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ZnO:Sn Deposition by Sol-gel Method: Effect of Annealing on the Structural, Morphology and Optical Properties

(Pemendapan ZnO:Sn melalui Kaedah Sol-gel: Pengaruh Pertumbuhan Terhadap Struktur, Morfologi dan Sifat Optik)

H. ABDULLAH*, S. SELMANI, M.N. NORAZIA, P.S. MENON, S. SHAARI & C.F. DEE

ABSTRACT

Sn doped zinc oxide polycrystalline thin films were prepared by sol-gel process. The sol was prepared from zinc acetate dehydrate and tin chloride were used. 2-methoxyethanol and monoethanolamine were used as the solvent and stabilizer, respectively. The quantity of tin in the sol was 0, 15, and 25 at.% Sn with annealing temperature 400, 500 and 600°C. Structural investigation including surface morphology and microstructure was carried out by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). The films give a hexagonal wurtzite structure with diffraction peaks at (100), (002) and (101). Changes in particle size with an increase in annealing temperature were observed in the SEM micrograph. The optical properties were determined by photoluminescence (PL) and UV-Visible (UV-VIS-NIR) spectrometer. The band gaps increased (2.78 eV to 4.10 eV) as the concentration of Sn was increased and the increasing of annealing temperature. Annealing temperature plays a key role in the formation of defects which is strongly related to the nonradiative recombination centers. 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 cells.

Keywords: Annealing temperature; anti-reflecting coating; sol-gel

ABSTRAK

Filem nipis zink oksida didop Sn telah disediakan melalui proses sol-gel. Sol telah dibuat daripada zink asetat nyahhidrat dan timah klorida. 2-methoxyethanol dan monoethanolamine masing-masing telah digunakan sebagai pelarut dan penstabil. Kuantiti timah dalam sol adalah 0,15, dan 25 at.% Sn dengan suhu penyepuhlindapan 400, 500 dan 600°C. Struktur termasuk morfologi permukaan dan mikrostruktur telah dikaji dengan pengukuran pembelauan sinar-X (XRD) dan mikroskop elektron imbasan (SEM). Filem menunjukkan struktur wurzit bersegi enam dengan puncak belauan pada kedudukan (10), (002) dan (101). SEM menunjukkan perubahan dalam saiz zarah dengan satu peningkatan dalam suhu penyepuhlindapan telah dicerap. Sifat optik telah ditentukan oleh fotoluminesens dan analisis spektrometer UV-Vis-NIR (UV-VIS). Nilai jurang jalur yang diperolehi bertambah (2.78 eV to 4.10 eV) bagi peningkatan Sn dan juga dengan penambahan suhu penyepuhlindapan. Dicadangkan suhu penyepuhlindapan memainkan peranan penting dalam pembentukan kecacatan, yang berkait rapat untuk penggabungan semula pusat-pusat yang tiada radiasi. Penambahan peningkatan jurang jalur diterima sebagai lapisan anti pantulan yang baik. Oleh sebab itu, filem ini boleh diterapkan pada sel suria silikon.

Kata kunci: Lapisan anti-pantulan; sol-gel; suhu penyepuhlindapan

INTRODUCTION

Zinc oxide is a direct wide band-gap (Eg ~3.37 eV) semiconductor with a large exciton binding energy (60 meV) (Karamdel et al. 2010; Wang et al. 2008). Due to its high conductivity and high transmittance, ZnO thin film has attracted attention as a transparent electrode in applications such as amorphous silicon solar cell, liquid crystal display and heat mirrors. In recent years, great interests were focused on its potential application in optical devices because of its strong PL spectra and inexpensive substrates (Vinodkumar et al. 2009). To obtain high quality ZnO thin film, a variety of techniques including chemical vapor deposition (CVD) (Kashiwaba et al. 2000), magnetron sputtering (Li et al. 2008) pulsed laser deposition (PLD) (Kaushal et al. 2009) and sol–gel techniques (Zhang et al. 2009) have been adopted. With the advantages of low deposition temperature, simple processing, high growth rate, low-cost equipment and suitability for large areas deposition, magnetron sputtering is one of the most promising deposition techniques.

