Optical, Structural and Electrical Properties of Nanosized Zinc Oxide Sintered Films for Photovoltaic Applications

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Abstract:
Zinc oxide films have been deposited on ultra-clean glass substrates by screen-printing method followed by sintering process. Optimum conditions for preparing good quality screen-printed films have been found. The optical band gap of the films has been studied using reflection spectra in wavelength range 325-600 nm by using double beam spectrophotometer. X-ray diffraction studies revealed that the films are polycrystalline in nature, single phase exhibiting wurtzite (hexagonal) structure with strong preferential orientation of grains along the (101) direction. Surface morphology of films has been studied by scanning electron microscopy (SEM) technique. The electrical resistivity of the films was measured in vacuum by two probe technique.
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1. Introduction
Zinc oxide is an important II-VI group semi-conductor with a large direct band gap of 3.2-3.36 eV at room temperature. It is used as key material for photovoltaic devices, gas sensors, varistors, surface acoustic wave devices, electric transducers, piezo-electric materials and opto-electronic devices [1-3].

Research on renewable energies includes the photovoltaic conversion of solar energy and important investigations of novel materials and structures. Photovoltaic provide one of the most important routes for direct solar energy conversion. Thin film solar cells meet the cost goals [4].

It is generally recognized that any large-scale applications must rely on cheap polycrystalline materials. The use of thin film polycrystalline semiconductors has attracted much interest an expanding variety of applications in various electronic and opto-electronic devices. The technological interest in polycrystalline based devices is mainly caused by their very low production costs [4].

Several techniques have been used to produce ZnO thin films such as chemical precipitation technique [2], sol gel [5, 6], spray pyrolysis [7, 8], R.F magnetron sputtering [9], SILAR [10], thermal evaporation [11] and screen printing technique [1, 3, 12].

Screen printing is a very simple and viable technique compared to other costly
methods. It is less time consuming, less polluting and ensures maximum material utility and offers a suitable method for preparing films on large area substrates [13, 14]. The formation of ZnO films by screen printing technique has been reported by several researchers [1, 3, 12]. A.V. Patil et.al [1] has reported screen printed ZnO films on alumina substrate. Bindu Krishan et al [12] has reported nanosized ZnO thick films by polyol synthesis. B. Ismail et al. [3] has also reported ZnO films on glass substrate by screen printing technique using ZnO paste (with ZnCl₂ and propylene glycol) and studied only structural and electrical properties of prepared films. In this paper, we have presented the formation of ZnO sintered films on glass substrate using ZnO paste (with ZnCl₂ and ethylene glycol). Our intention is to study the optical, structural and electrical properties of ZnO films and to employ this material for the fabrication of photovoltaic devices.

2. Experimental Procedure

In the present investigation, ZnO films were prepared by the screen-printing technique followed by sintering process [13, 14]. A commercially available ZnO powder with 99.999% purity was used as the starting material. A slurry consisting of ZnO powder, with 10% wt of ZnCl₂ and an appropriate amount of ethylene glycol were thoroughly mixed. ZnCl₂ was used as an adhesive and ethylene glycol as a binder. The paste thus prepared was screen-printed on ultra-clean glass substrates, which are cleaned by emery powder and acetone and finally washed with distilled water. The prepared samples were dried at 120°C for 4 hours in open air. The reason of drying the sample at lower temperature was to avoid the cracks in the samples. The organic materials were removed at about 400°C, so sintering temperature can not be less than 400°C. Zinc chloride is hygroscopic and its melting point is 283°C. To get stable sintered films, zinc chloride and ethylene glycol should not remain in the samples. We optimized the sintering temperature and sintering time by performing the experimental process for different values of these two parameters and concluded that samples should be sintered at 500°C for 10 min in a temperature-controlled furnace. All the films were synthesized under the same experimental conditions.

Thicknesses of films were determined after sintering by an optical interference technique. The ZnO films prepared in this way were found to have a thickness of the order of 10µm. The optical reflectance versus wave length traces of the films were recorded in 325-600 nm wavelength range using a double beam UV-VIS spectrophotometer. The X-ray diffractograms (XRD) were recorded using a philips X-ray diffractometer with CuKα (λ=1.5418Å) radiation. Surface morphology was characterized using a scanning electron microscope. The electrical resistivity of the films was measured in vacuum by two-probe technique.

3. Results and Discussions

3.1. Optical Properties

The optical band gap of these films was determined with the help of reflection spectra [14, 15]. Almost all II-VI semiconductors have direct band gaps. According to the Tauc relation [16], the absorption coefficient for direct band gap materials is given by:

\[ \alpha h \nu = A (h \nu - E_g)^n, \]

where \( h \nu \) is the photon energy, \( A \) is the constant which is different for different transitions, \( E_g \) is the band gap, and \( n \) is equal ½ for direct band gap semiconductors.

To measure energy band gap from reflection spectra a graph between \((\alpha h \nu)^2\) versus \( (h \nu) \) is
plotted. Absorption coefficient $\alpha$ is proportional to $\ln \left[ \frac{(R_{\text{max}} - R_{\text{min}})}{(R - R_{\text{min}})} \right] [14, 15]$ where reflectance falls from $R_{\text{max}}$ to $R_{\text{min}}$ due to absorption by the material and $R$ is the reflectance for any intermediate energy photons. So $\alpha$ is used in terms of reflectance as $\ln[\hbar \nu (R_{\text{max}} - R_{\text{min}})/(R - R_{\text{min}})]$ and extrapolation of straight line to $(\alpha \hbar \nu)^2 = 0$ axis gives the value of energy band gap of film material. Fig. 1 shows the reflection spectra of sintered ZnO film.

