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ZINC OXIDE NANOSTRUCTURES AS TRANSPARENT WINDOW LAYER FOR PHOTOVOLTAIC APPLICATION

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ZnO films have been prepared by oxidizing thermally evaporated Zn metal. Crystallization appears to be influenced by both annealing temperature and time. XRD result reveals the presence of (100), (002) and (101) diffraction peaks for films annealed at 250^0 C , also intensity of the peaks show an increase with increase in post-annealing temperature to 400 and 550 °C. FWHM of the peaks decrease with increase in annealing temperature which reveals that crystallinity of films is improved. The transparent sample has been characterized by SEM, XRD UV-VIS spectroscopy and RT measurements. Electron microscopy confirms platelets shaped crystals parallel to the substrate with average width of about 0.33-0.64 μm. The optical band gap lie in the range 3.06-3.30 eV showing an improvement in transparency with annealing temperature for window application. The annealing temperature appears to be important parameters for molecular packing in the solid state structure and influence the properties of the films. Films annealed at elevated temperatures show comparatively higher electrical resistivity and optical band gap which is due to the transformation of Zinc to Zinc Oxide at higher annealing temperature.

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Keywords: zinc, photovoltaic, oxide, films

1. Introduction

Transparent conducting oxides (TCOs) are an increasingly important component of photovoltaic (PV) devices, where they act as electrode elements, structural templates and diffusion barriers and their work function controls the open-circuit device voltage. For a TCO to be of interest for PV electrode applications, it must transmit freely across the solar spectrum [1].The first TCO was reported in 1907 by Baedeker [2] ,who used a primitive vapor deposition system to deposit thin-film CdO that was both optically transparent and electrically conducting. As CdO is not recommended frequently because of its highly toxic nature and effects on the environment and human health have recently been regarded as one of the top priorities. Therefore, developing alternatives to severely toxic cadmium-containing materials attracted much attention as a prime issue in the research field of semiconductor [3]. Since then, three oxides have emerged as commercially important transparent conductors: indium oxide, tin oxide, and zinc oxide. Among these Indium is very costly and Unlike of In and Cd, ZnO find preferences always because of it low cost and environment friendly nature. Manny techniques have been developed to prepare ZnO films for its use as TCO window layer [4-7] however scaling up of device quality transparent coating for industry is a big challenge. Keeping these point in view we explored the thermal oxidation method which has possibilities to develop large area device quality coating for photovoltaic applications. In this work we have exploited thermal oxidation of Zn films deposited by sublimation of Zn metal on glass substrate. The effect of annealing temperature and time in Oxygen environment has been studied on growth morphology and properties of these films for their possible applications as window material in Photovoltaic devices.

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2. Experimental

Zn films were prepared by thermal evaporation technique onto the corning glass substrate. The glass substrate was etched in dilute HF (2–3%) solution and rinsed in deionized water. The substrate was then cleaned ultrasonically with trichloroethylene and placed in the vacuum chamber of a coating unit. The substrates were mounted on the substrate holder with a heating arrangement and the temperature was measured with the help of a K-type thermocouple obtained from Omega Engineering Inc. (USA).Thefilms were prepared from the material by a conventional thermal evaporation technique using a vacuum coating unit (high vacuum coating unit 12A4H) . Molybdenum boats were used for evaporation. The pressure of the order of 10^{-5} mbar was maintained in the chamber throughout the deposition. Thefilm thick ness was controlled during deposition by means of a quartz crystal thickness monitor and was kept around at 1.5 µm. spectra were recorded Bruker X ray diffractrometer. The optical studies were carried out on ZnO films grown on glass substrates using the Perkin elmer UV-Vis spectrophotometer The surface morphology of thefilms was studi ed by JEOL JSM-6100 (Japan) scanning electron microscope with an electron beam accelerated by 20 kV. The electrical conductivity of the films were determined in the temperature range 290–405 K . The temperature of the film was measured using K-type thermocouple. The steady state value of current was recorded at regular intervals of 5 K using an electrometer (Keithley 6517 A). Silver contacts were used to connect electrical leads to the films. The contacts were verified to be ohmic from the symmetric straight lin e of current–voltage (I–V) characteristic passing through the origin. To study the optical properties, the transmittance and absorbance spectra of the samples were obtained in the photo energy range 1.12–4.13 eV by using UV-1601PC (Shimadzu, Japan) spectrophotometer.