In order to develop material for special applications, doped ZnO films have been fabricated and investigated by many research groups. It was reported that Sn is one of the most efficient elements utilized to improve the opto-electrical properties (Tokumoto et al. 2000). Thermal annealing is also a widely used method to improve crystal quality and to decrease structure defect in materials. During the annealing process, dislocations and other

structural defects move in the material and adsorption/ decomposition may occur at the surface, thus the structure and the stoichiometric ratio of the material will change (Yang et al. 2008). In this study, ZnO:Sn films prepared by sol-gel were annealed at the temperature ranging from 400 to 600°C in air and the effect of the annealing temperature on the crystal properties, morphologies, transmittance and PL spectra of ZnO:Sn films have been studied.

Experimental Details

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

The solution was dropped onto quartz substrates, which were rotated at 1000 rpm for 30 s. After depositing by spin coating, the films were 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 were repeated three times until the thickness of the sintered films was approximately 200 nm. The films were then annealed in air at 400, 500 and 600°C for 1 h.

The crystallinity of each ZnO film was measured using the XRD with CuK_α radiation. The surface morphology of the films was observed with a scanning electron microscop (SEM) and the changes in the optical properties by UV-Vis measurement and photoluminescence.

Results and Discussion

SEM images of undoped and doped ZnO thin films on quartz substrates are displayed in Figure 1. 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 different shapes and sizes were mixed. The film annealed at 400ºC had particles size approximately 48 nm. When the annealing temperature was at 500ºC, the particle size decreased and the microstructure of the film became denser. The 600ºC annealed film consisted of small particles forming a layer where the large ones lying on the layer. The particle size forming a layer reduces with increasing annealing temperature (Abdullah et al. 2009).

TABLE 1. Estimation of grain sizes measured from SEM micrographs

Anealling Temperature (ºC)	Grain Size (nm)	
	15 at.% Sn	25 at.% Sn
400	30	31
500	73	43
600	34	56

Additionally, a microstructure with a larger difference in size between the large and small particles is observed in films annealed at 600ºC. In cases where films was doped smaller ionic radius than zinc, particles formed matrix became smaller with increased annealing temperature. This is because the grain growth was disturbed by compression stresses due to the difference in ionic radii between zinc and tin ($r_{Sn}^{4+} = 0.069$ nm, $r_{Zn}^{2+} = 0.074$ nm). The change in particle size with an increase in annealing temperature was 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 is also observed by Lee and Park (2003) for film annealed at 500°C.

X-ray diffraction patterns of undoped ZnO and Sn doped ZnO films are presented in Figure 2. For the as-prepared ZnO nanoparticles, there are many dangling bonds related to the oxygen vacancies of the grain boundaries. Those grains tend to merge during the annealing process. The doping of Sn into ZnO thin film destroys the crystallinity of the thin film. Water might destroy the bonding of grains and crystallinity as unvaporized water drops migrate into the surface at high temperatures. It is uncoverable even after annealing at 400, 500 and 600°C. The undoped ZnO thin film gives a hexagonal wurtzite structure by with diffraction peaks for (100), (002) and (101). The crystallinity of undoped ZnO thin film was improved when it was annealed at 500 and 600°C. The effect was not observed for the ZnO thin films doped with 15 and 25 at.% of Sn.

The room-temperature PL spectra of ZnO films annealed at different temperature are displayed in Figure 3. Excitation and emission spectra at room temperature were recorded using a Perkin-Elmer LS-55 (Perkin-Elmer Co., USA) luminescence spectrometer with a xenon discharge lamp. From this figure, an ultra-violet (UV) near-band edge emission peak near 480 nm and defect related deep-level emission around 500-520 nm from the ZnO films were observed, similar to those reported elsewhere. The UV emission peak originated from excitonic recombination as shown by other researchers, and the UV peak intensity varies with annealing temperatures. Defect-related green emission is believed to come from oxygen vacancies (Kang et al. 2003). Generally, the quality of ZnO films improves with increasing annealing temperature. However, it is noted that the 15 at.% Sn doped ZnO thin films annealed at 500ºC shows the strongest excitonic related UV emission, and the UV emmision intensity monotonically decreases

