Synthesis and Characterization of Undoped and Aluminum Doped Zinc Oxide Thin Films using Thermal Evaporation Method

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Abstract

The undoped and Aluminum doped Zinc Oxide (AZO) thin films were prepared on ultrasonically cleaned glass substrates by thermal evaporation method at a pressure of 1.33×10^{-5} Pascal (~10^{-6} Torr). The film thickness was kept constant at 100 nm and the substrate temperature was also kept constant at 350^0C with only varying the doping concentrations. The deposited thin films were annealed at 350^0C for 15 minutes. The transmittance of the films increased and the absorbance decreased with the increase of Al incorporation up to 1.2 at % but after further increase of Al content they showed reverse behavior. The maximum transparency was found 86.48% for 1.2 at % Al doped ZnO thin film. The refractive index showed slight variation in the visible region with the incorporation of Al but extinction coefficient decreased. The band gap varied from 3.06 eV to 3.49 eV for the variation of Al concentration in ZnO with the minimum band gap occurring for 0.3 at % of Al content. The conductivity at the room temperature varied from 5.26 $\Omega^{-1}cm^{-1}$ to 3.05×10^3 $\Omega^{-1}cm^{-1}$ for variation of Al concentration with a maximum conductivity occurring for the film with 0.3 at % Al content. The results can be used for optimizing the optical and electrical properties of AZO films by tuning the Al concentration. .

Keywords: Al doped ZnO thin film, thermal evaporation method, optical properties, electrical properties

1. Introduction

ZnO thin films have attracted considerable interest in recent years for application as a transparent conducting material in liquid crystal displays [1], solar cells [2], etc. Zinc Oxide (ZnO) is a direct band gap semiconductor with a band gap of 3.37 eV and large excitation binding energy of 60 meV at room temperature [3, 4]. The conventional transparent conductive oxide (TCO) material is indium tin oxide (ITO). However, ITO materials are very expensive and toxic, as well as unstable to H_2 plasma. In contrast, undoped and doped ZnO thin films are widely used in transparent conducting layers because of their non-toxicity, thermal stability and better resistance against H_2 plasma processing damage [5, 6]. The high heat capacity, heat conductivity and high melting temperature of ZnO are beneficial for ceramics. Among the tetrahedral semiconductors, ZnO has the highest piezoelectric tensor, or at least one comparable to that of GaN and AlN. This property also makes it a technologically important material for many piezoelectric applications. Among the possible dopants, Al (group-IIIA) is a popular one because of high-quality, low-resistivity properties of the AZO thin films [7].

Various techniques such as molecular beam epitaxy (MBE) [8], pulsed laser deposition (PLD) [9], magnetron sputtering [10], thermal evaporation [11-13], chemical vapor deposition (CVD) [14], sol-gel [15], spray pyrolysis [16] have been applied to AZO thin film preparation. Thermal evaporation has distinct advantages over other techniques. It is a simple, suitable and economically attractive deposition technique, in which the quality of the films grown is quite superior. Usually in this method we get uniform deposition of the coating material and hence the film shows smooth variation of the properties with respect to wavelength of the incident electromagnetic wave. Furthermore, in our experimental set up, thickness of the film can be controlled using a thickness monitor and hence the film thickness remains uniform over the exposed area of the substrate. The materials sublime at lower temperature under vacuum and it does not demand any catalyst.

In this work, undoped ZnO and AZO thin films were prepared by thermal evaporation with a wide range of Al concentrations. The surface morphological, optical and electrical properties of the AZO thin films were investigated. The present work is limited to variation of the doping concentration only, in order to isolate the effect of the Al doping on ZnO thin films.

