

DETERMINATION OF THE BAND-GAP ENERGY OF CERAMIC ZnO DOPED WITH MnO BY PHOTOPYROELECTRIC TECHNIQUE

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ABSTRACT

Photopyroelectric spectroscopy (PPES) is used to study the band-gap energy (E_g) of ZnO doped with MnO of 0.1 to 2.0 Mol % and sintered at various isothermal sintering temperature ranged from 850°C to 1300°C. The wavelength of incident light is kept in the range from 300 nm to 800 nm at a modulation frequency of 9 Hz. The photopyroelectric spectrum with reference to the doping level and sintering temperature is discussed. E_g is estimated from the plot $(\rho h\nu)^2$ vs $h\nu$ and is about 3.0 eV for samples with 850°C sintering temperature at all doping levels. At higher sintering temperatures the value of E_g decreases with the MnO mol %; beyond 1 mol % E_g becomes constant at about 2.0 eV. The x-ray diffractometry shows that the crystal structure of ZnO doped with different mol % of MnO at all sintering temperatures remains to be of hexagonal type but a small peak is found related to the new phase $ZnMn_2O_4$ only at 1050°C sintering temperature at 2 mol % of MnO doping level. Density is decreased from 95.5% to 87% with the increase in sintering temperature and doping level.

INTRODUCTION

The ZnO based ceramic semiconductors are widely used as gas sensors (Lin et al, 1998), piezoelectrics, electrodes for solar cells, phosphors, transparent conducting films (Look, 2001), and varistors. Varistors possess high energy absorption capability against various surges. They are extensively used as protective devices to regulate transient voltage surges (Choon, 2003) of unwanted magnitudes which refer to the damaging voltage transients that exceed more than 10% of the operating voltage of the equipments being protected. ZnO based varistors have super-fast response to over-voltage transients as they sense and clamp transients in nano-second speed, repeatedly in thousands of times without being destroyed (David,1999). They can perform surge-suppressing functions equally in both polarities even in ac and dc circuits over a wide range of voltages. They have high energy-absorption capability with energy density up to 300 J/cm³ with low power loss of only 10-100 mW/cm³ with long life spans under hostile

environments of more than 10 years. They are compact, small size and low price. The varistors are typically fabricated by sintering of ZnO with other metal oxides of small amounts such as Bi₂O₃, Co₃O₄, Cr₂O₃, MnO and Sb₂O₃. Much have been done in I-V studies on ZnO based varistor by previous workers (Eda, 1989; Choon, 2003) and in this paper we present the optical study of ZnO and the variation of band-gap energy with MnO dopant by using photopyroelectric technique.

MATERIALS AND METHODS

ZnO (99.9% purity, Alfa Aesar) was doped with MnO (99.5% purity) varied as 0.1, 0.4, 0.7, 1.0, 1.3, 1.6, 2.0 mol %. The 30 g product at each mole percentage was mixed with ethanol solution and was stirred for 24 hours. The slurry was filtered and dried in air for 48 hours. The mixture was ground to make a powder of fine particles before pre-sintering. The powder of each mole percent was divided into three parts and was pre-sintered at temperatures 800°C, 1000 °C and 1250°C for 2 hours at the rate of 10 °C min⁻¹. Then each sample was ground and mixed with Polyvinyl alcohol as a binder to give strength and to avoid cracks in the final pressed product. The mixture was pressed under a force of 2 tons using zinc stearate as a lubricant to form a pellet of 10 mm diameter with 1 mm thickness. Finally the pellets were sintered at 850°C, 1050°C and 1300°C for 1 hour in air at heating and cooling rate of 4°C min⁻¹. The density of the ceramic ZnO doped with MnO was measured by the Archimedes method. The disk from each sample was ground for 2 hours to make fine powder for the PPES and XRD analysis.