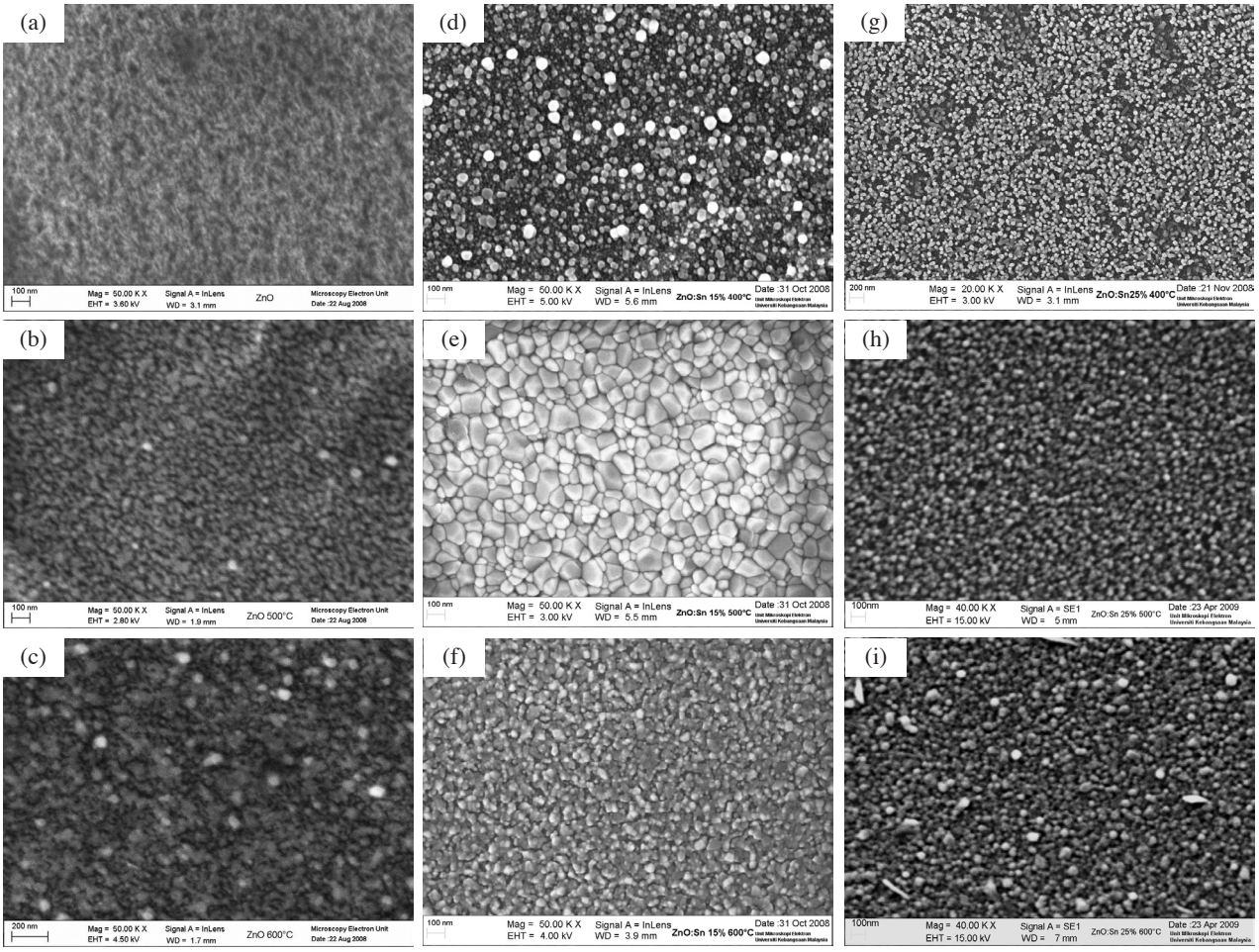

FIGURE 1. SEM images of undoped and doped ZnO thin films with Sn dopant content, (a) undoped, annealed at 400°C, (b) undoped, annealed at 500°C, (c) undoped, annealed at 600°C, (d) 15 at %, annealed at 400°C, (e) 15 at %, annealed at 500°C, (f) 15 at %, annealed at 600°C, (g) 25 at %, annealed at 400°C, (h) 25 at %, annealed at 500°C and (i) 25 at %, annealed at 600°C