3. Result and discussion

After the deposition of Zn onto glass the films were preheated at 250 °C for 2 hours and post-heated further for 2 h at different temperatures in presence of oxygen at atmospheric pressure. The films become dark gray after first annealing process and luster of the films decreases which indicates that Zn starts to convert into ZnO. In the two steps annealing process choice of temperature and time was justified from preliminary investigation. Fig. 1 shows XRD patterns of films after post-annealing process at 250°C for 2 hours. There are three peaks, which belong to the (100), (002), and (101) planes of the ZnO wurzite structure. With increase in annealing temperature to 400°C for 2 hours the colour of the films starts to whiten. The intensity of (100), (002) and (101) peaks gradually increased indicating more ordered structure. Fig. 3 shows XRD patterns of Zn films post-annealed at 550 °C shows that the intensity of (002) peak is increased more relative to other two peaks (100),(101) . The well-defined diffraction peaks from these patterns indicate polycrystalline structure of ZnO. FWHM of the peaks decrease with increase in annealing temperature (table.1) reveals crystallinity of films is improved. Variation of particle size with annealing temperatures is shown in fig 4. XRD Peak near 2θ=31.66 is chosen for Scherrer calculation using equation

$$\beta_{hkl} = \frac{K\lambda}{L_{hkl}\cos\theta_{hkl}} \tag{1}$$

where, β is the width of the peak at half maximum intensity of a specific phase (hkl) in radians , K is a constant that varies with the method of taking the breadth and shape of crystallites (0.89<K<1) [8] , λ is the wavelength of incident x-rays, θ is the centre angle of the peak and L is the particle size.

Table 1. Variation of FWHM and particle size with annealing temperature.

S. No	Annaling Temperatue °C	FWHM (radian)	Particle Size(nm)
1.	250	0.01058	12.75
2.	400	0.00765	17.63
3.	550	0.00567	23.80

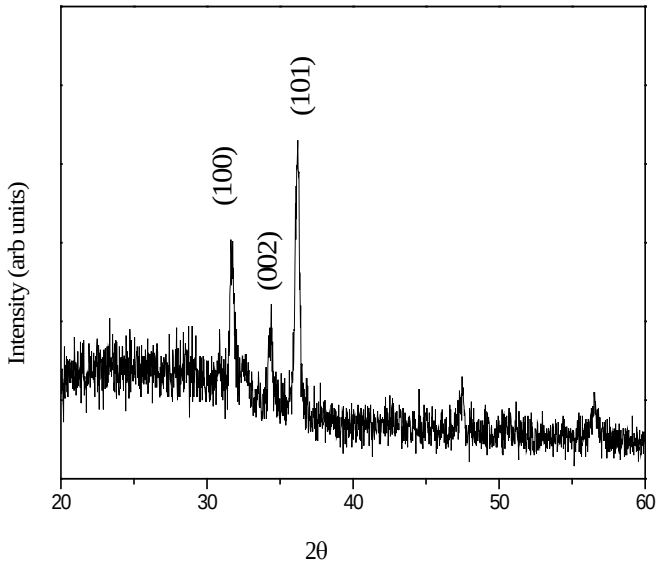

Fig. 1. XRD pattern of the oxygen doped Zn films annealed at 250 °C.

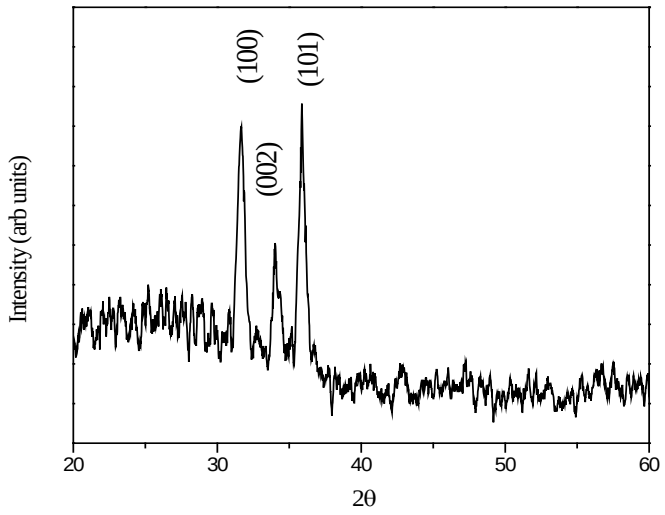

Fig. 2. XRD pattern of the oxygen doped Zn films annealed at 400 °C.

