition rates and process stability and reliability [12,13]. In this work, in order to obtain an excellent transparent conductive oxide (TCO) film for transparent electrode in solar cells, as a window material in antireflection coatings and optical filters with low resistivity and high optical transmittance, aluminium-doped zinc oxide films are deposited on glass substrates by a dc magnetron sputtering method. The influence of substrate temperatures, argon pressures and the effect of impurity doped into the ZnO:Al film on the structural, electrical and optical properties are discussed. X-ray diffraction (XRD), scanning electron microscopy (SEM), the I-V method and spectrophotometer are used to characterize microstructure, electrical and optical properties of the ZnO:Al transparent electrode films.

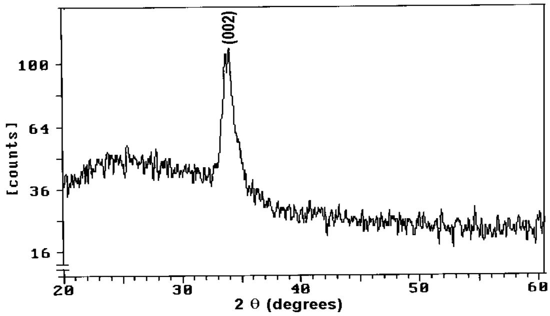
EXPERIMENTAL METHODS

The glass substrates are ultrasonically cleaned by using acetone, methanol and deionized water, and then dried by blowing nitrogen over them. A 60 mm-diameter disc of sintered ZnO powder (purity, 99.98%) and a sintered disc composed of a mixture of ZnO powder and < 2.0 wt % Al_2O_3 (purity, 99.98%) dopant are used as the target. Sputtering is carried out at a pressure of 8×10^{-2} - 1.2×10^{-1} torr in pure argon gas with a power of 40 W and the optimum deposition time of 90 min. A magnetic field from the external solenoid coil was varied up to about 200 G. The glass substrates are placed parallel to the target surface at a distance of 35 mm. Substrate temperatures are varied from 100 ^oC to 400 ^oC and the surface temperature of the substrate is monitored by a thermocouple and controlled by a heater during the deposition. ZnO:Al films are deposited onto a heated glass substrates in the temperature region from 100 up to 400 ^oC, and under optimum argon gas pressure of 9×10^{-2} torr. The electrical resistivities are measured at room temperature by using a I-V method; the crystallographic structures are determined by an X-ray diffractometer and the surface morphologies of the films are characterized by a scanning electron microscopy. The optical transmittance is measured in the wavelength range of 300-800 nm with a UV-vis spectrophotometer.

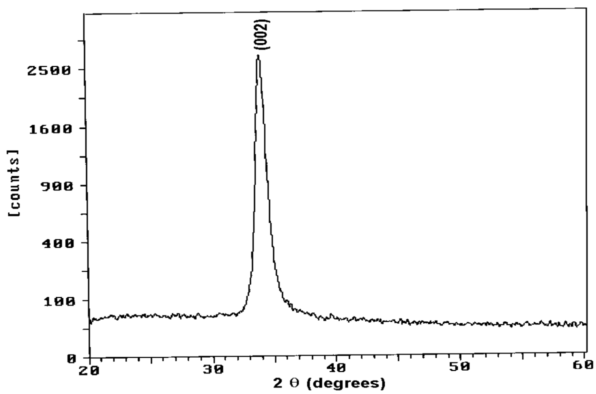
RESULT AND DISCUSSION

The most important parameter required for the application of ZnO:Al films as an excellent transparent conductive oxide (TCO) film for transparent electrode is its low electrical resistivity or high electrical conductivity and high optical transmittance. Hence, emphasis is placed in this study on optimizing of the deposition conditions for substrate temperature and argon pressure, the influences of substrate temperature and argon pressure on the X-ray diffraction patterns, electrical resistivity and optical transmittance of ZnO:Al films.

Variations of X-ray diffraction patterns of ZnO:Al films with Al/Zn = 0.9 at.% deposited at various substrate temperatures are shown in Figure 1. X-ray analysis indicated that the ZnO:Al films deposited at 200, 250, 300 ^oC exhibited the c-axis orientation perpendicular to the substrate surface, as can be seen in Figure 1a, 1b and 1c, respectively. The crystallographic structures are evaluated from the intensities and full width at half-maximum of the (002) diffraction peak and the peak becomes more intense and sharper with increasing substrate temperature. This means that the crystallinity of the ZnO:Al films is improved and the grain size of the crystallites becomes larger with increasing substrate temperature up to 300 ^oC as shown in the Figure 3. This result indicates that the substrate heating leads to an improvement in the crystallinity of the ZnO:Al thin films.