2. Experimental Details

AZO thin films were deposited on ultrasonically cleaned glass substrates by thermal evaporation method. An Al wire was used for Al source and ZnO powder were used for ZnO source. The vacuum chamber was very carefully cleaned with clothes soaked in acetone and was let to dry. The source material, ZnO powder was inserted in a Molibdenum boat and Al wire was kept in a Tungsten boat of turret source. The substrate with the mask was then mounted with a clamp above the boat. The substrate was placed at a distance of 10 cm above the sources and this distance was kept constant for all the films. Vacuum was created in the chamber by using Rotary and Diffusion pumps. When high vacuum was achieved (~ 10^{-6} Torr), the substrate was heated with the help of a radiant heater to a certain substrate temperature which was kept fixed for a particular substrate. A low tension (LT) voltage source was switched on and a current of 30~32 Amps was passed through the boat making the boat red-hot and the materials in the boat evaporate. The

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thickness of the films was monitored. After getting the desired thickness, the evaporation was stopped by placing a shutter above the evaporator source. The boat was replaced by using a rotator to bring the Al containing boat in that position and Al was also deposited in a similar way. A pure ZnO thin film was prepared of thickness 100 nm keeping the substrate temperature at 350^0C. Then it was annealed at 350^0C for 15 minutes. Then we prepared another eight samples (0.3, 0.6, 0.9, 1.2, 2.0, 5.0, 10.0 and 20.0 at % Al doped ZnO) of the same thickness keeping the same substrate temperature and annealing time and temperature as in the pure ZnO film.

The surface morphology of the thin films was studied using JEOL JSM-6490LA analytical scanning electron microscope (SEM) [X20,000]. The optical properties of the films were investigated using a UV-3100 (dual beam) recording spectrophotometer. The wavelength range of the spectrophotometer is 310 nm to 3000 nm. The electrical properties were investigated using KEITHLEY 2401 source meter by linear four point probe method.

3. Results and Discussion

Surface morphology: Figure 1 shows SEM micrographs of the Al-doped ZnO thin films with different Al concentrations: (a) 0, (b) 2, (c) 10 and (d) 20 at %. All the Al-doped thin films exhibited a rough surface with three-dimensional (3D) island growth due to the lattice and chemical mismatches between the thin films and substrates whereas the undoped thin film had a relatively smooth surface. This may be due to the degradation of crystal quality or the presence of defects. Some grains are observed clearly for high Al contents.

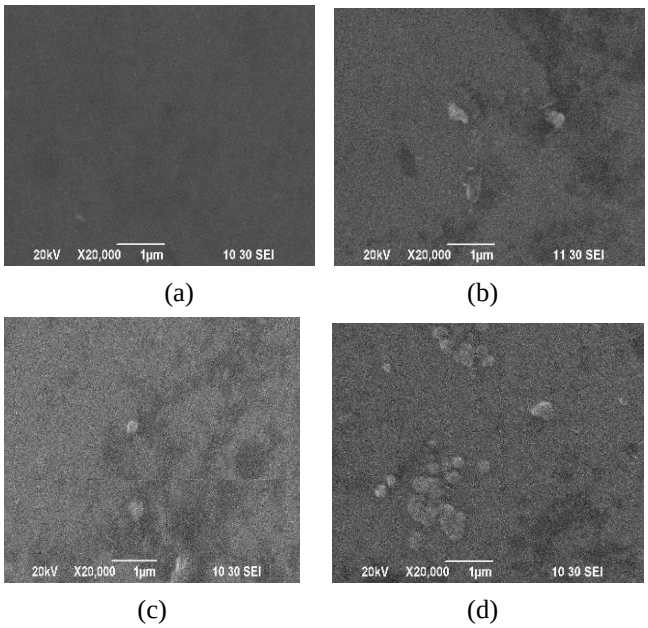
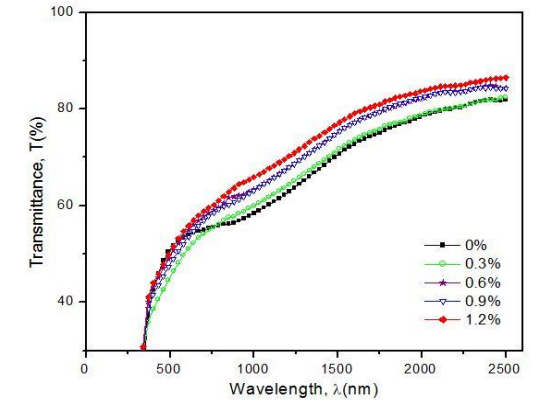
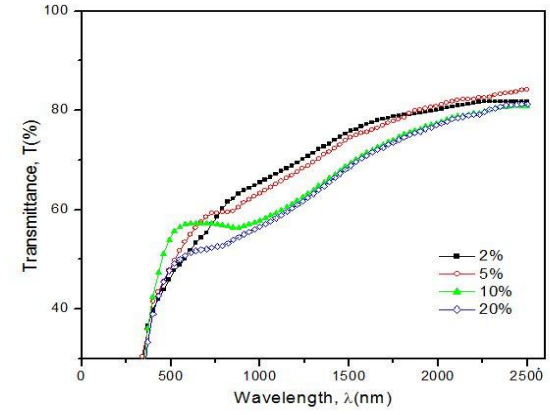