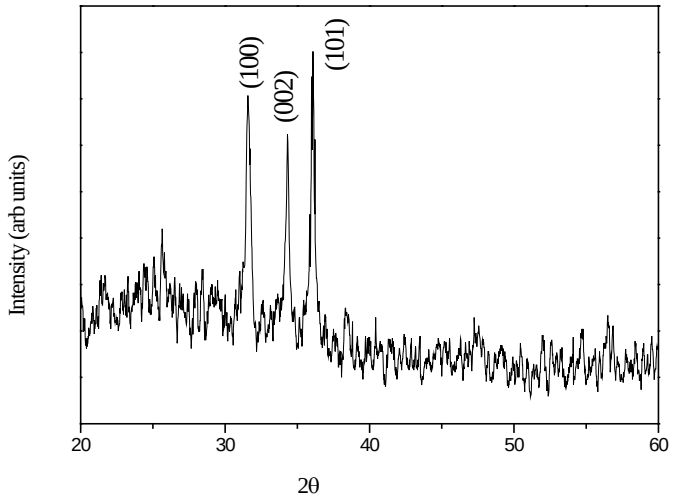

Fig. 3. XRD pattern of the oxygen doped Zn films annealed at 550°C.

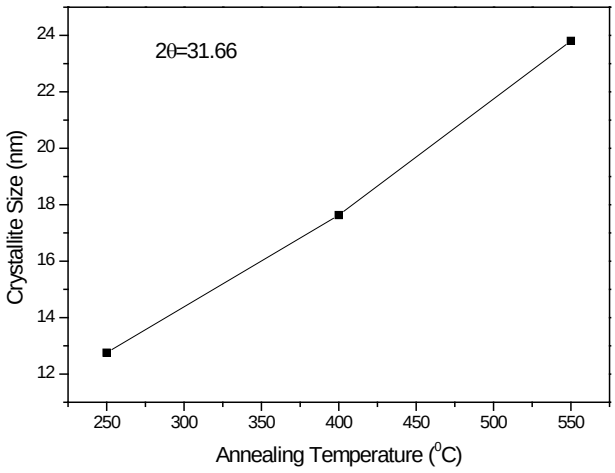

Fig. 4. Variation of particle size of the oxygen doped Zn films with increase in annealing temperature.

Fig. 5 shows the SEM pictures of Zn films produced by the thermal evaporation and annealed by two step process at the fixed experimental condition to improve the crystallinity of the films. Each oxidation temperature yields a particular surface morphology characteristic of that particular temperature. The grain boundaries are clearly seen and have platelets shaped crystals perpendicular to the substrate. The average diameter obtained from the SEM pictures is about 0.33 μm for films annealed at 250 C and increased to about 0.64 μm by increasing the annealing temperature to 550 °C. SEM and XRD results are in agreement and reveals that improvement of crystallinity of films with increase in annealing temperature as reported for studies on chalcopyrite films [9]. The averaged grain size visualized by SEM is around 0.33–0.64 μm, which is quite higher than the particle size deduced from the FWHM. This difference is due to the reason that SEM visualization allows only seeing grains, which are constituted of more or less disordered atoms and particles, while XRD gives the coherence length of atoms.[10]

Table 2. Change in optical band gap and grain size (calculated from SEM) with annealing temperature.