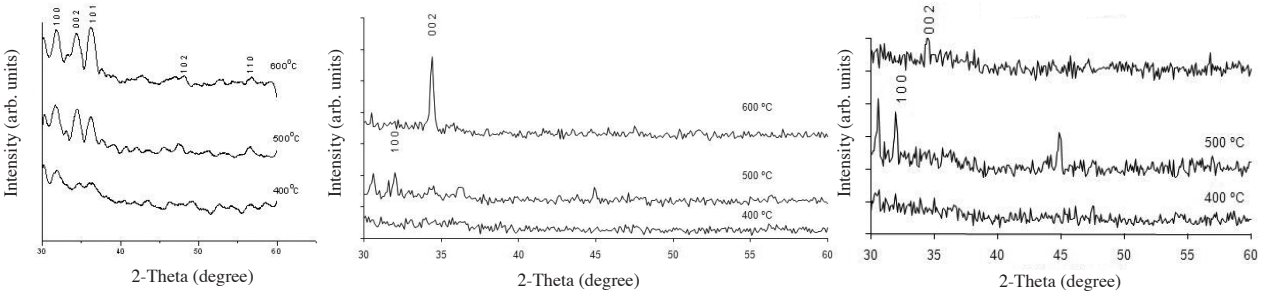

FIGURE 2. X-ray diffraction patterns of undoped and Sn-doped ZnO thin films annealed at different temperature for 1 h (a) undoped, (b) 15 at % and (c) 25 at %

from 600 to 400ºC. This behavior can be understood by considering the formation of defects. While the ZnO film was annealed at 500ºC, the rate of formation point defects, which is responsible for radative recombination is low at low temperature. The Pl spectrum showed two emision peaks for T=600ºC, the first at λ=340 nm refer to band to band transition, and it is due to the oxygen vacancies in tha lattice as reported before. The second peak at λ=650 nm which refer to inter-band transition is attributed to the zinc vacancies and this can be explained as follow.The additional of tin to ZnO may cause the following reaction (Ursaki et al. 2007):

$$SnO\ (s) \rightarrow Sn_{..Zn} + O_o + V''_{Zn}, \quad (1)$$

where Sn_{Zn} is tin subsituting Zn^{2+} in zinc oxide lattice, Oo is O in site, V''_{Zn} is zinc vacancy. The subtitution of the Zn^{2+} atom by the Sn^{4+} atom results in the formation of V''_{Zn} defects that can provide a charge carriers which may decay from the host ZnO to Sn^{4+} energy levels.

Accordingly, efficient excitonic emission can be easily achieved. For temperature higher than 400ºC for 15 and 25 at.% Sn doped ZnO, more defects responsible for nonradiative transition will be introduced into the films. This is why film annealed at these concentrations around 400ºC show poorer UV emission than that lower cencebtration. Futhermore, higher annealing temperatures (between 500 and 600ºC) facilitate the migration of grain boundries and promote the coalescence of small crystals, and thus favor a decrease of the concentration of nanradiative recombination centers.

The absorption coefficient (α) is calculated by using the following equation (Miao et al. 2006):

$$\alpha = \frac{\ln(I/T)}{d}, \quad (2)$$

where T is the transmittance index and d is the film thickness. In the direct transition semiconductor, the optical band-gap dependence on the absorption coefficient is given by the following equation (Shinde et al. 2006):

$$(\alpha h\nu)^2 = A(h\nu - E_g), \quad (3)$$

where A, E_g and $h\nu$ are constant, optical band gap, and photo energy, respectively. E_g can be determined by plotting the curve of $(\alpha h\nu)^2$ versus photo energy $h\nu$ and extrapolating the linear portion of the curve to the $h\nu$-axis. This technique is complementary to absorption measures transitions from the ground state to the excited state. Band-gap energy estimated from the absorption edge of the films is shown in Figure 4 and a band gap from 1.11 to 5.28 eV was obtained. The band gaps of all the films obtained are higher than those of the bulk ZnO. The ZnO film has a band gap of 2.78 eV at 400ºC, and it increases to 3.185 eV after annealing at 500ºC, and decreases again to 3.165 eV at 600ºC, which might be due to relaxation of growth induced strain in them. The band gap of Sn doped ZnO increases from 3.97 to 4.10 eV and decreases again to 3.77 eV with concentration of 15 at.%. While, at 25 at.% it was increases from 2.62 to 3.12 eV but the increment of the band gap is lower than 15 at.%. From the figure, we can see that the background absorption at the higher concentration increased drastically. Such an increase in background absorption is due to higher scattering of light at the rough surfaces of the doped nanostructures as can be seen from Figure 1.

