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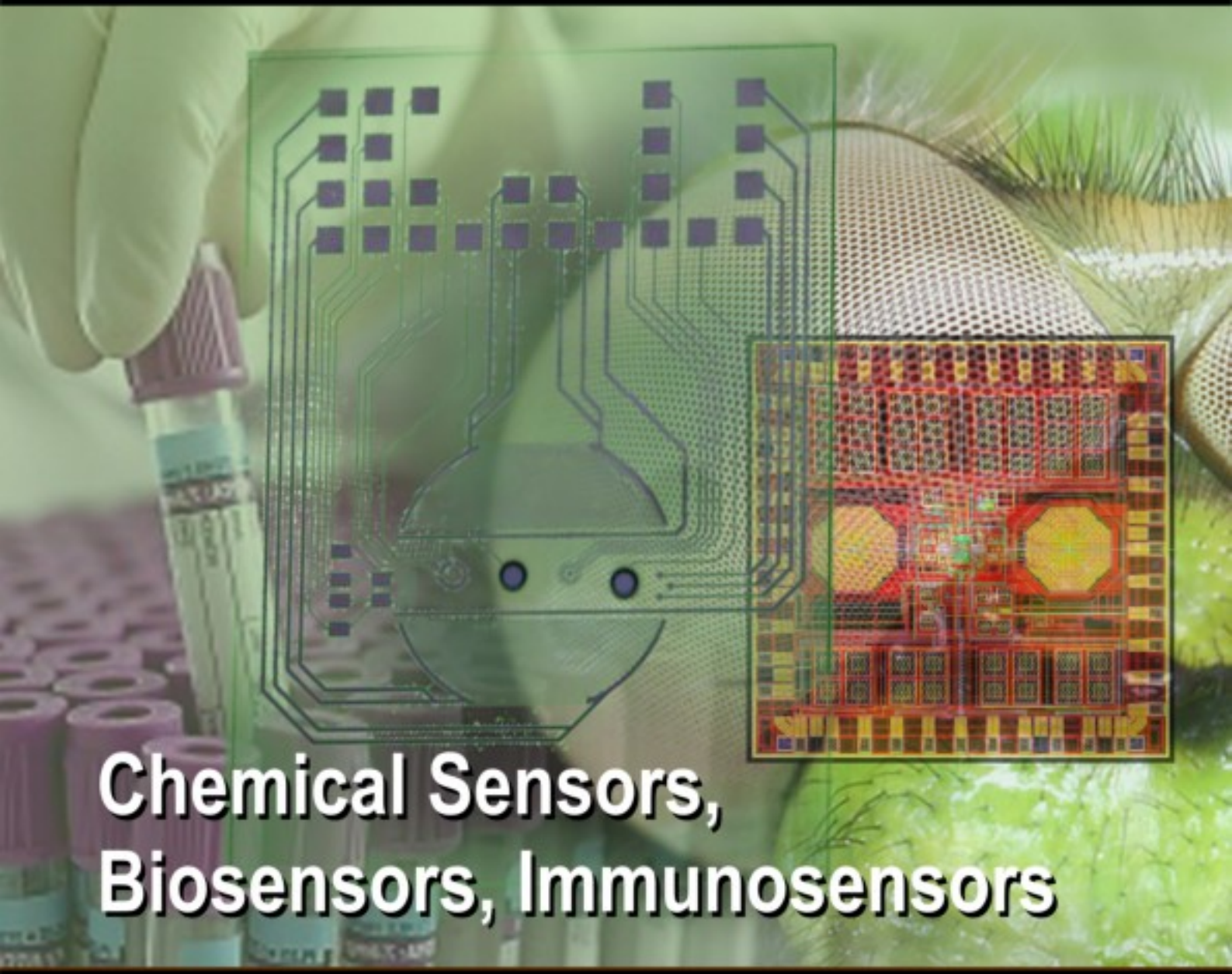

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Heat Treatment of Nanocrystalline ZnO and AZO Films Grown by Pulsed Laser Deposition

