American J. of Engineering and Applied Sciences 3 (1): 171-179, 2010
ISSN 1941-7020

Low-doping Effects of Nanostructure ZnO: Sn tin films annealed at different temperature in Nitrogen ambient to be applied as an Anti-reflecting coating (ARC)

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Abstract: Problem statement: The focus of this research is to discover the significant influences of substituting low concentration Sn at Zn-site as an Anti-Reflecting Coating (ARC) for $Zn_{1-x}Sn_xO$ compound. The effects of tin dopants on the structural and morphology properties of ZnO thin films prepared using the sol-gel method were investigated. **Approach:** The effects of annealing temperature on the deposited films were also investigated at three different temperatures of 400, 500 and 600°C. The composition of the $Zn_{1-x}Sn_xO$ sample are x = 0.00, 0.05, 0.10 and 0.15. As a starting material, zinc acetate dehydrate was used; 2-methoxyethanol and mono ethanolamine were used as solvent and stabilizer, respectively. The dopant source was tin chloride. **Results:** Microstructural and surface morphology of samples were characterized by using Scanning Electron Microscopy (SEM). The crystallinity and defects are studied using X-Ray Diffraction (XRD). Molecular bonding is carried out using Raman spectroscopy and optical study of band gap is investigated using UV-VIS measurement. **Conclusion:** The value of band gap obtained increased slightly as the concentration of Sn increased. The increment of the band gap is acceptable as a requirement for good anti-reflecting coating element. Therefore these films can be applied on silicon solar cell.

Key words: Zinc oxide, sol-gel method, thin films, doped Sn, annealing

INTRODUCTION

Metal oxide semiconductor films have been widely studied and have received considerable attention in recent years due to their optical and electrical properties. Some of them are good prospects as transparent conductive oxide films. Among them, ZnO is one of the metal oxide semiconductors that are suitable for use in optoelectric devices. It is an alternative material to tin oxide and indium tin oxide, which is most used to date (Lee and Park, 2003). ZnO is an n-type wide band gap semiconductor (E_g = 3.2 eV). Its large exciton binding energy of 60MeV at room temperature and electrical conductivity are due to intrinsic and extrinsic defects. The conductivity of pure ZnO is produced by the former defects such as zinc excess at the interstitial position and the lack of oxidation. Since pure ZnO thin films are sensitive to oxidation, absorption of O_2 in the films is inclined to decrease its electrical conductivity. In cases where ZnO is doped with different dopants, the electrical properties are enhanced by extrinsic defects and these trials have been attempted. Additionally, electrical properties of ZnO can be modified by thermal treatment in a reducing atmosphere. The optical properties of ZnO were mainly affected by a surface morphology and the change of the optical energy band gap followed by heavy doping. The material's morphology was also modified by thermal treatment in a reducing atmosphere and by an appropriate doping process (Lee

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and Park, 2003). ZnO is one of the metal-oxide semiconductors that has been utilized to be very useful functional materials for devices such as UV-light emitters, varistors, transparent high power electronics, surface acoustic wave devices, piezoelectric transducers, gas sensing, solar cells and structural materials such as window material for display (Shan *et al*., 2003). As grown, ZnO usually exhibits n-type conductivity with a wide band gap. The n-type conductivity might be caused by intrinsic defects, interstitial zinc and oxygen vacancies. Its electrical conductivity can be increased by doping it with group III elements such as aluminum, boron, gallium and indium, or group VII elements such as fluorine (Nunes *et al*., 2002). ZnO thin films can be prepared by a variety of thin film deposition techniques, such as pulsed-laser deposition (Shim *et al*., 2002), RF magnetron sputtering (Nunes *et al*., 2002), chemical vapor (Kashiwaba *et al*., 2000), spray pyrolysis (Paraguay *et al*., 1999) and the sol-gel process (Lee and Park, 2003). While physical deposition such as pulsed-laser deposition and RF magnetron sputtering produces films with good electrical and optical properties at lower deposition temperature, it has the disadvantage of a relative low deposition rate and expensive equipment. However, the sol-gel technique offers the greatest possibility of preparing small as well as large area coating of ZnO thin films at low cost for technological applications and is widely compatible with microelectronic technology, circuit and anti reflecting coating for solar cells (Lee and Park, 2003).

As one of the promising metal oxide materials in the semiconductor field (due to its potential properties), ZnO has received considerable attention in the recent years (Shan *et al*., 2004; Look, 2001). In this study, the effects of dopant and their doping concentration on the microstructure and morphology properties of doped ZnO thin films were investigated to produce films that can be applied on thin solar cells with improved efficiency.

MATERIALS AND METHODS

ZnO thin films are prepared by the sol-gel method. As a starting material, zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) is used. Two-methoxyethanol and Monoethanolamine (MEA) are used as a solvent and a stabilizer, respectively. The dopant source of tin is tin chloride ($SnCl_4$). Zinc acetate dehydrate and dopant is first dissolved in a mixture of 2-methoxyethanol and MEA solution at the room temperature. The molar ratio of MEA to zinc acetate ($Zn(CH_3COO)_2$) is maintained at 1.0 and the concentration of zinc acetate was 0.5 M. The solution is stirred at 60°C for 2 h to yield a clear and homogeneous solution, which served as the coating solution after it cooled to the room temperature. The coating is usually made 2 days after the solution is prepared.