Conclusion

In sum, we have discussed the effect of post-annealing temperature on the structure, optical properties and

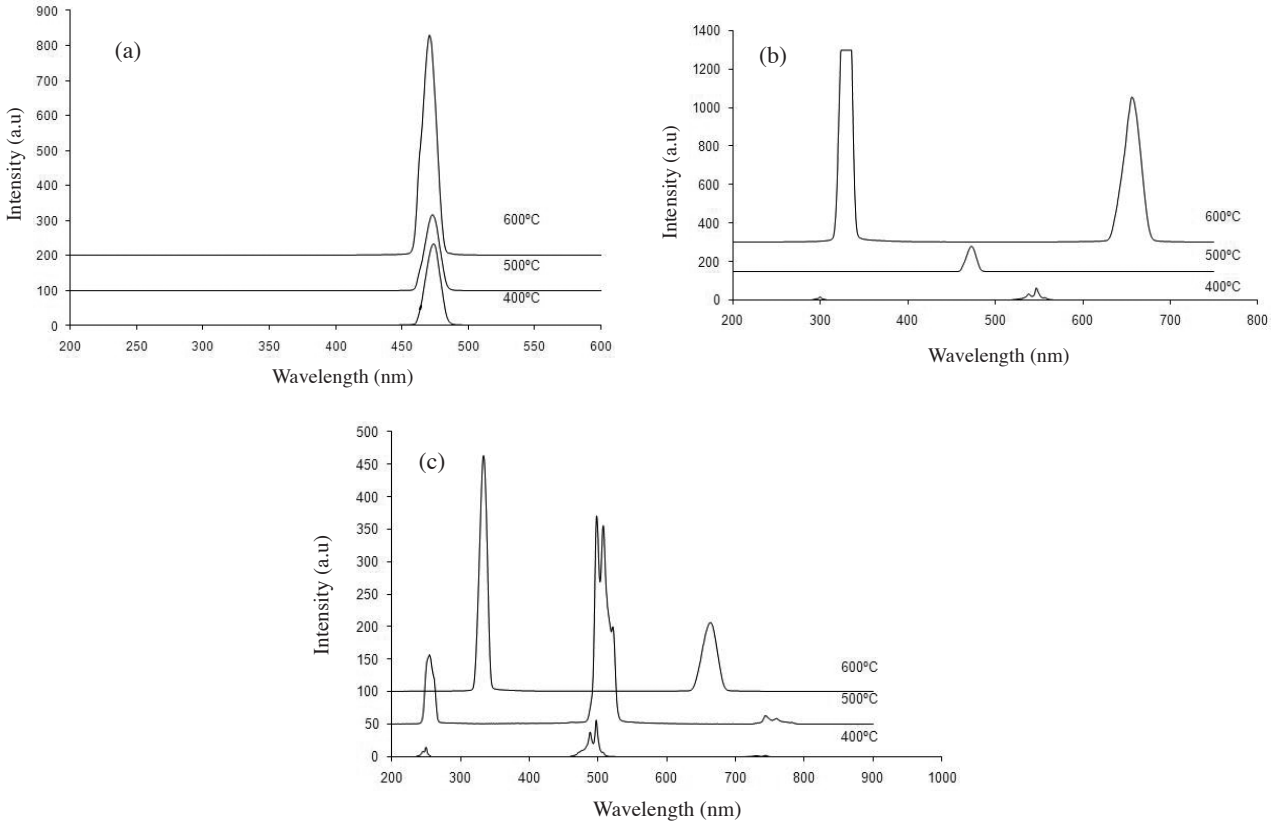

FIGURE 3. PL spectra of the undoped and Sn doped ZnO films annealed at different temperatures (a) undoped, (b) 15 at % and (c) 25 at %