Fig. 1 SEM images of AZO thin films with different Al concentration: (a) 0, (b) 2, (c) 10 and (d) 20 at %

Optical properties and transmittance: Figure 2 gives the transmittance spectra for all the AZO thin films. For convenience of illustrations, they are displayed in figure 2(a) and 2(b). The optical transmittance spectra of all AZO films seem very similar and the transmittance in the UV region (310 - 380 nm) dropped abruptly for all the films as this is the absorption region. In this region, the incoming photons have sufficient energy to excite electrons from the valence band to the conduction band and thus these photons are absorbed within the material to decrease the transmittance. So this region carries the information of the band gap of the material [17]. In the visible region (380 - 700 nm), the transmittance increases logarithmically and all the films showed medium transmittance (40% - 55%). The variation of Al content does not show significant change in transmittance in this region. At higher wavelengths (2000 - 2500 nm) transmission exceeds 80%. In the near infrared region (700-2500 nm) all the films have high transmittance and which increase with the increase of Al content up to 1.2 at %. We get the highest transmittance (86.48%) at 2500 nm for 1.2 at % Al-doped ZnO thin film. But for 10 and 20 at % AZO film, the transmittance decreased slightly which might be due to the increment of scattering of photons by crystal defect [18]. These results imply that the optical transmittance can be increased by Al incorporation in the ZnO thin film but higher incorporation may degrade the crystal quality which will eventually decrease the transmittance.



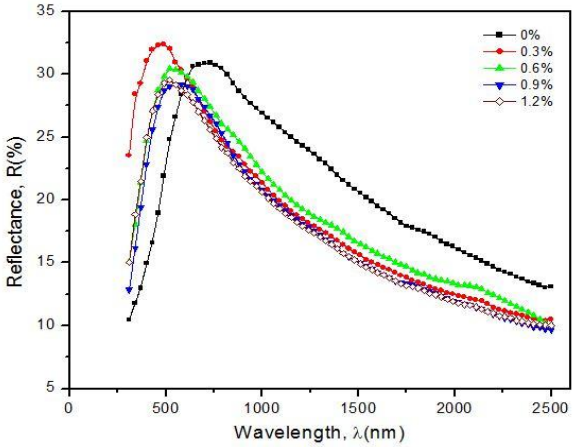
2(a)



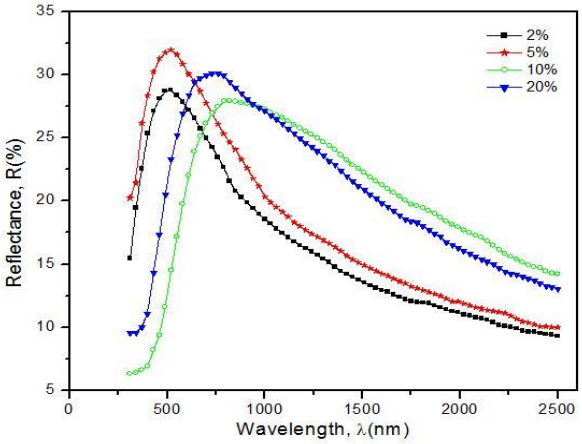
2(b)

Fig. 2 Optical transmittance spectra of AZO thin films prepared with different Al concentration