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Abstract: Repeated heating and cooling of the pulsed laser as-deposited ZnO and Aluminium doped ZnO (AZO) films at temperatures below the deposition temperature modifies their structural, optical and electrical properties while maintaining the c-axis orientation. Heat treatment affects the AZO films only slightly and the minimum electrical resistivity occurs for 2at% Al doped film. The electrical resistivity of undoped ZnO film decreases by a factor of more than half after heating. Unlike as-deposited films the lattice constant decreases linearly with increased Al doping and the maximum grain size is observed at 2at% Al doping. Absorption edges of the heat treated films show a small red shift in comparison as-deposited films. Interestingly, for heat treated films minimum resistivity and the largest grain size both occur at 2at%Al doping in ZnO. *Copyright © 2010 IFSA.*

Keywords: Heat treatment, Undoped and doped ZnO, Transparent conducting oxide, Pulsed laser deposition

1. Introduction

Zinc oxide (ZnO) is n type semiconductor with optical transparency in visible region. ZnO offers itself as transparent conducting electrode material for various applications such as solar cells, organic light emitting diodes, flat panel display and gas sensors [1-4]. Recently, the lasing action was observed in ZnO thin films which resulted into several studies on the application of ZnO in ultra violet (UV) lasers and photo detectors [5]. ZnO is a non- toxic, inexpensive [6] and abundant material having chemical

and thermal stability. The notable properties of ZnO are its direct band gap 3.27 eV at room temperature and the high exciton binding energy of ~ 60 meV as compared to ZnSe (20 meV) [7] and GaN (25 meV) [8]. In the past decades several techniques - pulsed laser deposition (PLD), molecular beam epitaxy [9], thermal evaporation, organic chemical vapour deposition [10-12] magnetron sputtering [13-15], atomic layer epitaxy [16, 17] have been employed to deposit thin films. However, PLD has been realized to be comparatively more useful, in growing thin films of oxide material, owing to its maintenance of stoichiometry, simplicity and control achieved by adjusting the laser fluency and the pulse rate [18]. Authors have earlier reported the properties of as-deposited undoped and aluminium doped ZnO films [19]. These films may associate metastable phases, inhomogeneity, stress and other defects with themselves. Therefore the films were heat treated after a gap of one year. Effect of cyclic heat treatment on the structural, transmission and electrical characteristics of these films have been reported in this paper.

2. Deposition of Nanocrystalline Films

Ceramic pellets of undoped zinc oxide (ZnO) and Al doped zinc oxide (AZO) are prepared using conventional cold pressing technique. Level of the doping is kept at 2, 3, and 5 at% respectively. Zinc oxide and Alumina powder both are obtained from Aldrich chemical company, Inc. and are of 99.999 and 99.997 % purity respectively. The pellets are sintered at 800 ^{0}C for 4 hours for densification and then polished to avoid occurrence of particulates due to their rough or irregular surface. The pellets were ablated by third harmonic of Q switched Nd:YAG laser (Quantel YG 980) to obtain undoped and doped films. The wavelength of laser pulses is 355nm, repetition rate is 10Hz and pulse duration is 6ns with a fluence of 2J/cm^{2}. Float glass substrate is kept at 6 centimetres from the target and its temperature is maintained at 400 ^{0}C. Base pressure in the deposition chamber is 10^{-6} torr and oxygen partial pressure is maintained at 10^{-3} torr. Thickness of each of the four films i.e. ZnO, 2at%Al: ZnO, 3at%Al: ZnO and 5at%Al: ZnO is nearly 250 nm. All the films are subjected to post-deposition heat treatment. Structural and electrical characterization along with optical transmission study of these four film samples has been performed.

