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Changes of structural, optical and electrical properties of sol-gel derived ZnO films with their thickness

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Zinc oxide (ZnO) films having thickness in the range from 15 nm to 208 nm have been fabricated by the sol-gel technique by varying number of sequentially deposited layers. The structural, optical and electrical properties of ZnO films were investigated as a function of film thickness. The crystallinity and degree of orientation of the ZnO films were closely related to the film thickness. The textures of the films improved only at an optimum thickness. At lower thicknesses, the roughness of the film became very large and led to the presence of possible voids having porous microstructure. The absorption in UV region depended strongly on sequential layers and increased with the increase of film thickness. Films thinner than ca. 60 nm exhibit morphology and behaviour different from thicker ones. A marked increase in resistivity for thinner films can predominantly be attributed to surface scattering and the decrease in carrier concentration.

Key words: *sol-gel; ZnO*

1. Introduction

ZnO, a direct band gap semiconductor with the band gap of 3.37eV [1] and high exciton binding energy of 60 meV [2] has a variety of potential applications such as bulk acoustic and surface acoustic wave (SAW) devices [3, 4]. It is also a promising candidate for spintronics applications. ZnO films have low electric resistance and high transparency in the visible light. Several deposition techniques have been used to grow ZnO thin films, including sol-gel process [5], spray pyrolysis [6], molecular beam epitaxy (MBE) [7, 8], chemical vapour deposition (CVD) [9] and sputtering [10, 11]. In comparison with other techniques, the sol-gel technique has the advantage of being low cost and low substrate temperature deposition. Certain applications require ZnO films with some specific structure characteristics, orientation, stress relief, smooth surface and high packing density. In the present work, these characteristics are examined as a function of the thickness of the film. It has been observed that the crystallite size and the density of film increases when ZnO films deposited increase in

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thickness. The influences of thickness variation on the crystalline structure, surface morphology, optical and electrical properties of ZnO films have been investigated, with the aim to analyze the films growth mechanism.

Single crystalline substrates provide nucleation for the growth of ZnO, however in the case of amorphous substrates the first few layers of ZnO crystallites are developed, which act as nucleating centres for a further growth of the film. It has been reported that strong self-texture is effective in obtaining a highly oriented and single crystalline epitaxial growth [12]. If the lower layer is crystalline, it provides a nucleation step for a further crystallization of the upper layers and there could be a competition between upper layer and lower layer [13]. That may act as a substrate for ZnO film to be grown with a minimum lattice mismatch. A minimum thickness with less structural defects and impurity in the material may essentially be required to provide a good self texture for further growth of a good crystalline quality film.

2. Experimental

The solutions were prepared by dissolving zinc acetate, ($Zn(CH_3CO_2)_2\cdot 2H_2O$, purity 99.5%) in anhydrous methanol. The obtained mixture was mixed ultrasonically for about two hours. The clear solutions were used for spin coating after 24 hours of aging on Corning glass (7059) substrates. The substrates were cleaned ultrasonically, first in acetone, and subsequently in methanol for 10 minutes each. They were further cleaned with ion exchanged distilled water for 20 minutes and kept in an oven at 80 °C for 30 minutes. The films were dried at 300 °C for 20 minutes each. This process was repeated several times to deposit films of the desired thickness. The films were annealed for one hour at temperature from 575 °C for decomposition and oxidation of the precursors. X-ray diffraction pattern of the films were recorded with a Philips PW 1830 diffractometer, using a monochromatized X-ray beam with nickel-filtered CuK_{α} radiation (λ = 1.5418 Å) in 2θ from 20° to 60°, with a 0.02 sample pitch. The thickness of the films was determined by a Dektak^{-3} ST surface profiler and was observed to vary in the range 0.015–0.21 μm for various films. The surface morphology of the films was analyzed based on atomic force microscopy (AFM) micrographs using an SPI 3700. Optical transmittance measurements were carried out using a Shimadzu UV-260 spectrophotometer in the range of 300–800 nm. The electrical sheet resistance was measured with the four-probe method.