The solution is dropped onto quartz substrates, which are rotated at 1000 rpm for 30 sec. After depositing by spin coating, the films are dried at 150°C for 10 min over a hot plate to evaporate the solvent and remove organic residuals. The procedures from coating to drying are repeated three times until the thickness of the sintered films is approximately 200 nm. The films are then inserted into a furnace and annealed with 5% nitrogen at different temperatures which are 400, 500 and 600°C for 1 h. The crystallization of each ZnO film is measured using an X-ray diffractometer with CuK_a radiation. The surface morphology and chemical composition of the films are observed with a Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX). The changes in chemical bonding are measured by a Raman spectroscopy and the optical properties by UV-Vis measurement.

RESULTS

Figure1 shows the X-ray diffraction patterns of ZnO thin films undoped and doped with tin at 5%. The temperature differential for each sample changed from 400-600°C. X-ray diffraction spectra of all the films are taken at room temperature. The peaks, with the Miller indices given belong to the ZnO. The presence of sharp structural peaks in these X-ray diffraction patterns confirmed the polycrystalline nature of the films. All films, undoped and doped, regardless of dopants and their temperature differential, are thin films and have (0 0 2) as the preferred orientation. The 5% tin doped ZnO at 500°C, 5% tin doped ZnO at 500°C and 15% tin doped ZnO at 600°C thin film had the highest (0 0 2) diffraction peak intensity than that of the others. Moreover, the peak intensities of those films increased with increased temperature of those films. This indicates that an increase in temperature deteriorates the crystallization of films, which may be due to the formation of stresses by the difference in ion size between zinc and the dopant and the segregation of dopants in grain boundaries (for high doping concentrations). This (0 0 2) preferred orientation is due to the minimal surface energy which the hexagonal structure, c-plane to the ZnO crystallites, corresponds to the densest packed plane as we can see in morphology structure. Overall, another orientation presented at (1 0 1) and (1 0 0), also seen in Fig. 1.

SEM images of undoped and doped ZnO thin films on quartz substrates are displayed in Fig. 2. These SEM images show that the surface morphology of the films is strongly dependent on the annealing and concentration of the dopant. A particular structure is observed in SEM images for all films. For tin doped films, particles with