3. Heat Treatment of ZnO and AZO Films

The as-deposited films are subjected to thermal cycles in air atmosphere. Heat treatment of the films is carried out at temperatures quite below the deposition temperature since at temperatures near or above deposition temperature, partial loss of material due to re-evaporation of film or a discontinuity in the film may occur. All the above as-deposited samples are heated up to 150 ^{0}C and then cooled back to room temperature i.e. 30 ^{0}C. Samples are again heated to 150 ^{0}C and cooled back. Three cycles of heating and cooling is repeated to stabilize the variation in the resistance. Variation in resistance of each of the samples during the thermal cycles is recorded directly using two probe pressure contacts and is plotted in Fig. 1. The resistance of the undoped ZnO film at room temperature is 947 Ω. As the temperature of sample is raised gradually to 150 ^{0}C its resistance decreases to 855 Ω along the curve a as shown in Fig. 1. Further when the sample is cooled back the resistance starts increasing along curve b showing a value of 949 Ω at room temperature which is very near to its initial value. As the thermal cycle is again repeated the film resistance follows the curve b**.** Again in next cycle the film resistance varies along the curve c. Thus the electrical resistance of the sample film measured during heating and cooling between room temperature and 150 ^{0}C, shows a hysteresis type of graph for resistance vs. temperature. These traces of paths, however, come closer with repeated cyclic heating and cooling and after three such cycles eventually follow the same path up to 70 ^{0}C during further heating and cooling.

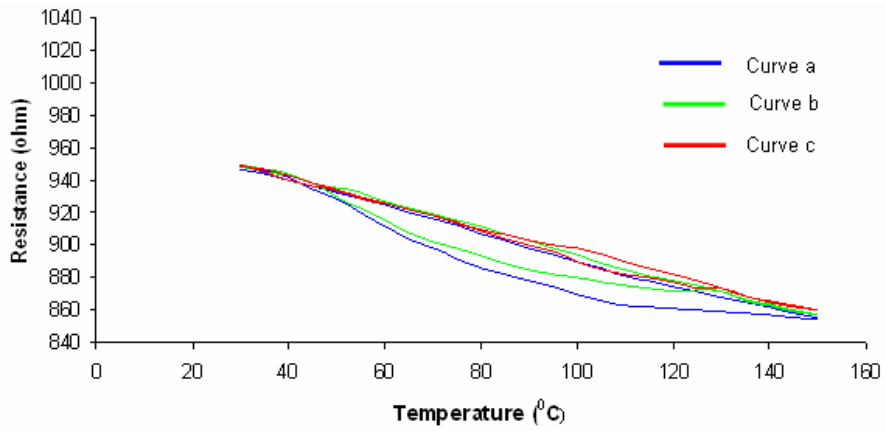


Fig. 1. Variation of resistance with temperature for as-deposited undoped ZnO film during repeated heating and cooling between 30 and 150 ^{0}C. Curves a, b and c represent the first, second and third cycle of heat treatment respectively.

The highly conducting as-deposited AZO films with a doping of 2, 3, and 5 at% have high conductivity. Variation in the film resistance when these films are subjected to heating cycles is negligible.

4. Characterization of the Films

The XRD patterns of the films are taken using X-ray powder diffractometer (SEIFERT ISO–DEBEYEFLEX2002) using Cu-K_α1 (λ=1.540568 Å) radiation. Surface morphology of films has been carried out using Scanning Electron Microscope. The transmittance of the films is obtained in 200-900 nm region using UV-VIS spectrophotometer from Systronics.

4.1. Structural Properties

The X-ray diffraction patterns of the heat treated ZnO and AZO films are shown in Fig. 2**.** The ZnO related reflections (2θ~34^0) in each pattern are obtained in (0002) plane, indicating a strong c-axis orientation with hexagonal wurtzite structure. Each of the four films has retained their single crystalline nature. The XRD peaks which occur at 34.51^0, 34.54^0, 34.57^0, and 34.60^0 for ZnO and AZO samples respectively shift to higher values of θ with increasing Al concentration in ZnO films. The trend is opposite to that obtained for as-deposited films [19]. The c-lattice constant of heat treated samples are 0.5194, 0.5190, 0.51846 and 0.51794 nm respectively. For ZnO sample it is equal to the JCPDS value of 0.5194 nm and for AZO the lattice constants are lower. The respective grain sizes are calculated to be 32.1, 36.9, 32.1 and 33.6 nm using Debye-Scherer equation.