3. Results and discussion

The X-ray diffractograms (Fig. 1) show that ZnO films of different thicknesses annealed at 575 °C are polycrystalline in nature with (002) plane in preferred mode. Figure 2 shows the increase of peak intensity and decrease of the full width of their half maxima (FWHM) as the thickness of ZnO film increases, since the peak intensity and grain size are associated with the crystallinity of the film. Poor crystallinity in a thinner ZnO film could be associated with an incomplete growth of the crystallites as only few atomic layers of disordered atoms constitute the bulk of the film [14].

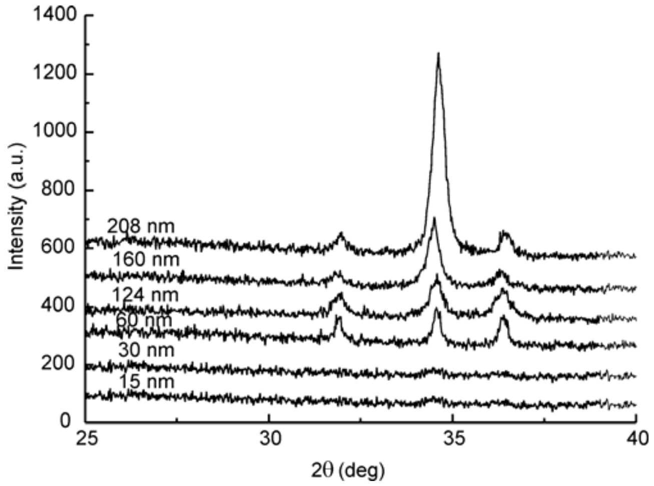

Fig. 1. X-ray diffraction patterns of ZnO films differing in thicknesses

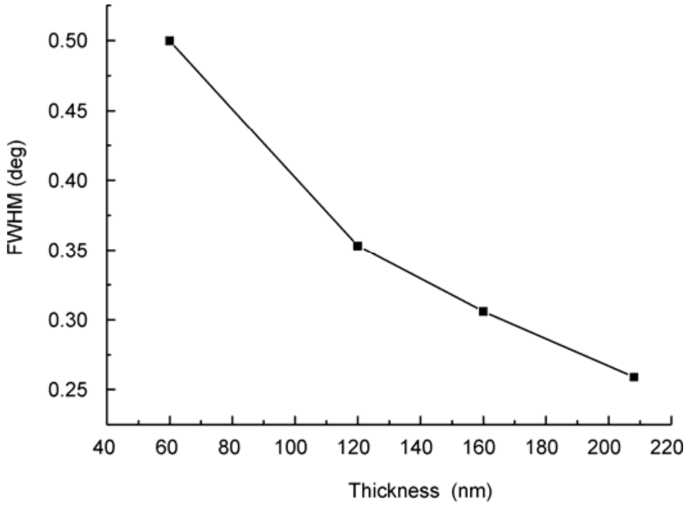

Fig. 2. Dependence of FWHM on the thickness of ZnO films

According to the mechanism of crystal growth [15, 16], the growing faces of crystallites correspond to the crystal shape at equilibrium and are determined by the orientation of the crystal. A growth competition can start among the neighbouring crystals according to their growth types (i.e., to their orientation). The faster growing crystals will grow over the slower growing ones. This competition is terminated when only crystals exhibiting the same type of crystal faces proceed to form the free surface.

This competitive crystal growth represents an orientation selection resulting in the competitive growth texture [17]. This was probably why the crystallinity was increased when ZnO film was thicker. The crystallite size has been estimated from the FWHM of (002) diffraction peak by the Scherrer relation [18]:

$$l = \frac{0.94\lambda}{B\cos\theta}$$

where λ is the wavelength of X-ray radiation θ is the Bragg angle of the (002) peak, B is the angular width of the (002) peak at a half of its maximum intensity (FWHM). The film thickness varying from 60 nm to 208 nm has the grain size of the crystallites between 16 nm to 32 nm.