S. No	Annealing Temperature °C	Band Gap(eV)	Grain Size(μm)
1.	250	3.06	0.33
2.	400	3.12	0.52
3.	550	3.30	0.64

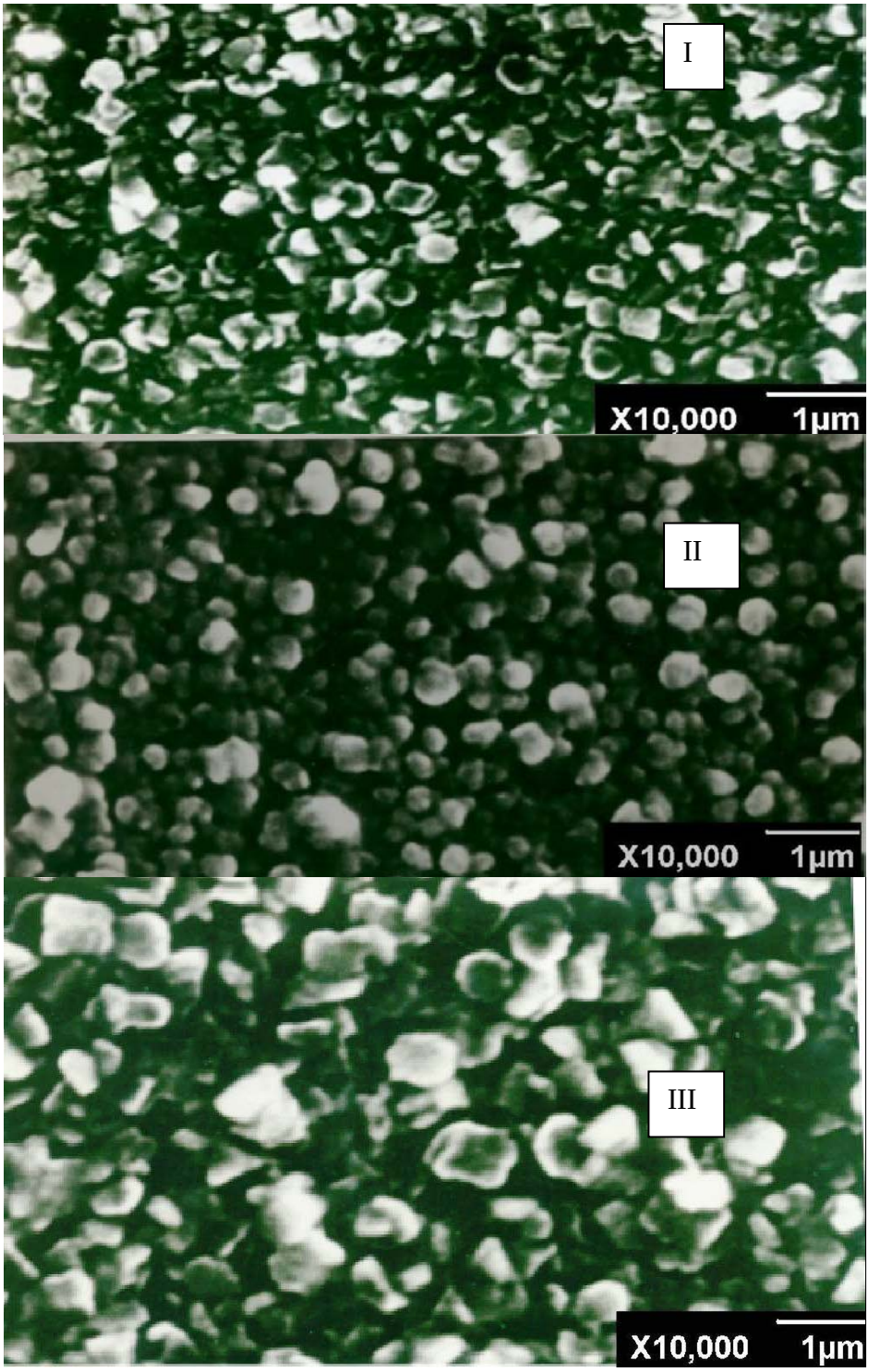

Fig. 5. SEM of oxygen doped Zn films at annealing temperatur (I) 250 °C (II)400 °C(III)550 °C.

The optical absorption coefficient (α) of ZnO films is determined over the energy range 1-4.2 eV at room temperature 296 K. This absorption region has been examined in terms of an interband transition and the dependence of absorption coefficient upon energy [11] of incident photon is given as equation

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

where B is the constant, E_g is the band gap and ν is the frequency of the incident light. The plot of square of the absorption coefficient vs. photon energy of the films prepared by different annealing temperatures is shown in the figs (6-8)

The extrapolation of the straight line to αhν = 0 give the optical transitions which lie in the range 3.06-3.30 eV. The results indicate that band gap energy of films increases with the increase in the annealing temperature which can be understood by the facts that the films annealing at higher temperatures are more ordered and thus leading to less absorption and better transparency. Also this shift of band gap to higher value is due to the oxidation Zn. The change in optical band gap of films annealed at temperature is reported in table 2 .

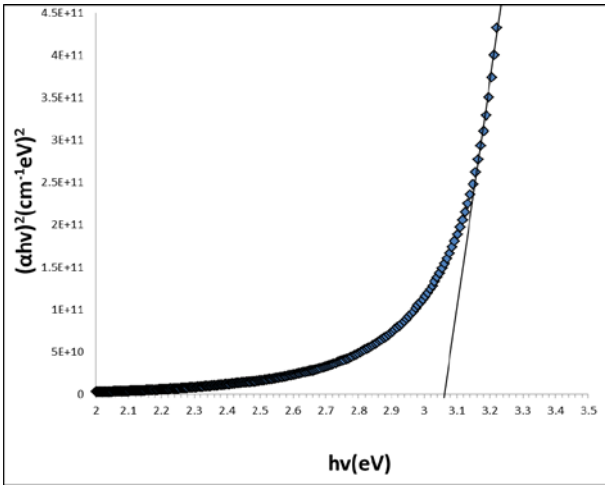

Fig. 6. Typical $(\alpha h\nu)^2$ vs (hν) dependence for oxygen doped Zn films annealed at 250 °C.