4.2. Surface Morphology

Figs. 3a, b and c show the surface morphology of as-deposited undoped ZnO, 2at% Al:ZnO and 3at% Al:ZnO respectively. All the SEMs show uniform growth throughout the substrate with occasional darker patches. For doped samples these patches become deeper. Cyclic heat treatment of these films changes their surface structure. Cracks appear in the undoped film (Fig. 4a) due to segregation and shrinking whereas the morphology of 2 at% Al:ZnO changes considerably (Fig. 4b) showing uniform rod-like structures which may be due to grouping of grains. For 3at% Al:ZnO film (Fig. 4c) rectangular structures of random sizes are seen.

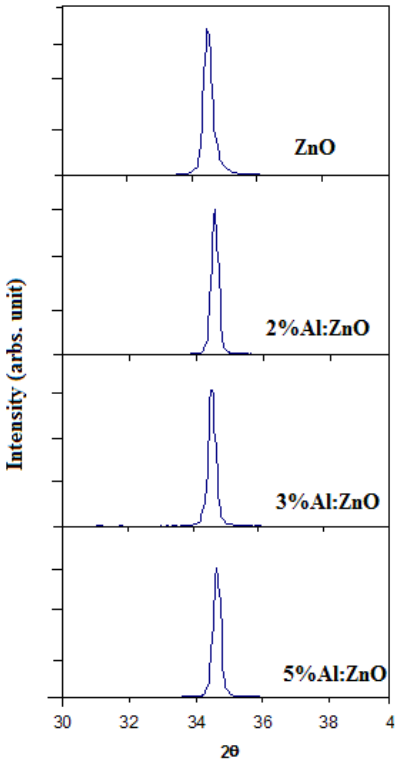
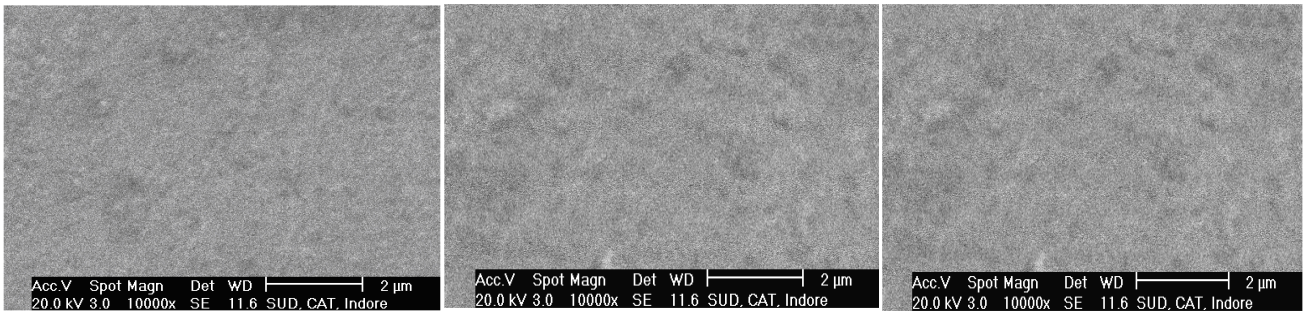
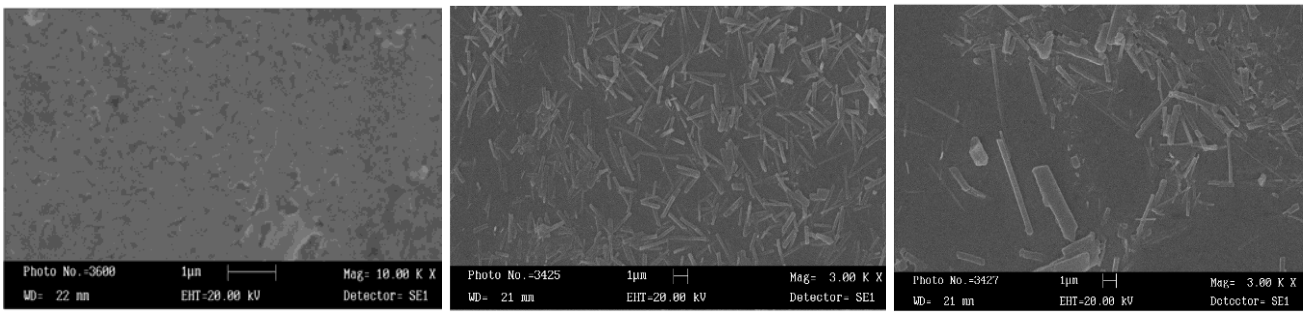


Fig. 2. XRD patterns of heat treated films ZnO and AZO films.