(a)



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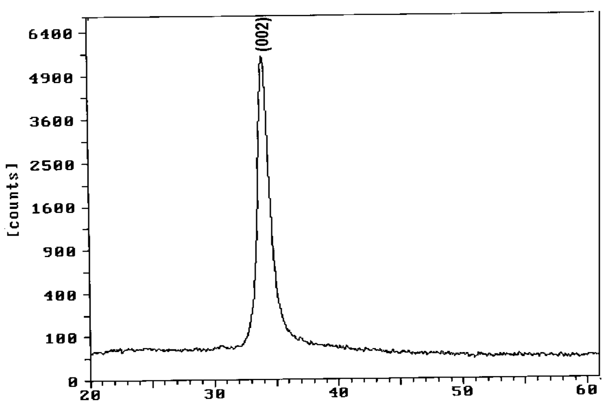
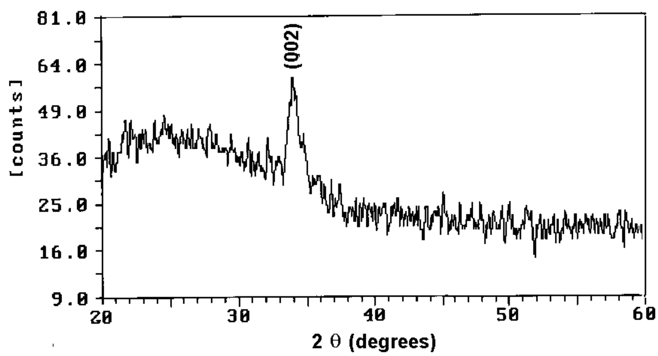


(c)

Figure 1. X-ray diffraction patterns measured on ZnO:Al films deposited at substrate temperatures of (a) 200 ^{o}C, (b) 250 ^{o}C and (c) 300 ^{o}C respectively.



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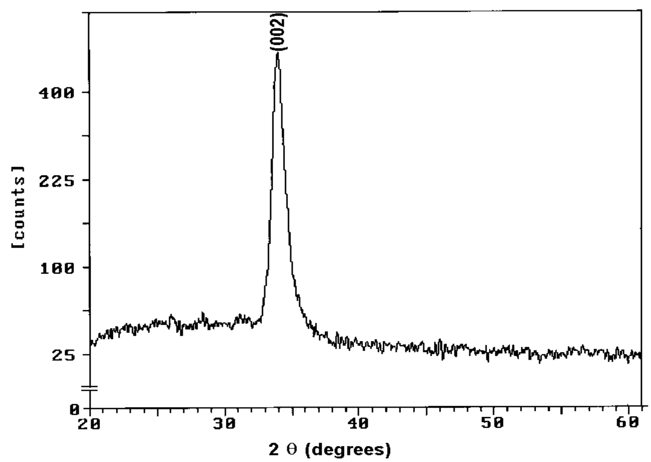


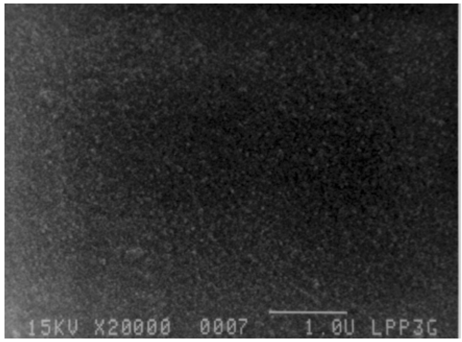
(b)

Figure 2. X-ray diffraction patterns of (a) ZnO and (b) ZnO:Al films, at substrate temperature of 300 ^{o}C.