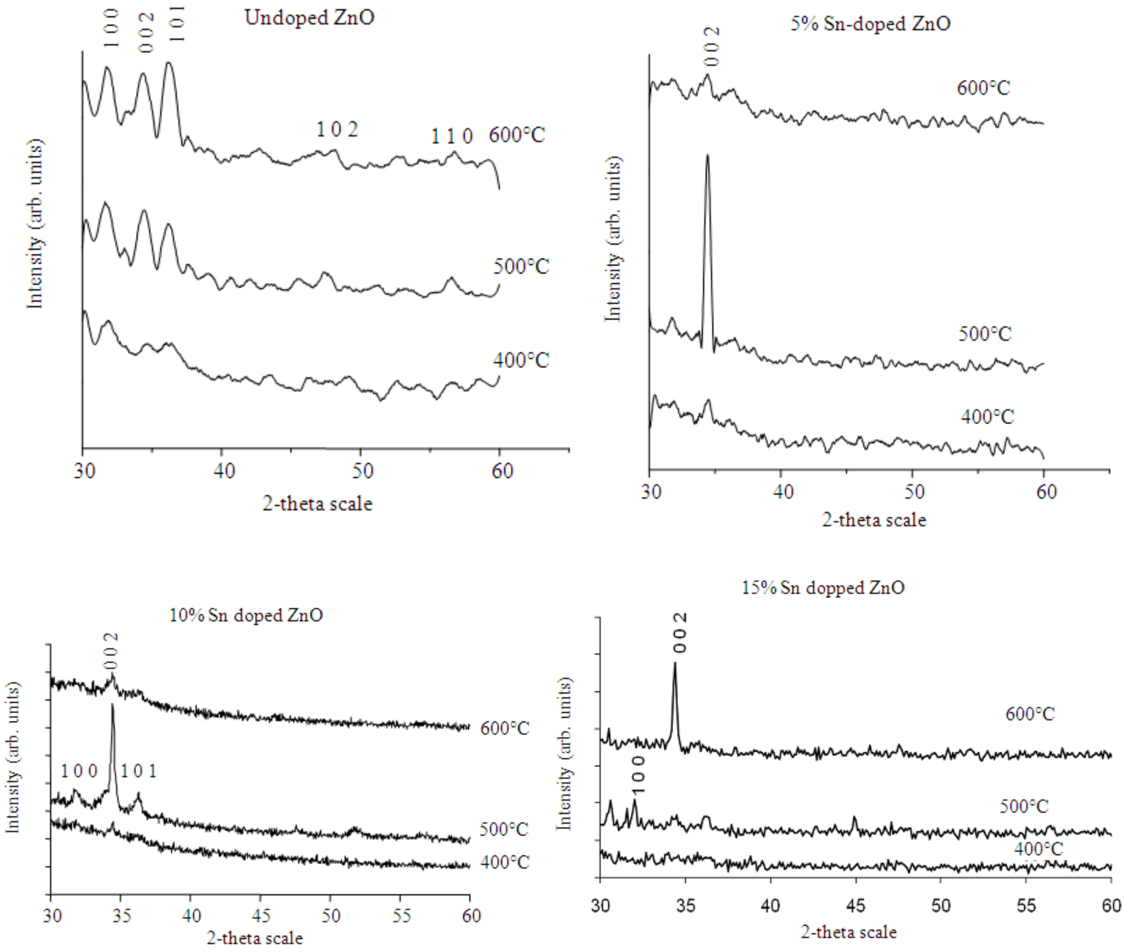
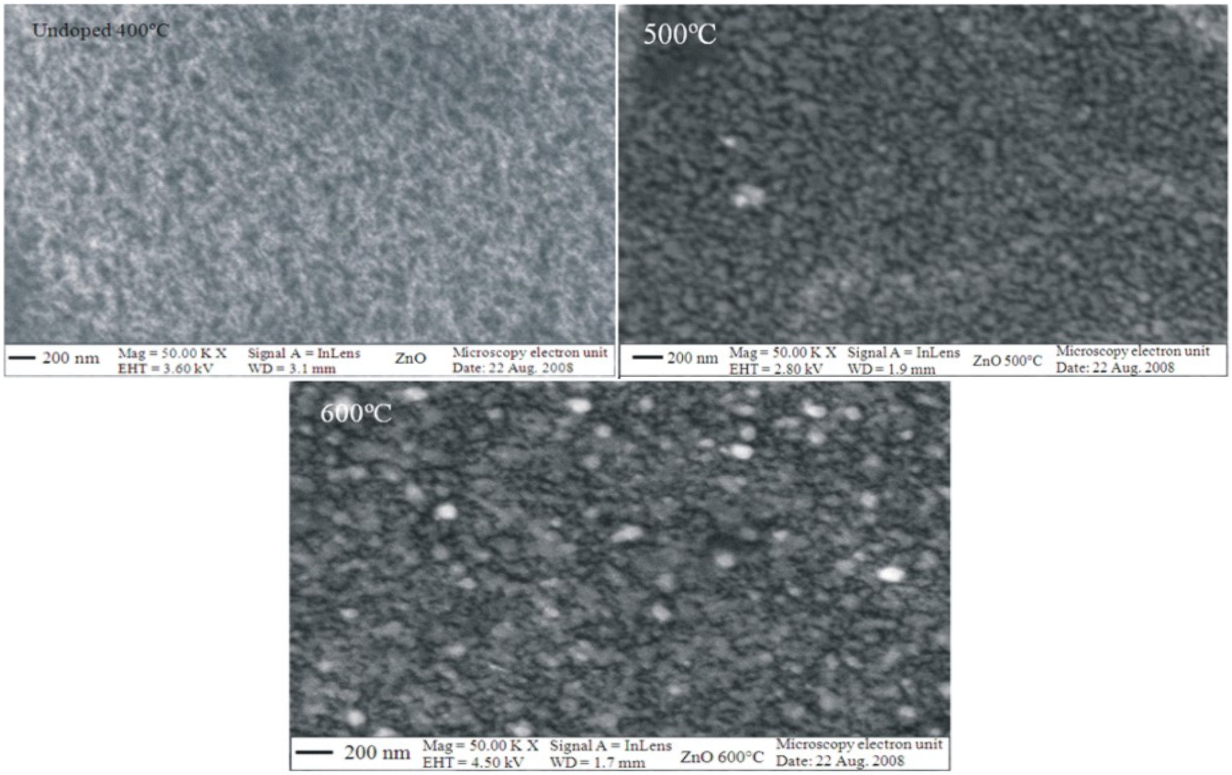


Fig. 1: X-ray diffraction patterns of ZnO doped with tin at 5, 10 and 15% thin films as a function of temperature differential