(a) (b) (c)

Fig. 3. SEM of as-deposited (a) undoped ZnO film; (b) 2at% Al:ZnO film; (c) 3at% Al:ZnO film.



(a) (b) (c)

Fig. 4. SEM of heat treated (a) undoped ZnO film; (b) 2at% Al:ZnO film; (c) 3at% Al:ZnO film.

4.3 Optical Properties

The optical transmittance of the heat treated films is measured at normal incidence taking air as reference and is shown in Fig. 5**.** ZnO, 2at% Al:ZnO, 3at%Al:ZnO and 5at%Al:ZnO films show an average transmission of nearly 65, 74, 75 and 80 % respectively, between 450 to 900 nm. Thus 5at% Al: ZnO shows the maximum transmission among all the films. This trend is similar to that obtained before heating the films. The respective sharp absorption edges occur at 384, 346, 334 and 330 nm. All the films show a small red-shift as compared to their corresponding values for as-deposited films. The band gaps for the respective samples are obtained as 3.23, 3.54, 3.59, and 3.61 eV as shown in the inset.

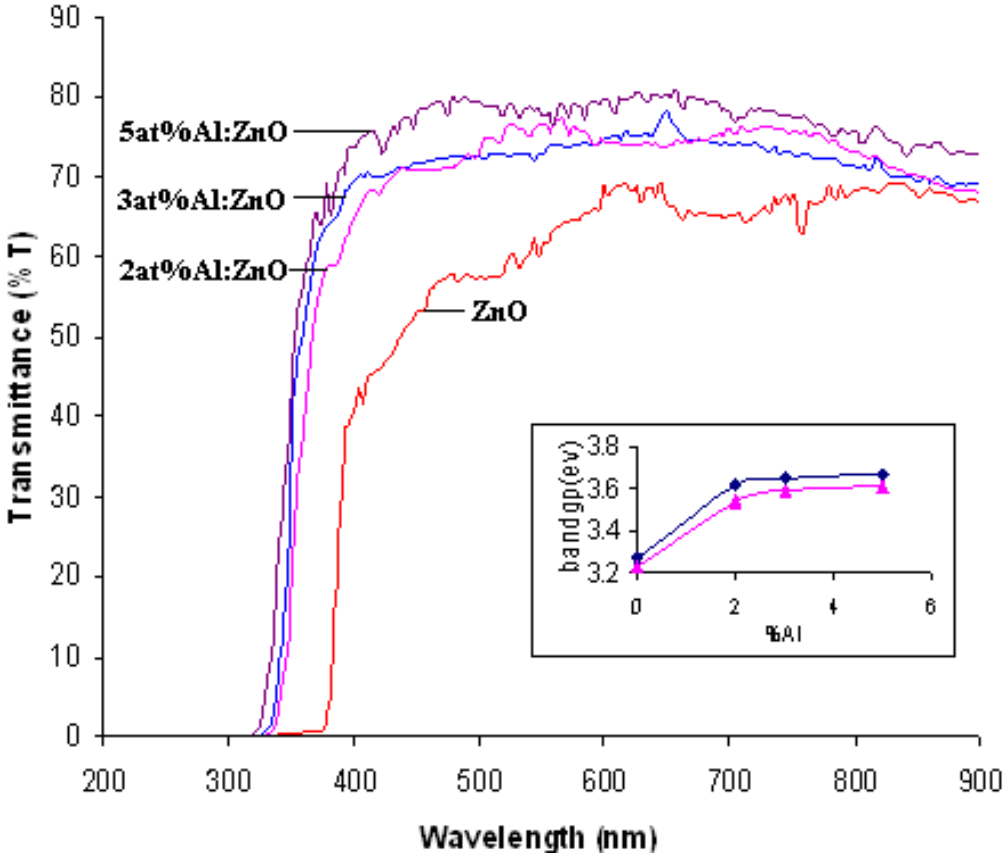


Fig. 5. Transmission spectra of undoped and Al doped ZnO films. Inset shows the optical band gap with variation in Al doping in ZnO for as-deposited and heat treated films.