Reflectance: Figure 3(a) and 3(b) shows the reflectance spectra of Al-doped ZnO thin films. It is observed that in the UV region the reflectance increases smoothly for all the as-deposited thin films and lies in the range of 6% to 29%. The increasing points of reflectance shift gradually towards the lower wavelength with the increase of Al content in the films. The nature of increase gives an idea about the nature of the energy gap, which is ascertained further by the spectra of absorption coefficient. In the visible region we observe peaks for all the samples. These peaks indicate the maximum reflectance value for the respective films. The reflectance values start decreasing in the near infrared region as this region has high transparency. From both figures we see that, with the introduction of Al content in the film, the reflectance of the film has a decreasing trend. But all the AZO films have nearly equal reflectance values except 10 and 20 at % AZO. These two films have the reflectance values greater than other films in this region. A possible explanation for this is the increase of scattering of photons by crystal defects. Hence,



3(a)

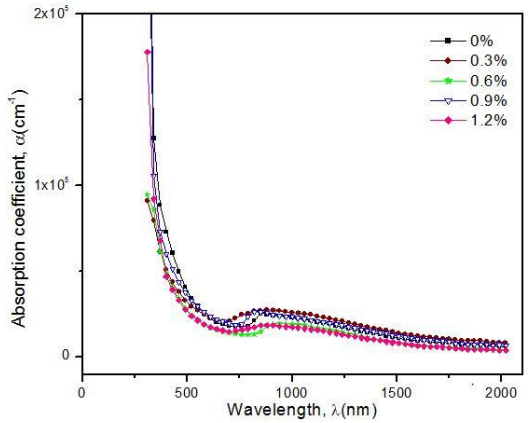


3(b)

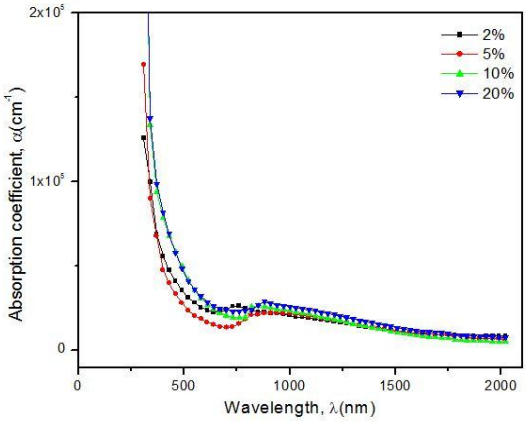
Fig. 3 Optical reflectance spectra of AZO thin films prepared with different Al concentration

it can be said that the reflectance can be increased initially by incorporating Al in the ZnO thin film for the UV region and can be decreased by doing the same for the near infrared region. But higher incorporation of Al (≥ 10 at %) gives the opposite result in both cases.

Absorption Coefficient: The absorption coefficient characterizes how easily a material or medium can be penetrated by a beam of light and it can be obtained through $I = I_0 e^{-\alpha t}$, where I and I_0 are the intensities of the transmitted and incident light, respectively, and t is the thickness



4(a)



4(b)

Fig. 4 Optical absorption coefficient spectra of AZO thin films prepared with different Al concentration

of the AZO thin films. Figure 4(a) and 4(b) shows the absorption coefficient (α) of the AZO thin films with different Al concentrations. We see that the absorption coefficient is in the range of 1×10^5 to 3.5×10^5 cm^{-1} in the UV region and it is also observed that in this region the absorption coefficient exhibits higher values which clearly indicate that there is a large probability of the allowed direct transitions. The absorption coefficient falls exponentially in the visible region. With the increase in Al content the absorption coefficient decreases slightly but for 10 and 20 at % AZO thin film it increases. In the near Infrared region the absorption coefficient decreases with increasing photon wavelength and remains approximately constant at higher wavelengths. Al incorporation does not

affect α in this region. These results imply that the optical absorption in the visible region of the ZnO thin film can be reduced by incorporating low amount of Al and can be increased by incorporating higher amount of Al.