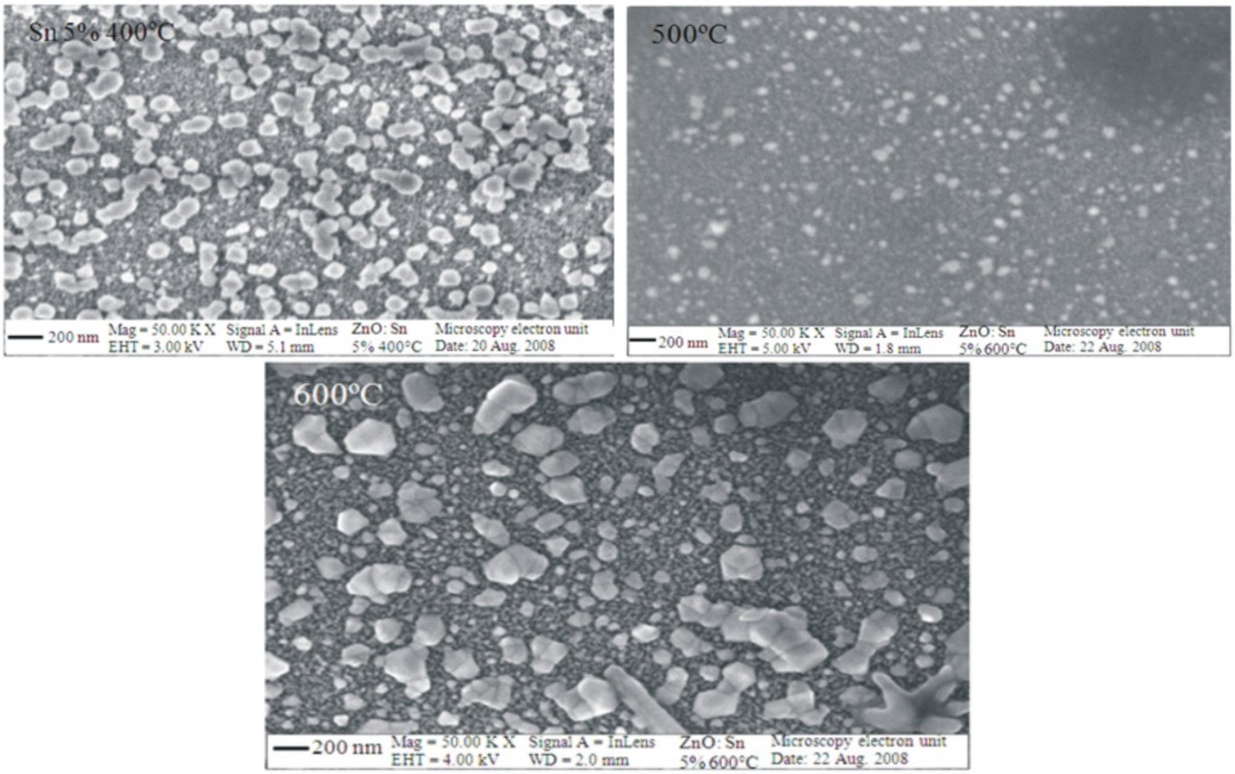
different shapes and sizes were mixed. The film with annealed 400°C had particles size of approximately 48nm. When the annealing temperature was at 500°C, the particle size decreased and the microstucture of the film became denser. The 600°C annealed film consisted of small particles forming a matrix where the large ones lying on the matrix. The particle size forming a matrix reduces with increasing annealing temperature.

Additionally, a microstructure with a larger difference in size between the large and small particles is observed in films annealed at 600°C. In cases where films doped with tin with smaller ionic radius than zinc, particles forming matrix became smaller with increased annealing temperature. This is because the grain growth is disturbed by compression stresses due to the difference in ionic radii between zinc and tin (r_{Sn}^{4+} = 0.069 nm). The change in particle size with an increase in annealing temperature is observed to occur more in the tin doped films than in the undoped films. This is due to a higher difference in ionic radius between zinc and tin, this behavior also has been observed by Lee and Park 2003 annealed at 500°C.

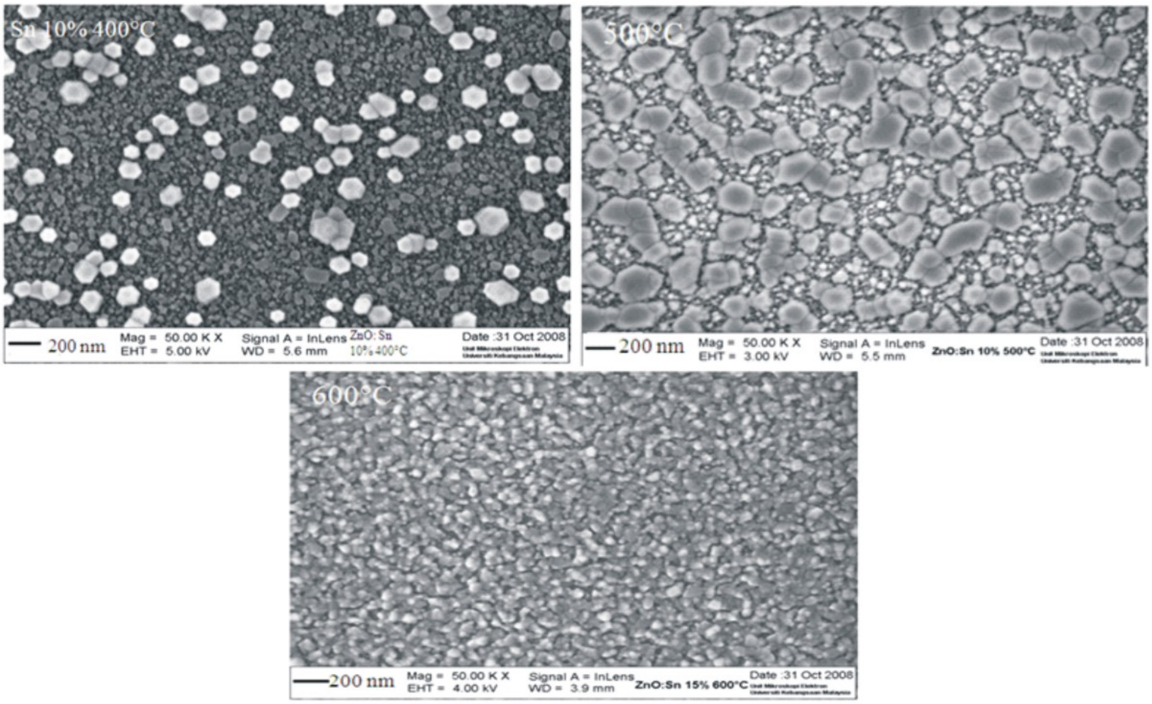
ZnO crystallizes in the hexagonal wurtzite structure, which belongs to the space group C^{4}_{6v}. It is generally agreed that stress arises from the mismatch of thermal expansion coefficients of the films and the substrates, or the lattice mismatch and distortion. Doping is considered to be the main factor that causes the lattice distortion of the crystals, for it is usually different from the atomic radii of different elements (Huang *et al*., 2003). Figure 3 shows the Raman band of the undoped ZnO and doped with Sn at 5, 10 and 15%. Most positions of the modes are shifted. This indicates that the addition of Sn strengthens the tensile stress of the ZnO crystals. Theoretically, it is difficult to substitute Zn^{2+} with Sn^{4+}