4.4. Resistivity at Room Temperature

The resistivity of the films is measured using four point-probe method. Variation of resistivity, ρ, of the films after heat treatment with variation of Al content in the AZO samples at room temperature is shown by curve a, Fig. 6. Resistivity of these films at the same temperature before heat treatment is shown by curve b in the same figure. Minimum value of ρ is 2.79×10^{-4} Ω-cm and it occurs for heat treated 2at. %Al: ZnO film. For undoped ZnO resistivity falls from 3×10^{-2} Ω-cm to 1.47×10^{-2} Ω-cm after heat treatment. The change in resistivity for different concentrations in ZnO can be attributed to granularity in the samples.

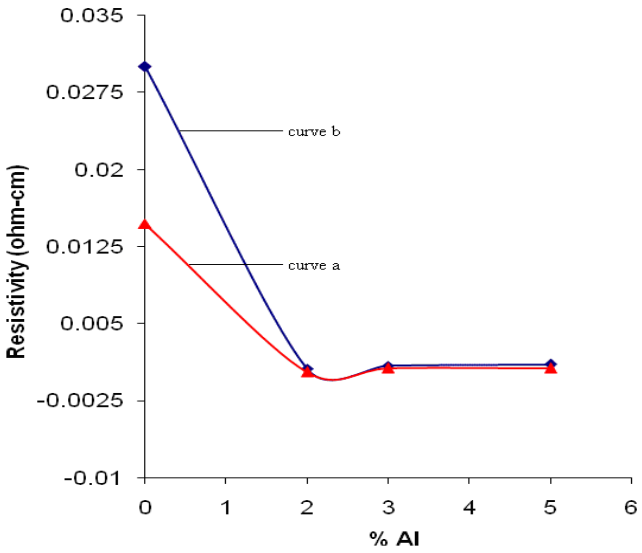


Fig. 6. Variation in resistivity of as-deposited , heat-treated (curve a & curve b) undoped and doped ZnO films.

4.5. Sensitivity to Temperature

Sensitivity of heat treated films to temperature is investigated by four point probe method by studying the variation in resistance of the film with variation in its temperature. For the purpose, voltage developed across two probes placed linearly on the film is measured at every 5 ^{0}C between 30 to 150 ^{0}C for three different values of currents i.e. for 0.01, 0.1 and 1 mA. Variation in the sheet resistance for undoped heat treated ZnO film is shown in Fig. 7. The curve shows negative temperature coefficient of resistance (TCR) showing the semiconducting behaviour of undoped ZnO film. Such variation for heat treated AZO films with 2, 3 and 5 at% doping are also shown in the same figure. As the temperature rises from 30 to 150 ^{0}C the sheet resistance of AZO films increases showing a positive TCR with a maximum change of 3 ohm in resistance. This indicates an absence of activation carrier and confirms that all Al doped ZnO films are degenerate semiconductors where the conductivity is mainly dominated by temperature independent scattering processes, such as ionized impurity scattering and tunnelling through the grain boundaries.