Fig. 1. Reflection spectra of ZnO sintered film.

Fig. 2. Energy band gap determination of ZnO sintered film from reflectance measurement.

Fig. 2. shows plot between $[\hbar \nu \ln (R_{\text{max}} - R_{\text{min}})/(R - R_{\text{min}})]^2$ versus $h \nu$ for sintered ZnO film. The extrapolation of straight line to energy axis gives the value of direct band gap. From this plot, the value of energy band gap for ZnO sintered film come out to be 3.25 eV, which is in good agreement with the earlier reports [5, 17].
3.2. Structural Properties

3.2.1. X-ray diffraction analysis

X-ray diffraction studies were carried out on these samples and diffractograms were analyzed to obtain information about various crystallographic aspects. XRD traces of all samples were taken at room temperature and found to show almost similar trends. The XRD pattern of ZnO sintered film deposited on glass substrate is shown in fig. (3). The experimental d-values for ZnO film are calculated from the Bragg’s relation $2d_{hkl} \sin \theta = n\lambda$, by taking $\theta$ values from the peaks of XRD patterns. These d-values are compared with the standard d-values (JCPDS Data for ZnO) for the confirmation of structure of film material.

The prepared ZnO films were found to exhibit Wurtzite (hexagonal) structure (JCPDS-36-1451) with a preferred orientation along certain crystallographic planes which have been identified as (100), (002), (101), (102), (110), (103), (201) planes respectively, of which the intensity of (101) orientation in predominant. The presence of sharp structural peaks in the XRD confirms the polycrystalline nature of the ZnO films. By recording the full width at half maxima (FWHM) of these peaks, the average crystalline size was estimated using Scherrer formula:

$$D = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2)

where K is the shape factor that was taken equal to 0.9, $\lambda$ is the wavelength of X-ray source, $\beta$ is the full width at half maximum (FWHM) of (101) peak and $\theta$ is the Bragg’s diffraction angle in degrees. The estimated size of ZnO crystallites was 20 nm.

3.2.2. Scanning electron microscope (SEM) analysis

Scanning electron microscopy is a convenient method for studying the microstructure of thin films. Fig. (4) shows SEM image of ZnO film sintered at 500°C. SEM indicated that the microstructure is polycrystalline, granular and porous in nature. The SEM image clearly illustrates the formation of sub micrometer crystallites distributed more or less uniformly over
the surface.

Fig. 4. SEM image of ZnO sintered film.

3.3. Electrical properties

The electrical transport properties are of great importance in determining whether the studied material is congruent with our necessities or not. The electrical properties are dependent on various film or growth parameters such as composition, thickness, and substrate temperature and deposition rate. For photovoltaic application, important properties include electrical resistivity [14, 15].

3.3.1. Electrical resistivity

The electrical resistivity of ZnO films was measured in temperature range 330-550 K using two point probe method in vacuum. Fig. (5) Shows the variation of log of resistivity (log\(\rho\)) with reciprocal of temperature \(\frac{1}{T}\times10^3\). The resistivity of semiconductor at any temperature T is given by the Arrhenius relation:

\[
\rho = \rho_0 \exp \left( \frac{E_a}{kT} \right)
\]

where \(\rho_0\) is constant, \(k\) is Boltzmann’s constant and \(E_a\) is activation energy required for conduction.

Linear behaviour of graph (Fig. 5) shows that the film resistivity is in good agreement with the Arrhenius relation. The activation energy of ZnO sintered film calculated from slope of the graph is \(\sim 0.30\) eV which is in good agreement with the reported values of activation energy of ZnO films [1]. The straight line nature of graph suggests that grain boundary limited conduction is the dominant conduction mechanism. The grain boundaries are a consequence of imperfections associated with the polycrystalline nature of the films. Seto [18] explained the high temperature conduction mechanism in semiconductors.
4. Conclusions

The optical, structural and electrical properties of ZnO screen-printed films have been investigated. The films are polycrystalline in nature and have hexagonal (Wurtzite) structure with strong preferential orientation of grains along (101) direction. They have a band gap of 3.25 eV. SEM analysis has revealed polycrystalline, granular and porous morphology of ZnO sintered films. It has been observed that activation energy of ZnO comes out to be $\sim 0.30$ eV. The conduction in ZnO is through thermally activated process.

The band gap, large absorption coefficient, polycrystalline nature, stability and good value of activation energy make ZnO sintered film suitable for solar cells, wide band gap window material other photovoltaic devices.

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References


Садржај: Филмови цинк-оксида депоновани су на ултра-чист супстрат стакла методом скрин-принтинга и синтеровањем. У раду су изложени оптимални услови за припрему квалитетних скрин-принтинг филмова. Оптички процеп филма проучаван је рефлексионим спектрама у опсегу 325-600 нм спектрофотометром. Рендеңска дифракција је откривена да су филмови поликристални, једнофазна вурицита (хексагонална) структура са јаком преференцијалном оријентацијом зрна дуж (101) правца. Морфологија површине филмова је проучавана скенирајућом електронском микроскопијом. Електрична отпорност филмова мерена је у вакууму техником две пробе.

Кључне речи: Енергетски процеп, скрин принтинг, рефлексиони спектри, полупроводници, отпорност.