Undoped 400°C
200 nm
Mag = 50.00 K X
EHT = 3.60 kV
Signal A = InLens
WD = 3.1 mm
ZnO
Microscopy electron unit
Date: 22 Aug. 2008
500°C
200 nm
Mag = 50.00 K X
EHT = 2.80 kV
Signal A = InLens
WD = 1.9 mm
ZnO 500°C
Microscopy electron unit
Date: 22 Aug. 2008
600°C
200 nm
Mag = 50.00 K X
EHT = 4.50 kV
Signal A = InLens
WD = 1.7 mm
ZnO 600°C
Microscopy electron unit
Date: 22 Aug. 2008

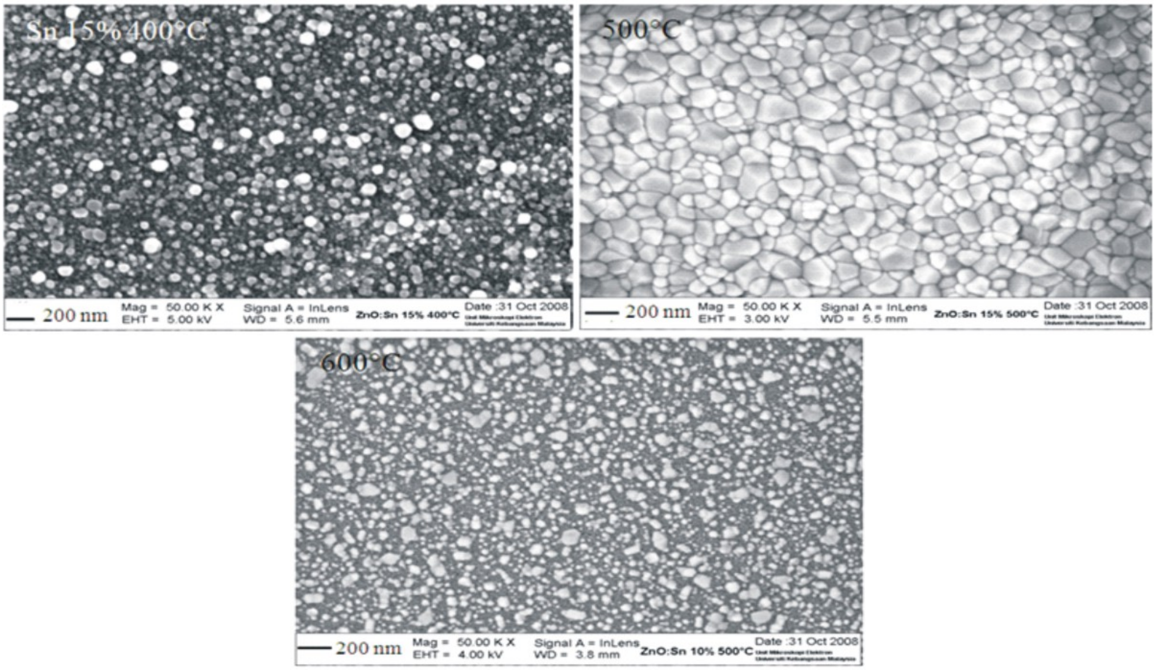
(a)


Sn 5% 400°C
200 nm
Mag = 50.00 K X
EHT = 3.00 kV
Signal A = InLens
WD = 5.1 mm
ZnO: Sn
5% 400°C
Microscopy electron unit
Date: 20 Aug. 2008
500°C
200 nm
Mag = 50.00 K X
EHT = 5.00 kV
Signal A = InLens
WD = 1.8 mm
ZnO: Sn
5% 600°C
Microscopy electron unit
Date: 22 Aug. 2008
600°C
200 nm
Mag = 50.00 K X
EHT = 4.00 kV
Signal A = InLens
WD = 2.0 mm
ZnO: Sn
5% 600°C
Microscopy electron unit
Date: 22 Aug. 2008

(b)



(c)



(d)

Fig. 2: SEM images of undoped and doped ZnO thin films with Sn dopant content, (a) undoped; (b) x = 0.05; (c) x = 0.10 and (d) x = 0.15

in ZnO crystal, for the radius of Sn^{4+} is much larger than that of Zn^{2+}. The liquid phase penetrates into the boundaries between ZnO grains and enhances the grain growth and the densification of the film. This process