3.1. Surface morphology

Figure 3 shows AFM the images of ZnO films with various thickness. The surface of ZnO films exhibited hillocks with island-like growth with the decrease of thickness at 15 nm. It indicated that there would be more defects existing in thinner films with varying grain size and orientation distributions.

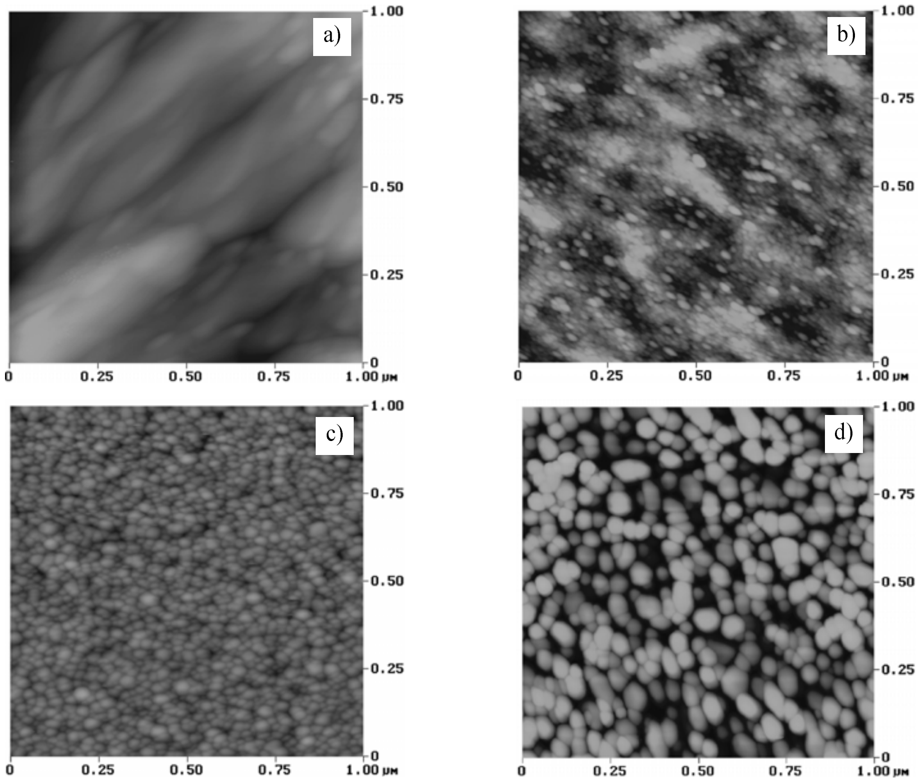

Fig. 3. AFM micrographs of ZnO films with various thicknesses:
a) 15 nm, b) 60 nm, c) 124 nm, d) 208 nm

Thinner films are observed to have smaller grains, non-uniform grain size and random orientation with poor degree of crystallinity. As the film thickness increases during deposition, the deeper layers of atoms are subjected to stronger interatomic forces and form a compact structure, whereas for thin films the atoms near the surface are subjected to a weaker interatomic force and thus form a spongy loose packed structure [19]. It is observed from the figure (3a) that film with a thickness of 15 nm showed no growth of grains and only hillocks are observed. The surface roughness of 38.8 nm was observed. Grains start developing at the thickness of 60 nm with the surface roughness decreased to 4.0 nm (Fig. 3a, b).