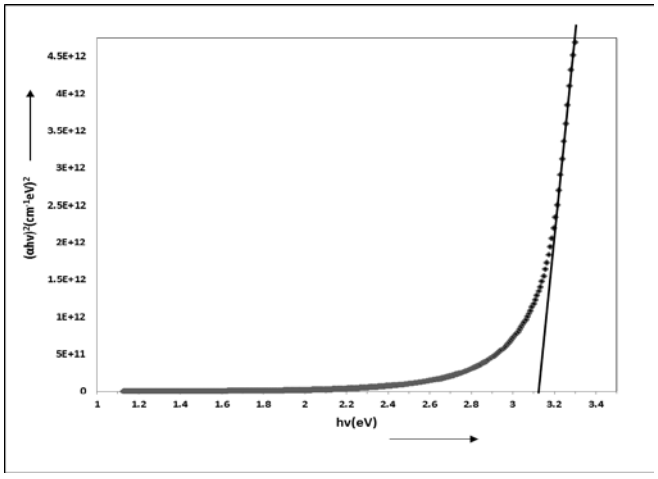

Fig.7. Typical $(\alpha h\nu)^2$ vs (hν) dependence for oxygen doped Zn films annealed at 400 °C.

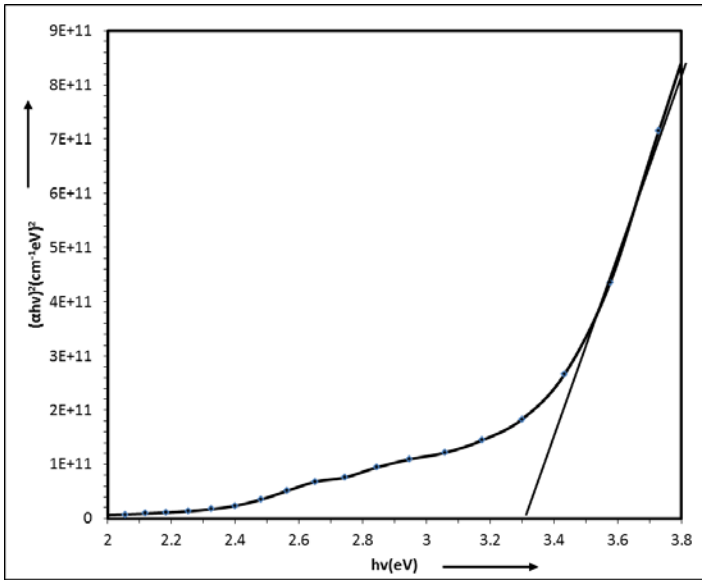

Fig. 8. Typical $(\alpha h\nu)^2$ vs (hν) dependence for oxygen doped Zn films annealed at 550 °C.

Electrical resistivity of the films annealed at 250,400 and 550°C for 2 h is measured by depositing two parallel silver electrodes with width 0.5 cm and separated by 2cm in vacuum on the films. Resistivity measurements were done by two probe method in range 293K-393K using relation ρ= Rbt /L where L is length t is thickness of films and b is electrode separation.. Observations reveal that, the resistivity of the films increases with increase in temperature, within the experimental range (290-393K) investigated. This shows that films have metallic behavior in investigation temperature range. The electrical resistivity of the films annealed at higher temperature 550 °C is high as compare to films annealed at temperature 400 °C . This may be due to the fact that as annealing temperature increases more and more Zn atoms are combined with O to form ZnO and concentration of Zn atoms decreases. It has been observed that the electrical resistivity increases with increase in the annealing temperature too. These results are in good agreement with SEM and XRD pattern of these films. From these measurements it is evident that samples are showing their metallic characters which may be due to the reason that only few Zn sites have transformed to ZnO and majority are left as Zinc. Thus it is proposed that the higher annealing temperature for complete transformation of Zinc lattice to Zinc oxide should be tried .Corning glass can not be used for this as we observed that it starts diffusing at 600^0 C. Another possible reason for this type of behaviour may be delocalization of electrons leading to metallic conductivity, which is