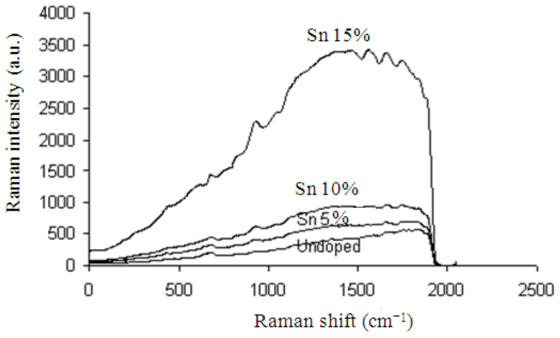
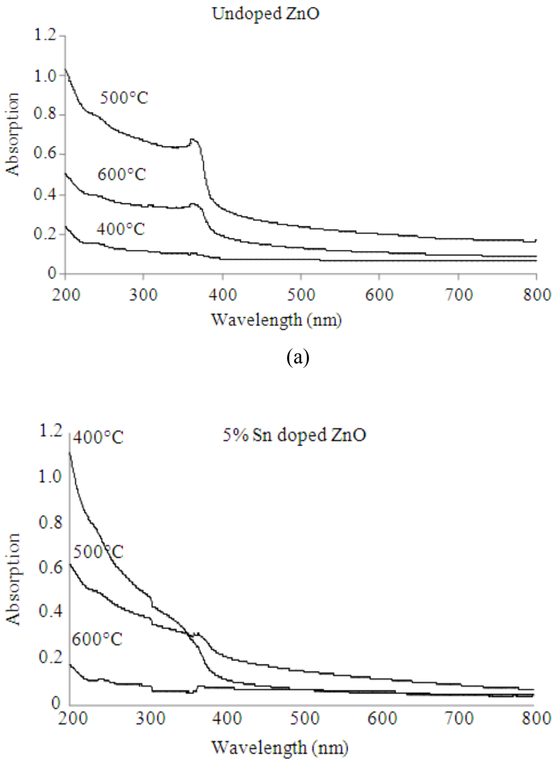


Fig. 3: Raman spectroscopy of undoped and doped ZnO with Sn at 5, 10 and 15% before annealing and in liquid form

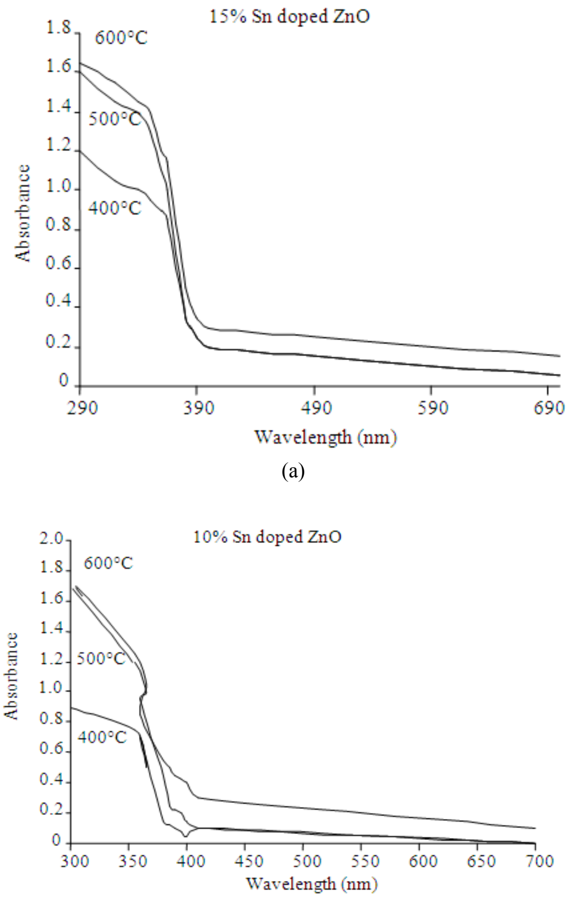


(a)

(b)

Fig. 4: Optical absorption spectra of undoped and doped ZnO with Sn at 5% thin films

can strengthen the interfacial stress of the ZnO grains, which may be the main cause of the shift of the modes in the Raman spectrum. Nevertheless, if there are any effects to the microstructure of ZnO crystal by Sn^{4+}, the possibility could not be excluded, for solid solubility of Sn in ZnO at 5, 10 and 15%.



(a)

(b)

Fig. 5: Optical absorption spectra of doped ZnO with Sn at 10 and 15% thin films

In the Raman spectra of Sn-doped ZnO films, there are additional modes that can be observed. Thus, we can relate it to the intrinsic host defects, for instance, oxygen vacancies. A higher intensity of the vibration mode indicating a higher concentration of oxygen vacancies might be in Zn-Sn-O films than that of ZnO films. As a donor, more oxygen vacancies lead to higher conductive band electron density, which will enhance the sp-d interactions and lead to a red-shift of the band gap.

The absorption spectra with wavelengths from 200-800 nm of the undoped and doped ZnO thin films are presented in Fig. 4 and 5. The absorption edges were defined as the wavelengths at intersections that were obtained by extrapolating the horizontal line and the sharply rising portions of the UV-Vis absorption curves as can be seen in Fig. 4 and 5 also have been reported by Wong and Xu (2004). The absorption of undoped ZnO films at 500°C, at 5% Sn at 400°C and 600°C for 10 and 15% Sn were higher than those of the others for each temperature. In the case of undoped ZnO films, the absorption at annealing temperature of 500°C was higher, but the absorption at temperatures 400 and 600°C were lower than 500°C. In particular, the absorption of tin doped films decreases with decreasing annealing temperature. As seen from the SEM images in Fig. 2, the lower absorption in tin doped films may be due to the increase in optical scattering caused by the mixing of small and large particles as well as its rough surface and morphology.