Band Gap: As a direct band gap semiconductor, ZnO has an absorption coefficient (α) obeying the following relation for high photon energies *(hν)*:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (1)$$

Where *h* is Planck's constant, *ν* is the frequency of the incident photon and *A* is a constant that depends on the electron-hole mobility. The direct band gap energy of the deposited thin films have been obtained from the intercept on the energy axis, after extrapolation, of the tangent to the curve of $(\alpha h\nu)^2$ vs. $(h\nu)$ curve at large photon energies. Figure 5 shows the plots of $(\alpha h\nu)^2$ vs. photon energy of AZO thin films with different Al concentrations whereas fig. 6 shows the optical band gap variation of the AZO thin films as a function of Al-content in the ZnO thin film.

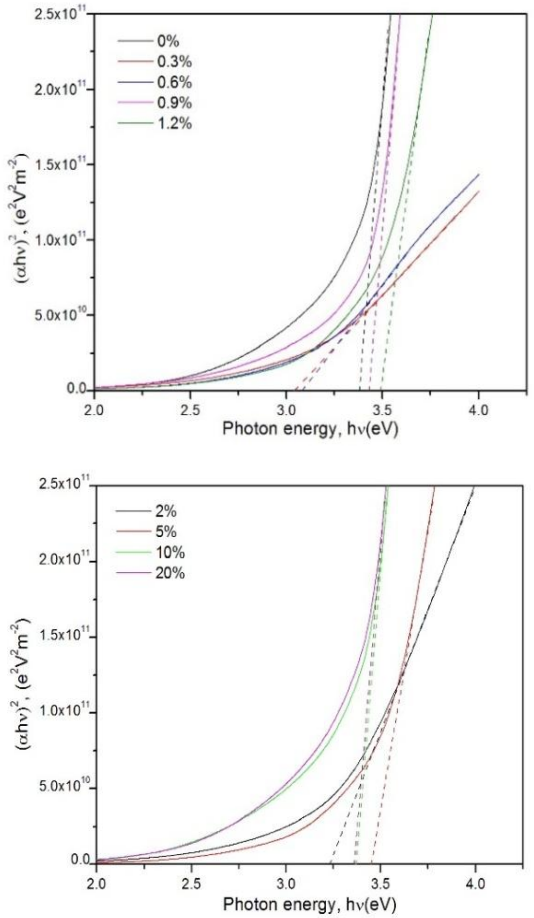


Fig. 5 Plot of $(\alpha h\nu)^2$ vs. photon energy (hν) of AZO thin films prepared with different Al concentration

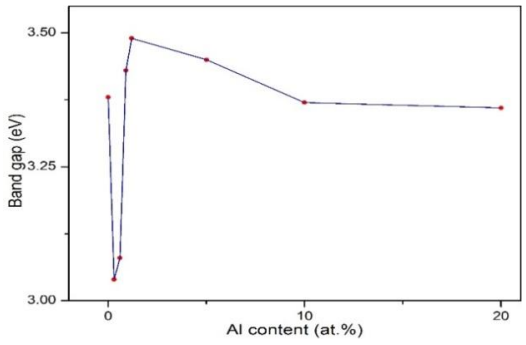


Fig. 6: Band gap of AZO films as a function of Al-content in the 0-20 at.% range

The optical band gap of the undoped ZnO thin film is found to be 3.38 eV. It is observed that the band gap sharply decreases for increase of Al-content at low concentration (~ 0.7 at.%) and increases up to a peak value 3.49 eV for concentration of 1.2 at.% and slowly decreases with further increase of Al-content. This movement of the band gap may be explained by the Burstein-Moss (BM) shift [19], an energy band widening (blue-shift) effect resulting from the increase of Fermi level in the conduction band of degenerate semiconductors [20].