Photopyroelectric spectroscopy (PPE) is a non-radiative useful tool (Minamide, 1998) to study optical properties of the materials. This method is based on photothermal effect where the pyroelectric transducer is used to detect the temperature variation from the light-induced periodic heating in the sample. The transducer possesses a temperature dependent spontaneous polarization below the Curie temperature that changes as the temperature of the material changes (Blackburn, 1970). When there is an absorption of incident light, the non-radiative de-excitation processes with in the solid will cause the sample temperature to fluctuate, through heat diffusion to the surrounding pyroelectric film. Due to this temperature change, a pyroelectric voltage (Almond, 1996) at modulation frequency (ω) is observed in the pyroelectric film and is given by,

$$V(\omega) = \frac{pI_d}{\varepsilon} \langle \Delta T \rangle$$

where p is the pyroelectric coefficient, I_d is the film thickness, ε is the film dielectric constant and $\langle \Delta T \rangle$ is the average temperature (John, 1986) rise in the film. Photopyroelectric signal amplitude was measured for a range of optical excitation wavelengths 300 nm to 800 nm to produce a PPE spectrum which is actually an excitation spectrum; other factors are usually kept or assumed fixed while the PPE spectrum is obtained. For sample treatment prior the photopyroelectric measurement,

fine powder was again ground in deionised water, then few drops of the each mixture were dropped on an aluminium foil of area 1.5 cm^2 and dried in air to form a thin layer of sample on the foil. The foil was placed in contact (Tam, 1984) to a Polyvinylidene Fluoride (PVDF) PPE sensor (Mandelis, 1984) using silver conductive grease in between two Perspex plates, Fig. 1. A 1 kW Xenon arc lamp (Oriel 6921) was used as the light source in the PPE spectrometer system, Figure 2. The light beam was mechanically chopped at 9 Hz modulation frequency and was focused on the sample in PVDF holder. The detected PPE signal was amplified by a low-noise pre-amplifier (SR560) and then analysed by a lock-in amplifier (SR530). The data of PPE amplitude signal from the lock-in amplifier and the scanning wavelength from a monochromator were accumulated in a personal computer. The raw signal from the sample was normalized with respect to the carbon black PPE spectrum. The effect of MnO doped in ZnO varistors was investigated at room temperature.

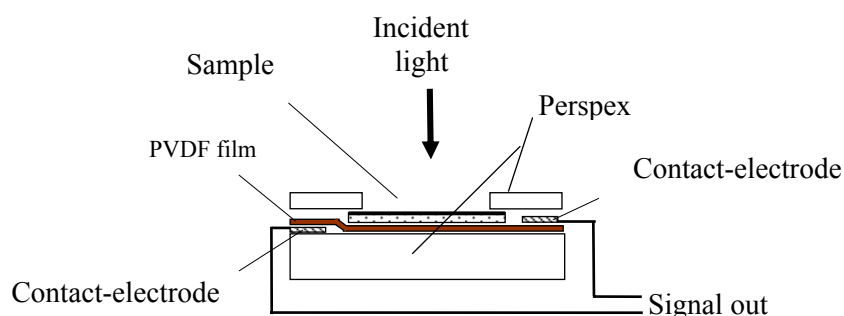


Figure 1: Schematic diagram of sample-PVDF holder.

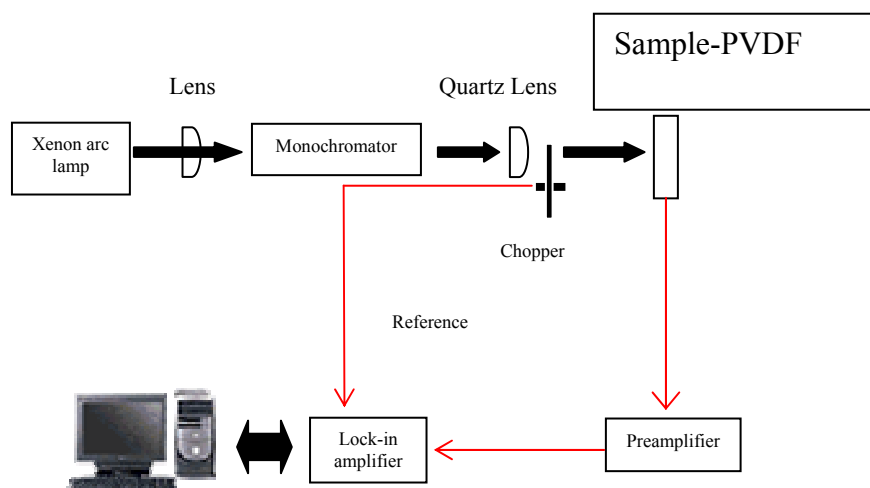


Figure 2: Schematic diagram of PPES.