The optical band-gap, E_g, is determined from the absorption spectra using equation (Tauc *et al*., 1966):

$$(\alpha hv)^2 = C(hv-E_g) \quad (1)$$

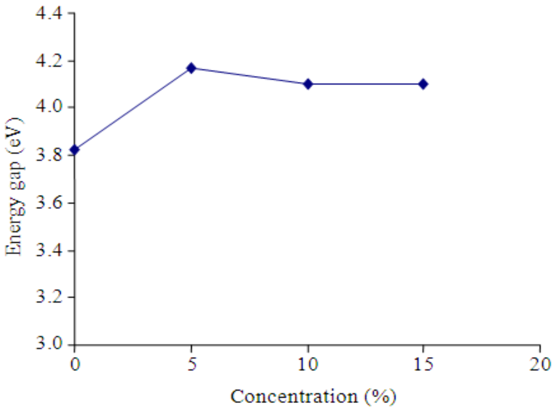


Fig. 6: Graph of different Sn concentration (%) Vs energy gap at 500°C

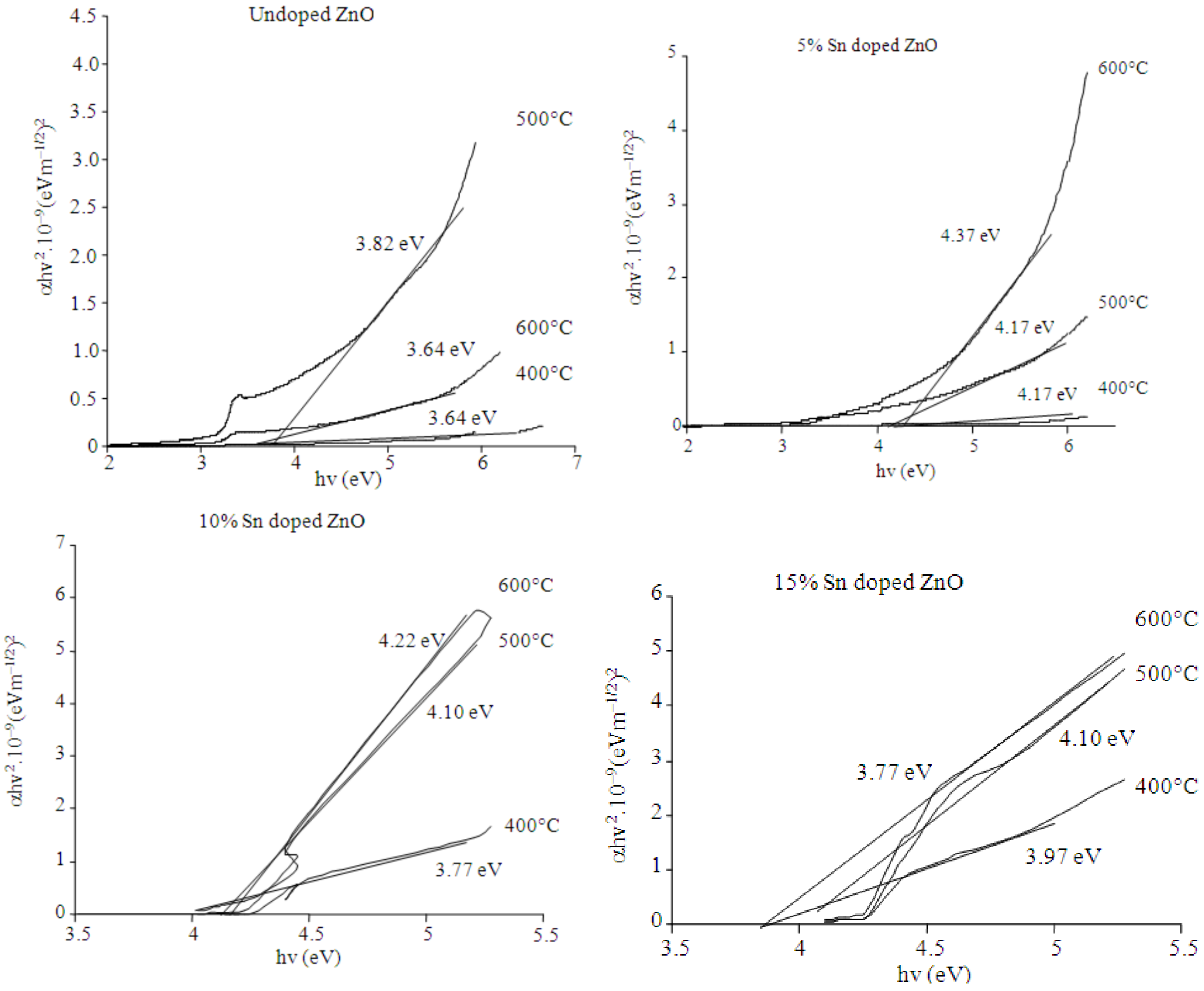


Fig. 7: Evoluation of $(\alpha hv)^2$ Vs hv curves of films prepared, at different annealed temperature

related to direct transitions in ZnO crystals, with constant C depending on the electron-hole mobility.