Refractive Index: The refractive index is an important parameter for optical materials and applications. In materials where an electromagnetic wave can lose its energy during its propagation, the refractive index becomes a complex function of the frequency of the light wave. It is described by the following relation:

$$n = n(\omega) + ik(\omega) \quad (2)$$

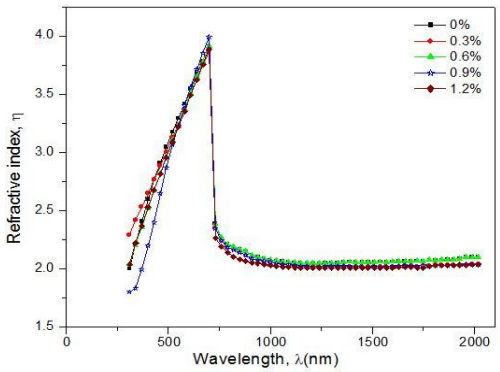
Where *n* is the real part and *k* is the imaginary part (extinction coefficient) of the complex refractive index. We have calculated refractive index by using the following relation [21, 22].

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (3)$$

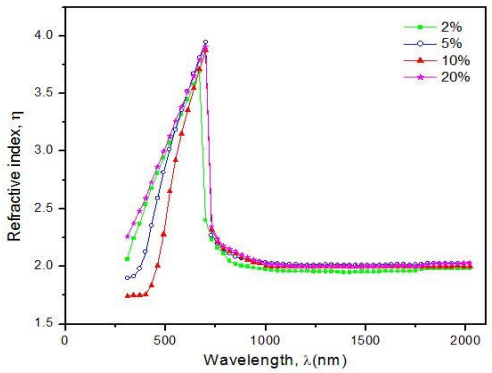
Where k $(k = \alpha\lambda/4\pi)$ is the extinction coefficient and *R* is the reflectance. Figure 7a and 7b show the refractive index (*n*) of the AZO thin films with different Al concentrations. Refractive indices of the as deposited thin films first increase gradually in the UV and visible region; attaining a maximum peak (~ 4.0) at 700 nm they fall abruptly and finally tend to be a constant at 2.0 in the near infrared region. Incorporation of Al in the ZnO thin films shows slight variation in the UV and visible regions. The initial gradual increase and peak is due to the interaction that takes place between photons and electrons. The rapid change after peak indicates a change in the absorption energy of the material, which depends on the surface and volume imperfections. Constant refractive index occurs due to successive internal reflections or due to the trapped photon energy within the grain boundary [23].

Extinction Coefficient: Figure 8(a) and 8(b) shows the extinction coefficient (*k*) spectra of the AZO thin films. The behavior of the extinction coefficient is nearly similar to the corresponding absorption coefficient for AZO thin films. It is observed that, extinction coefficient falls abruptly with the increase of wavelength in the UV region. It may be due to the absorption of light at the grain boundaries. In the visible region, the extinction coefficient first decreases and

then increases for all the as deposited thin films. This change is also due to the variation of absorbance. The extinction coefficient decreases slightly with wavelength in the near infrared region for all the thin films. It is also seen that with the increase of Al content the extinction coefficient decreases. The extinction coefficient describes the attenuation of light in a medium and higher *k* value indicates the probability of raising the electron transfer across the mobility gap with photon energy. Therefore, the higher values are the representation of greater attenuation of light in a thin film.



7(a)



7(b)

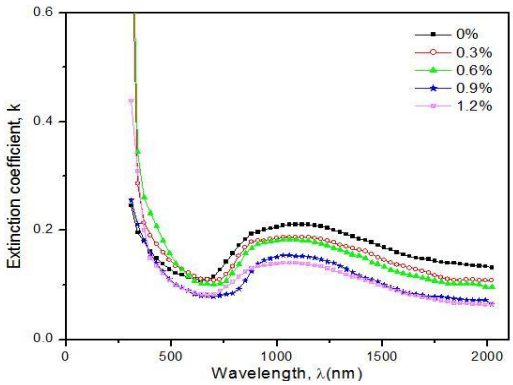
Fig. 7: Refractive index spectra of AZO thin films prepared with different Al concentration

Electrical properties: From the I-V characteristics curve we have calculated the slope of each curve by making them linearly fit. The inverse of the slopes give us the value of resistances for each of the thin films. Then we calculated the resistivity using the following equation:

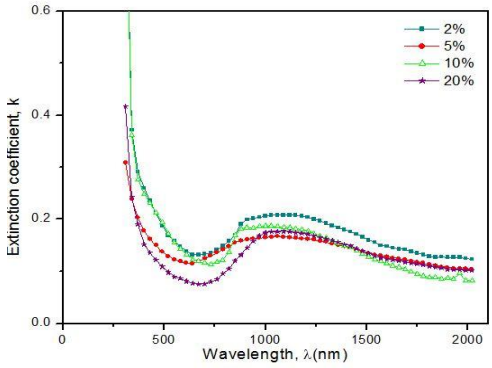
$$\rho = 4.532\, t\, (\frac{V}{I}) \quad (4)$$

Where *t* is the thickness of the sample, *V* is the applied voltage and *I* is the measured current. Then inverse of resistivity gives the value of conductivity and expressed by

$$\sigma = \frac{1}{\rho} \quad (5)$$



8(a)



8(b)

Fig. 8: Extinction coefficient spectra of AZO thin films prepared with different Al concentration

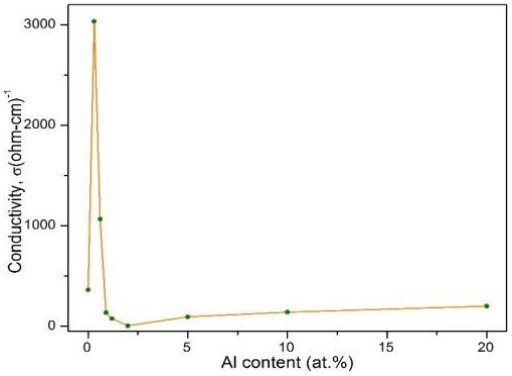


Fig. 9: Conductivity of the AZO films as a function of Al-content in the 0-20 at.% range

It is seen that by the introduction of 0.3 at % Al in ZnO, the electrical resistivity is reduced. With further increasing of Al up to 2.0 at % in ZnO, the resistivity increases. Then with the increase of Al content in ZnO the resistivity starts to decrease again and it continued to 20 at %. The resistivity of the AZO film is related to the Al doping concentration, intrinsic defects and various scattering centers [20]. Figure 9 shows the conductivity of the ZnO thin films as a function of Al content. It is seen that highly conducting AZO film is found in the low-Al content region. For 0.3 at % Al-doped ZnO thin film we found the highest conductivity which is 3.04×10^{3} $\Omega^{-1}cm^{-1}$. When a small

amount of Al impurities were added on ZnO, they mostly substitute Zn existing at lattice sites as donors, together with less Al atoms present at interstitial sites. However, when the Al content is around ~ 2.0 at.%, Al atoms in the film results in the intra-grain congregation and/or grain-boundary segregation forming Al–Al and Al–O clusters (e.g. AlO_x sub oxides) [20]. These Al atoms are electrically inactive, even acting as "electron killers" with such effects as donor passivation; thus the electron concentrations are limited. Similar suggestions were proposed by Chen et al. [24] and Choi et al. [25] for ZnO:Al and ZnO:Ga films, respectively. This is an indication that in order to get highly conducting AZO films, it is necessary to optimize the amount of Al in ZnO.

4. Conclusion

Al-doped ZnO thin films by thermal evaporation method in a wide range of Al - content from 0 to 20 at %. The AZO films were systematically studied for having a comprehensive knowledge of their behaviors. The SEM micrographs of Al-doped ZnO thin films have a rough surface with three dimensional island growths. Maximum transparency 86.48% was obtained for 1.2 at % Al-doped ZnO thin film in the near infrared region. For low Al-content (concentration < 2.0 at %), throughout the complete wavelength region, absorption coefficient decreases with increase of Al content. On the other hand, for moderate Al-concentration (> 2.0 at %), absorption coefficient slightly increases with increase of Al-concentration. Controlling Al-doping concentration, band gap of AZO thin film can be tuned at a suitable desired value. The refractive index (real part) shows slight variation with the incorporation of Al in the ZnO thin film in the visible region but extinction coefficient decreases with the increase of Al content in the ZnO thin films for all Al concentration. The conductivity also varied much for low-Al content region. Thus by varying the Al-content, we can tune band gap and can apply AZO thin films as front contact layer, buffer layer of thin film solar cell.

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