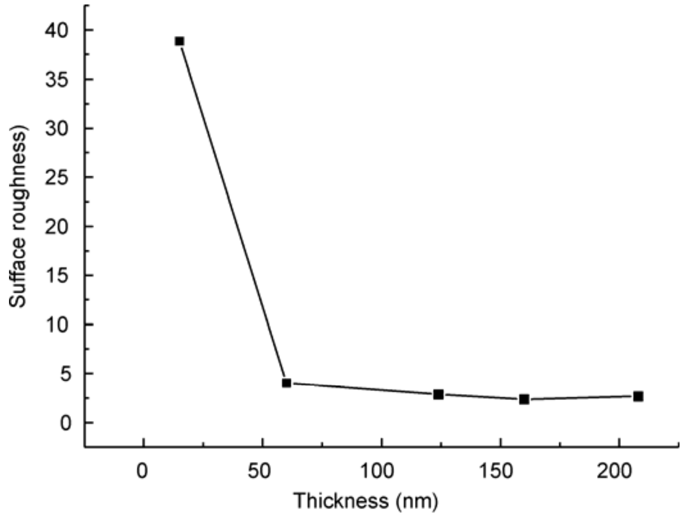

Fig. 4. Dependence of surface roughness on the thickness of ZnO films

The variation of the surface roughness is shown in Fig. 4. The drastic change in surface roughness is in conformity with the analysis of the growth of the film. This trend of growth continues with the further increase of thickness indicating the increase of grain sizes along with the decrease of surface roughness.

3.2. Optical properties

Figure 5 shows the UV–VIS–IR transmission spectra of ZnO films of different thicknesses. The optical transmission in the visible region was high (>80%) but it decreased substantially at short wavelengths near the ultraviolet range for films with different thickness. Generally, the visible transmission of film decreased with the increase of film thickness. However, the films 15 nm thick showed the lowest average visible transmission [20]. AFM pictures show clearly hillocks growth in films with thickness 15 nm. The surface morphology improved and structural defects decrease with increase in thickness, which is in agreement with the XRD analysis. The transmission of the film was found to depend upon the quality of the film, which in turn depends upon the thickness of the film. With the increase of thickness probably oxygen vacancies VO^{++} increase which results in slight decrease of transmission.

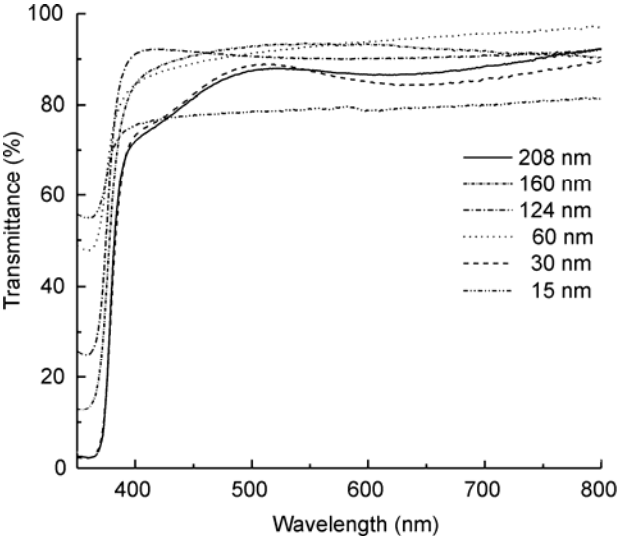

Fig. 5. Dependence of optical transmission on wavelength for ZnO films of various thicknesses

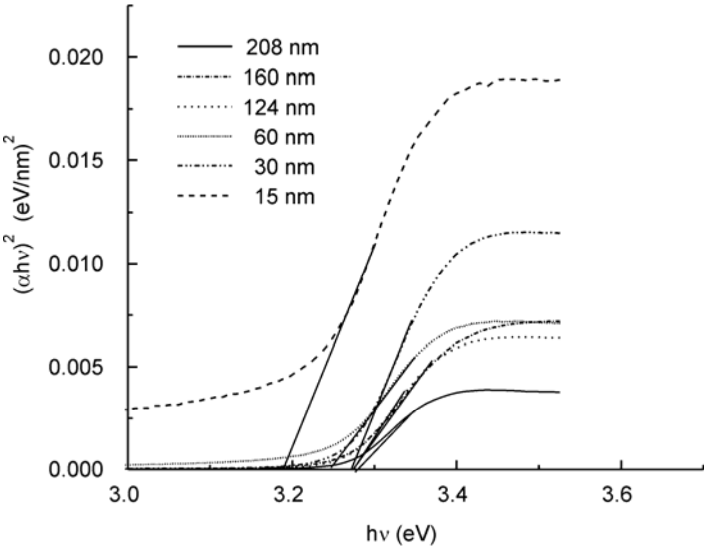

Fig. 6. The plot of $(\alpha h\nu)^2$ vs. $h\nu$ for ZnO film deposites from 15 nm to 208 nm thick

The band gap of the films was determined from the Tauc plots of $(\alpha h\nu)^2$ vs. photon energy. Figure 6 shows the $(\alpha h\nu)^2$ vs. photon energy curves of ZnO films with varying thickness.