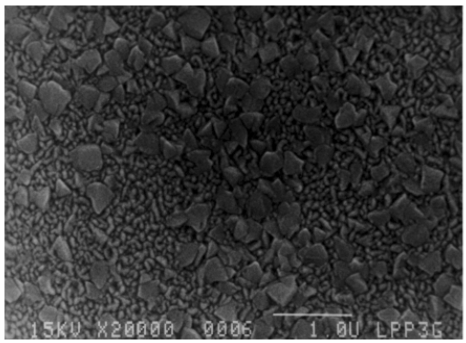
Figure 2 shows the X-ray diffraction spectra of the ZnO film and the ZnO:Al film with Al/Zn = 0.9 at.%, substrate temperature of 300 ^{o}C and argon gas pressure of 1×10^{-1} torr. X-ray diffraction analysis indicates that the deposited films are polycrystalline and oriented perpendicular to the substrate surface, i.e. c-axis orientation. The (002) diffraction peak intensity of the ZnO:Al film is higher and the half-width is smaller than that of the ZnO film, an indication that the grain size of the ZnO:Al film is larger compared to that of the ZnO film. The crystallographic orientation correlates with microstructure or morphology of ZnO:Al thin films as shown in

Figure 3. The ZnO:Al thin films deposited at lower temperature (200 ^oC) shown in Figure 3a. has a homogeneous distribution of small grain size which yields a uniform and smooth film. The lateral grain size become bigger at elevated substrate temperature (Figure 3b) of 300 ^oC due to the increasing mobility of the constituting atoms at high substrate temperature. In the ZnO:Al films deposited on the surface of substrate at a temperatures above 300 ^oC is produced a smaller grain size (Figure 3c). A mechanism to explain the reason why the higher substrate temperature caused a smaller grain size has not been clarified yet.

The electrical conductivity of ZnO:Al films as a function of the substrate temperature is plotted in Figure 4. During the deposition of ZnO and ZnO:Al films, the optimum argon gas pressure is set at 9×10^{-2} torr, the dc power is maintained constant, and the Al/Zn ratio of the ZnO:Al films deposited is about 0.9 at.%. It is shown that the electrical conductivity of the film increases with elevated substrate temperature and reaches a maximum value at 300 ^oC, and thereafter decreases slightly. The electrical conductivity of ZnO:Al films is higher than that of undoped ZnO films by about five orders of magnitude and the highest conductivity of the ZnO:Al film is about $0.2 \times 10^2\ \Omega^{-1}cm^{-1}$. The dependence of electrical conductivity upon substrate temperature can be explained by the change in microstructure and the presence of incomplete oxidation of the zinc to form ZnO films [12]. This result is different from the ZnO films prepared by using the spray pyrolysis method [14].



(a)



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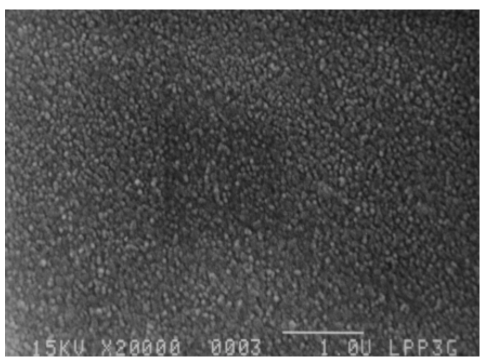

(c)

Figure 3. Scanning electron micrograph taken on the surface of ZnO:Al films deposited at (a) 200 ^{o}C, (b) 300 ^{o}C and (c) 400 ^{o}C.

Figure 5 shows the measured electrical conductivity of ZnO:Al thin films as a function of the Al/Zn ratio. The ZnO:Al films were deposited at the substrate temperature of 300 ^{o}C, and the argon gas pressure of 9×10^{-2} torr , as well as the dc power were maintained constant. It can be seen that the electrical conductivity increases rapidly at a low concentration of Al and reaches a maximum value at Al/Zn = 0.9 at.%, whereas above Al/Zn = 0.9 at.% the electrical conductivity decreases with increasing Al concentration. As the Al dopant concentration is increased, more dopant atoms occupy lattice sites of zinc atoms resulting in more charge carriers. Thus the electrical conductivity of ZnO:Al film increases with increasing dopant concentration. However, after a certain doping level the dopant atoms in the crystal grain and grain boundaries tend to saturation, resulting in a decreases in the conductivity of the ZnO:Al thin films. This result is different with the ZnO:Al films prepared by the spray pyrolysis method [15] and the sol-gel technique [6].

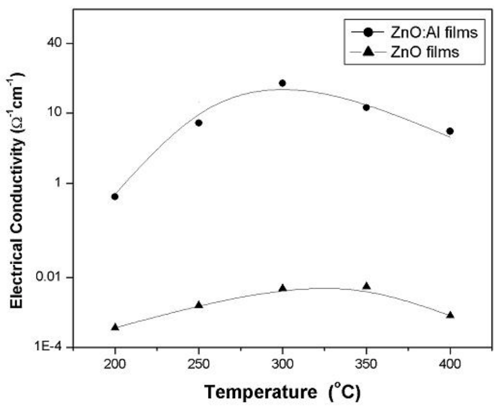

Figure 4. Electrical conductivity values of ZnO and ZnO:Al films as a function of substrate temperature.