Characteristic of a degenerate semiconductor [12]. Similar metallic behaviour has been observed for ZnO films deposited laser ablation by Gupta et. al. [13]

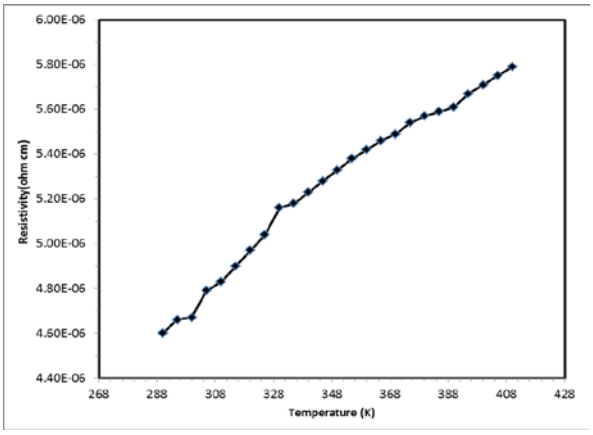

Fig. 9. Variation Resistivity with absolute temperature for oxygen doped Zn films annealed at 250 °C.

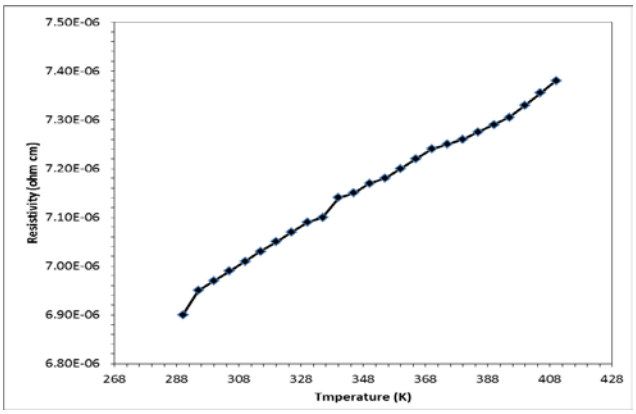

Fig. 10. Variation Resistivity with absolute temperature for ZnO films annealed at 400 C.

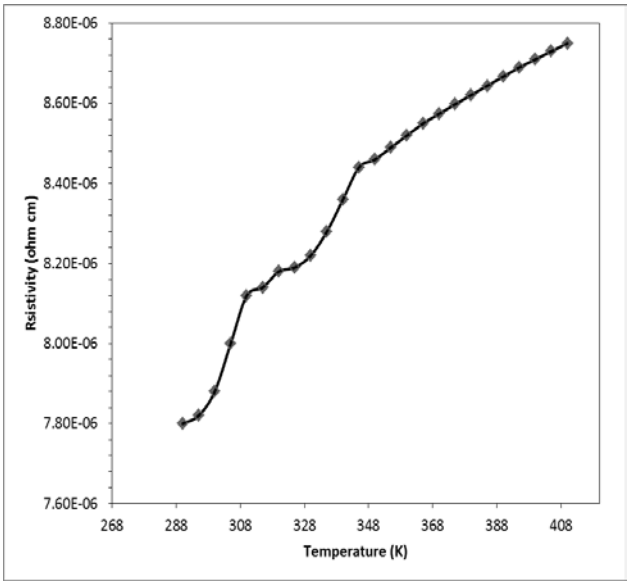

Fig. 11. Variation Resistivity with absolute temperature for oxygen doped Zn films annealed at 550 °C.

4. Conclusion

We observed that thermal oxidation technique have potential to develop transparent window materials and because of its simplicity and low cost this technique can be scaled to industry level. Optimizing the parameter like annealing temperature and time device quality ZnO nanostructures can be obtained which have potential for photovoltaic application. We found that for the post-annealed films at 250 °C, the (100), (002) and (101) diffraction peaks appeared and the intensity of the peaks goes on increasing with increase in post-annealing temperature to 400 and 550 °C. FWHM of the peaks decrease with increase in annealing temperature reveals crystallinity of films is improved showing particle size distribution in the range of 12-24 nm. The optical band gap is found to lie in the range 3.06-3.30 eV. The results indicate that band gap energy of films increases with the increase in the annealing temperature. The annealing temperature appears to be important parameters for molecular packing in the solid state structure and influence the properties of the films. Films deposited at elevated temperatures show comparatively higher electrical resistivity and optical band gap.

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