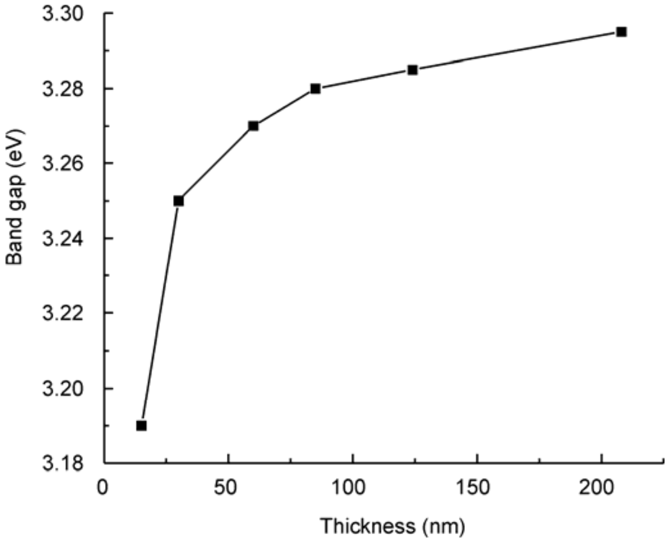

Fig. 7. Dependence of the band gap on thickness of ZnO films

Figure 7 shows the increase of optical band gap E_g from 3.19 eV to 3.27 eV for ZnO films with thicknesses varying from 15 nm to 60 nm, thereafter a slow increase to the value of 3.30 is observed for the thickness of 208 nm. The low energy band gap could be attributed to defects and impurities [21] such as interstitial zinc atoms. For films with thickness higher than 60 nm, the film grows with improvement in grain size which results in a little shift of the absorption edge.

The results suggest that the band gap of ZnO films does not depend significantly on the crystallographic orientation or degree of texturing. It is mainly affected by carrier concentration [22]. There is only a little change in the optical properties of ZnO films by varying the film thickness after the full growth of film at the thickness of more than 60 nm.

3.3. UV absorbance

Figure 8 shows the absorption spectra of ZnO samples with increasing thickness. It is observed that the increase of thickness results in higher absorption of radiation in the UV region. It is shown in Fig. (9) where the absorbance at 365 nm is plotted with the increase of thickness. Two distinct domains of absorption are observed. Apparently there is a critical film thickness ca. 60 nm, which seems to assure a good crystallinity of the film.