Figure 6 shows that the energy gap increases with the increase of Sn concentration at 500°C. The $(\alpha h\nu)^2$ Vs hv plots are shown in Fig. 7. Independent of the preparation method (undoped or doped with Sn) the determined optical band-gap of the samples varies depending on the annealing temperature i.e. between 3.64 and 4.37 eV. The largest values of E_g is determined for textured films ((0 0 2) orientation) prepared from films with 500°C annealed temperature (Fig. 1). The value of 4.37 eV is notably larger than that of the optical band-gap reported for monocrystalline ZnO. In general, blue shift of the absorption onset of Sn doped nanocrystalline films is associated with the increase of the carrier concentration blocking the lowest states in the conduction band, well known as the Burstein-Moss effect (Burstein, 1954). In order to describe the experimentally found blue shift in Sn doped films, the displacement polarization effects and structural disorder is considered as additional factors that affect the shape of the band tails. This theory of band-gap widening for polar semiconductors is proposed by Valle *at al.* (2004). Although the band-gap widening in most of the studied films can be justified by this model, the band-gap values of more than 4.3 eV found in textured samples containing relatively small crystallites are not well understood. It is suggested that the quantum confinement phenomena induced by the nanoscopic size of the crystallites also contribute to this effect.

As a result, as the film is oriented more preferentially along (0 0 2) direction, the grain size of the film increased, the Zn content decreased, the tensile stress of the ZnO crystals increased and the absorption increased as well.

CONCLUSION

The results of tin doped ZnO thin films prepared by the sol-gel method show that the nanostructure of films annealed at intermediate temperature (500°C) is clearly different than those prepared at lower or higher temperature. All films were oriented preferentially along the (0 0 2) direction. The XRD patterns of the samples are polycrystalline and exhibit single phase hexagonal structure. Films doped with at 5% tin concentration at 500°C had stronger c-axis orientation perpendicular to the substrate and smaller grain than the others. The surface morphology of the films showed that the films strongly depend on the annealing temperature. In Raman spectra, the modes shift to lower wavenumbers and to higher wavenumbers, respectively. When the films were doped with Sn, it is discovered that the tensile residual stress and the free carrier concentration increase with doping. The optical band-gap of about 4.3 eV is considerable larger than that of nanocrystalline ZnO and cannot be described by the standard theories for band-gap widening.

ACKNOWLEDGEMENT

The researchers would like to thank Photonic Technology Laboratory, Institute of Microengineering and Nanoelectronics, University Kebangsaan Malaysia. This study was partially supported by a grant from Ministry of Higher Education (UKM-RS-06-FRGS0001-2007).

REFERENCES

Burstein, E., 1954. Anomalous optical absorption limit in InSb. Phys. Rev., 93: 632-633.

Huang, Y., M. Liu, Z. Li, Y. Zeng and S. Liu, 2003. Raman spectroscopy study of ZnO-based ceramic films fabricated by novel sol-gel process. Mater. Sci. Eng., B97: 111-116.

Kashiwaba, Y., F . Katahira, K. Haga, T. Sekiguchi, H. Watanabe, 2000. Hetero-epitaxial growth of ZnO thin films by atmospheric pressure CVD method. J. Cryst. Growth, 122: 431-434.

Lee, J.H. and B.O. Park, 2003. Transparent Conducting ZnO: Al. In and Sn thin films deposited by the sol-gel method. Thin Solid Films, 426: 94-99.

Look, D.C., 2001. Recent advances in ZnO materials and devices. Mater. Sci. Eng., B80: 383-387.

Nunes, P., D. Costa, E. Fortunato and R. Martins, 2002. Performances presented by zinc oxide films deposited by RF magnetron sputtering. Vacuum, 64: 293-297.

Nunes, P., E. Fortunato, P. Tonello, F. Branz Fernandes, P. Vilarinho and R. Martins, 2002. Effect of different dopant elements on the properties of ZnO thin films. Vacuum, 64: 281-285.

Paraguay, F.D., W.L. Estrada, D.R.N. Acosta, E. Andrade and M. Miki Yoshida, 1999. Growth, structure and optical characterization of high quality ZnO thin films obtained by spray pyrolysis. Thin Solid Films, 350: 192-202.

Shan, F.K., B.C. Shin, S.C. Kim and Y.S. Yu, 2003. Substrate effect of ZnO thin films prepared by PLD. J. Eur. Cerm. Soc., 24: 1015-1018.

Shan, F.K., B.C. Shin, S.C. Kim and Y.S. Yu, 2004. Optical properties of as doped ZnO thin films prepared by PLD technique. J. Eur. Cerm. Soc., 24: 1861-1864.

Shim, E.S., H.S. Kang, J.S. Kang, J.H. Kim and S.Y. Lee, 2002. Effect of the variation of film thickness on the structural and optical properties of ZnO thin films deposited on sapphire substrate using PLD. Applied Surf. Sci., 186: 474-476.

Tauc, J., R. Gricorovichi and A. Vancu, 1966. Optical properties and electronic structure of amorphous germanium. Phys. Status Solidi, 15: 627-633.

Valle, G.G., P. Hammer, S.H. Pulcinelli and C.V. Santilli, 2004. Transparent and conductive ZnO: Al thin films prepared by sol-gel dip-coating. J. Eur. Cerm. Soc., 24: 1009-1013.

Wong, C. and B.Q. Xu, 2004. Synthesis and optical absorption property of the $Zn_2Ti_xSn_{1-x}O_4$ $(0 \le x \le 1)$ solid solutions. Sol. St. Phen., 177: 3448-3453.