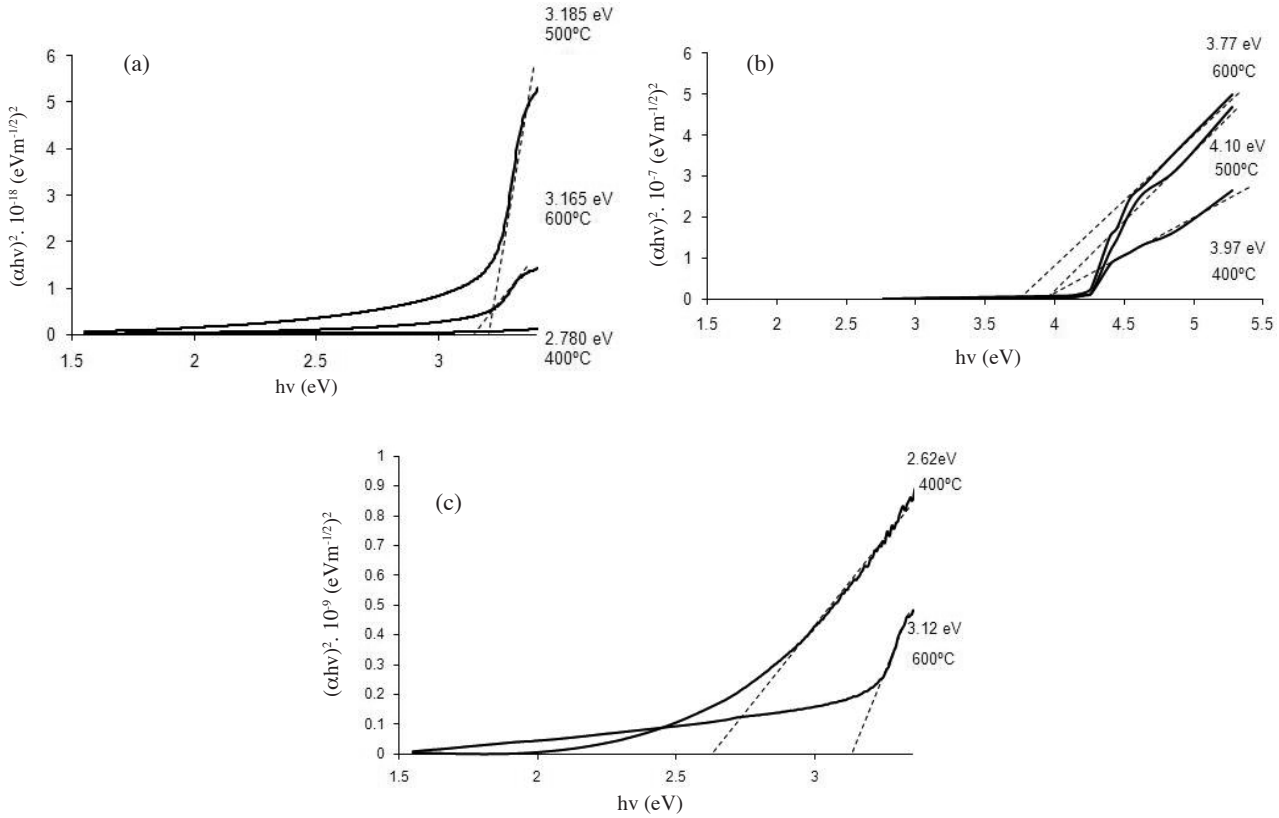

FIGURE 4. Evoluation of $(\alpha hv)^2$ vs. hv curves of films prepared, at different annealed temperature (a) undoped, (b) 15 at % and (c) 25 at %

TABLE 2. Energy gap determined from Figure 4

Temperature (°C)	Energy gap (eV)		
	Undoped ZnO	15 at.% Sn doped ZnO	25 at.% Sn doped ZnO
400	2.78	3.185	3.165
500	3.97	4.10	3.77
600	2.62	-	3.12

PL spectra of Sn doped ZnO thin films. The crystal quality of the films is highly dependent on the annealing temperature. It can be improved by annealing from 400 to 600°C. The morphology of ZnO nanostructure change drastically with the incorporation of tin. Incorporated tin in ZnO nanostructures substituted zinc from its lattice site. The average band gap increased from 2.78 eV to 4.10 eV with annealing temperature going up from 400 to 600°C and doping concentration at 15 at.%. The increase of the band gap was attributed to the decrease of the tensile strain in the films and a linear increment of the optical band gap with the strain was obtained. The oxygen vacancies increased with increasing annealing temperature and doping of the films. Sn doping not only formed the SnO_2 phase to reduce the structural defects but also enhanced the optical properties.

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H. Abdullah*, M.N. Norazia, S. Selmani & S. Shaari
Department of Electric, Electronic & System
Faculty of Engineering
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor D.E.
Malaysia

P.S. Menon, S. Shaari & C.F. Dee
Institute of Microengineering and Nanoelectronics (IMEN)
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor D.E.
Malaysia

*Corresponding author; email: huda@vlsi.eng.ukm.my

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