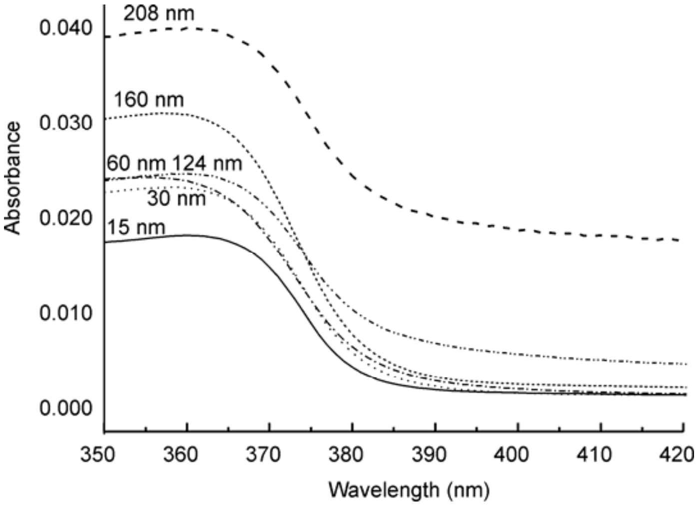

Fig. 8. Absorption spectra of ZnO films

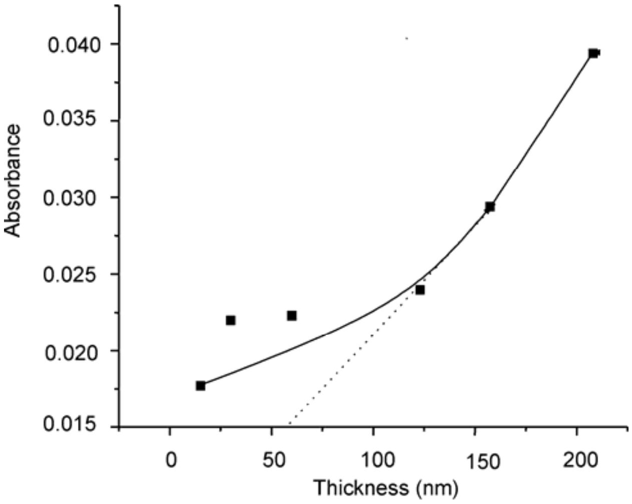

Fig. 9. Dependence of the absorbance of the excitonic band (at 365 nm) on thickness of ZnO films

3.4. The effect of thickness on resistivity of ZnO films

The variation of sheet resistance of ZnO films with different thickness and annealed at 575 °C is shown in Fig. 10. The sheet resistance decreases substantially with increase of thickness. A higher sheet resistance for thinner films could be attributed to surface scattering and the decrease in carrier concentration. For thinner films, more defects act as scattering centres which results in the formation of trapping states capable of trapping carriers and thereby immobilizing them. This reduces the number of free carriers available for electrical conduction. Also after trapping the mobile carriers, the traps became electrically charged, creating a potential energy barrier, which impeded the motion of carriers from one crystallite to another, thereby reducing their mobility [23, 24]. It is observed that a very high sheet resistance was observed for a film thickness of 15 nm, which decreases, rapidly with the increase of thickness.

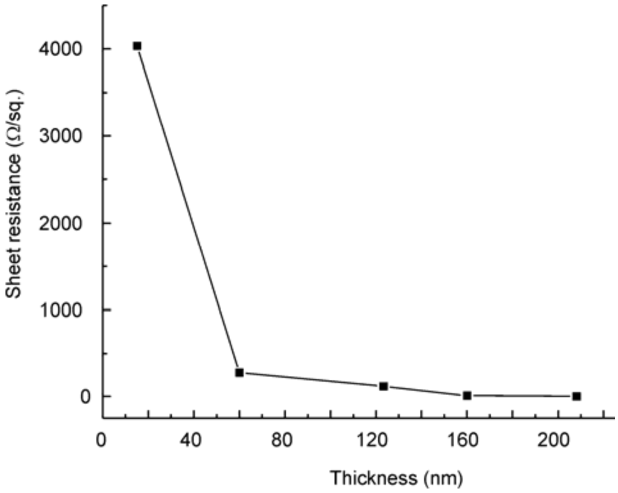

Fig. 10. Dependence of sheet resistance on the thickness of ZnO films

Sheet resistance R_{sh} is related to resistivity by the relation:

$$R_{sh} = \frac{\rho}{d}$$

It has been reported that the absorption edge shifts the Fermi level to a higher energy due to the Burstein–Moss (BM) effect [25]. The decrease in carrier concentrations for thinner films results in the increase of resistivity. The decrease in band gap for thinner films is due to lower carrier concentration in conformity with the BM shift given by the relation

$$\Delta E^{BM} = \left(\frac{\hbar^2}{2m^* e}\right)\left(3\pi^2 N\right)^{2/3}$$

where m^* is the effective mass of the electron and N is the carrier concentration.

4. Conclusion

ZnO films of varying thickness have been fabricated using the sol-gel process on a corning glass (7059) substrate. The structural, optical and electrical properties of the

ZnO films reveal two different zones of thickness. A critical minimum thickness of 60 nm ensures good crystallinity and low sheet resistance of the films. Incomplete growth of crystallites with structural defects was seen in films having thickness lower than 60 nm. Above the critical thickness of the film, no significant change in the band gap of ZnO is observed.

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