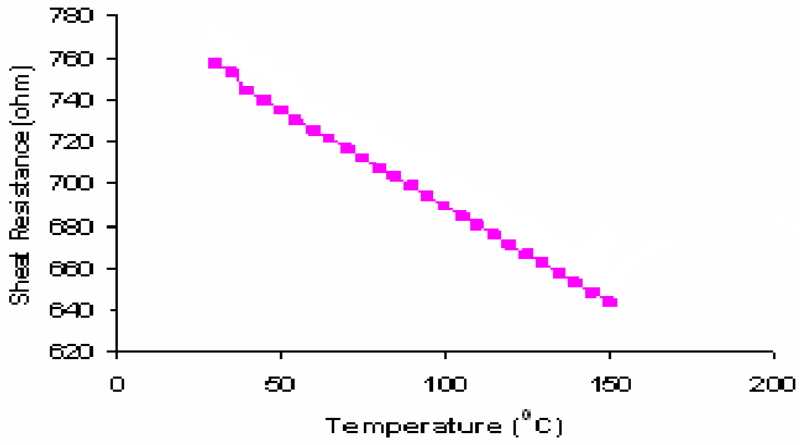


Fig. 7. Variation of sheet resistance with temperature for heat treated ZnO film show negative TCR.

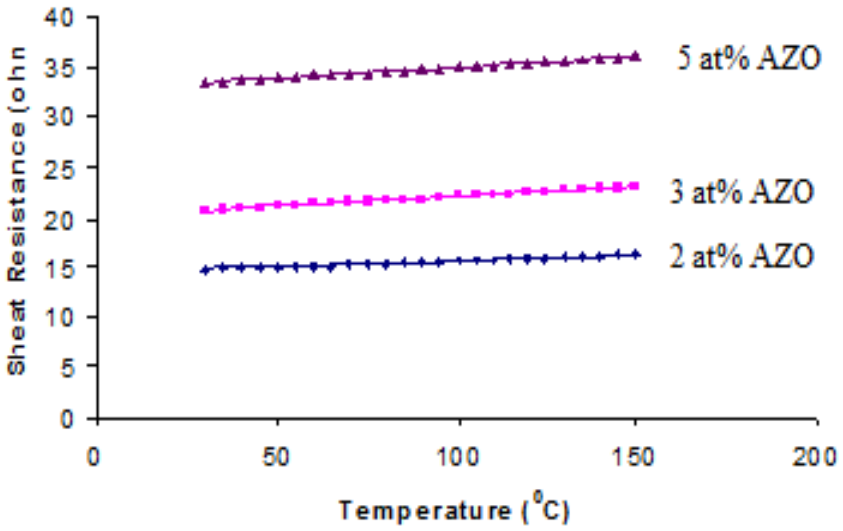


Fig. 8. Variation of sheet resistance with temperature for heat treated AZO films shows very small positive TCR.

5. Results and Discussion

The ZnO and AZO films when subjected to repeated heating and cooling between 30 ^{0}C and 150 ^{0}C i.e. at temperature below the deposition temperature their properties - structural, optical and electrical - get modified. For as-deposited films, the XRD peaks shifts to lower angles [19] with increasing Al doping whereas after cyclic heating this trend reverses and XRD peaks now shift to higher angles. This trend affects the interplanar spacing also as it decreases with increasing Al concentration for heat treated films whereas it was increasing for as-deposited films. Lattice constants also show similar behaviour. After heating, lattice constant decreases linearly with increased Al doping. This behaviour is attributed to the occurrence of substitutional incorporation of Al ion into Zn^{2+} sites. Since radius of Al ion (0.53Å) is lesser than that of Zn^{2+} ion (0.72Å), substitutional incorporation of Al ion into Zn ion sites leads to compression of lattice. As the film is heated the doped Al ion which got interstitially placed in the as-deposited films diffuses in and gets placed on Zn ion sites thereby leading to increase in the lattice parameter,. The grain size earlier showed increasing trend with increasing Al concentration in ZnO but after heating this trend breaks. The size firstly increases at 2at% Al doping, then decreases for 3at% Al doping and again increases for 5at% Al doping. The grain size is maximum at 2at% doping. The heat treatment decreases the transmittance of the films. The sharp absorption edges for corresponding films show a small red shift after heating in comparison to as-deposited films. Inset in Fig. 3 shows a comparison between the band gaps of heat treated and as-deposited films. The resistivity of heat-treated undoped ZnO film at room temperature drops drastically to 50 % as compared to as-deposited film. It is interesting to note that for heat treated films minimum resistivity and the largest grain size both occur at 2at% Al doping in ZnO.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

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