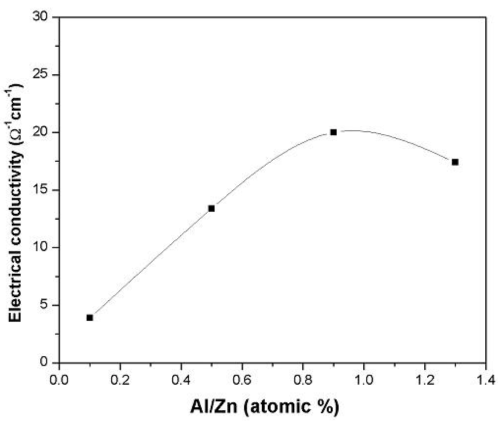

Figure 5. Electrical conductivity of ZnO:Al thin films as a function of the Al/Zn ratio at substrate temperature of 300 ^{o}C, and the sputter gas pressure was maintained constant.

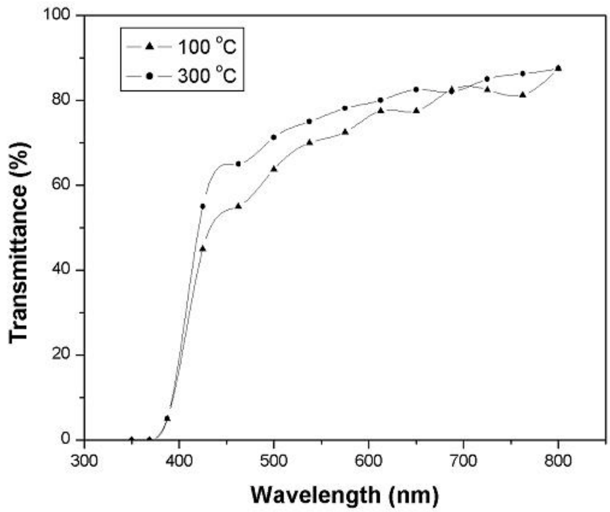

Figure 6. Transmittance spectra of ZnO:Al films (Al/Zn = 0.9 at.%) as a function of the wavelength for film thickness of about 400 nm.

The transmittance characteristics for ZnO:Al film is measured in the visible range of 300 – 800 nm in wavelength and the results are shown in Figure 6. This film is deposited at the substrate temperature of 100 °C and 300 °C each, whereas the sputter gas pressure and the dc power were maintained constant. From the optical transmittance spectrum can be observed that the increase of total transmittance of the film with an increase in growth temperature and a high transmittance in the visible range is obtained in the ZnO:Al films. The transmittance spectra of ZnO:Al films at wavelengths shorter than about 400 nm decreased sharply and the average transmittance over the 400 up to 800 nm is about 80% in the visible range. The optical transmission of ZnO:Al films depend on the deposition temperature. The increase of transmittance may be attributed to the decrease of film thickness, the increase of structural homogenity and the crystallinity of the films. This result is almost the same as the ZnO:Al films prepared by using the r.f. magnetron sputtering method [1] or the sol-gel technique [6].

CONCLUSION

Aluminium-doped zinc oxide transparent conducting films were prepared by the conventional dc magnetron sputtering technique. The influence of substrate temperature and dopant concentration on the structural properties, electrical conductivity and optical properties were investigated experimentally. It was determined that the dc magnetron sputtering technique is a good method to deposit transparent conductive ZnO:Al thin films. Transparent, high electrical conductivity, c-axis, highly oriented ZnO:Al thin films were grown on glass substrates by dc magnetron sputtering at different substrate temperatures. The degree of crystallinity, optical transmission, and electrical properties is strongly dependent on the substrate temperature. The glass substrate heating improves the structural and morphological properties of the film and leads to an improvement in carrier mobility by increasing the crystallinity of the film. The ZnO:Al thin films grown on the surface of substrates at a temperature of 300 ^{o}C showed a high conductivity value of $0.2 \times 10^{2}\ \Omega^{-1}cm^{-1}$. Doping with aluminium significantly increases the conductivity of these films by about five orders of magnitude, and a transmittance of about 80% in the visible range.

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