For the determination of band-gap energy (E_g), it was assumed that the fundamental absorption edge of ZnO-X metal oxide is due to the direct allowed transition. The optical absorption coefficient β varies with the excitation light energy $h\nu$ (Toyoda, 1985) and is given by the expression,

$$(\beta h\nu)^2 = C(h\nu - E_g)$$

near the band gap, where C is the constant independent of photon energy, $h\nu$ is the photon energy and E_g is the direct allowed energy gap. The PPE signal intensity ρ is directly proportional to β , hence $(\rho h\nu)^2$ is related to $h\nu$ linearly. From the plot of $(\rho h\nu)^2$ versus $h\nu$, the value of E_g is obtained by extrapolating the linear fitted regions to $(\rho h\nu)^2 = 0$, as shown in Fig. 4 for pure ZnO.

X-ray power diffraction with Cu K_α radiation using PANalytical (Philips) X'Pert Pro PW1830 was used to identify the crystalline phases. The XRD data were analysed by using X'Pert High Score software for the identification of the crystalline phases present in ZnO doped with MnO at different sintering temperatures.

RESULTS AND DISCUSSION

The XRD pattern Fig. 3 shows that the crystal structure of pure ZnO and ZnO doped with 2 mol % of MnO. At all sintering temperatures the crystal structures remained to be of hexagonal wurtzite-type structure. No extra peak was found at 850°C and 1300°C sintering temperatures at all doping levels, indicating the substitution of Mn^{2+} inside the lattice of ZnO and the absence of any free MnO. The presence of a small peak at the diffraction angle of 44.66° for the (220) plane found in the pattern, Fig. 2, related to the new phase $ZnMn_2O_4$ (ICSD code 01-071-2499) only at 1050°C sintering temperature at 2 mol % of MnO doping level, this indicates the significant amount of the new phase is only found at 1050°C sintering temperature. Therefore, it is considered that presence of second phase $ZnMn_2O_4$ and an amorphous Mn-rich thin film, in a nanometer scale, which is not detected in XRD pattern, is also formed at the grain boundaries at 850°C to 1300°C sintering temperatures. The presence of a second phase or amorphous film can benefit grain boundary diffusion, thus promoting the grain growth of ZnO at all sintering temperatures. Density was decreased from 95.5% to 87% with the increase of sintering temperature and doping level, and the decrement is very prominent with the temperature. Therefore it is expected that there is an abnormal grain growth with the increase of doping level and temperature. ZnO behaves as a n-type semiconductor, as its conduction band arises from the 4s orbital of Zn is wide enough to favour the effective charge transfer. Electron is excited from its valence state due to the absorption of light so this process generates the electron-hole pairs, which starts the conduction mechanism. Above the band-p energy the photopyroelectric signal is due to the phonon emission and below the energy is due to Urbach tail (Kimura, 2001). The value of band-gap energy (E_g) is about 3.0 eV at 850°C sintering temperature at all doping levels, Fig. 5; this indicates that the probability of the substitution of the Mn^{2+} ion is very low at this

temperature. In practice, there are a variety of inter grain conduction paths that operate in parallel (Levinson and Philipp, 1986). These can be through the grain boundary region or through the bulk inter-granular material, and are sensitive to the presence of chemical additives. It has been postulated that transition metal oxides, such as Mn, is involved in the formation of interfacial states and deep bulk traps at grain boundaries, providing large potential barriers to give better nonlinear characteristics when the I-V behaviour of the material was studied as a varistor (Eda, 1989). The change in band-gap energy for the 850°C, 1050°C, 1300°C sintering temperatures with doping mol % is shown in Fig. 6. At higher sintering temperatures, band-gap energy decreases with the increase of MnO mol %, indicating that the substitution of Mn^{2+} introduces the energy levels by the formation of interfacial states and deep bulk traps at grain boundaries. Beyond 1 mol %, band-gap energy becomes constant at 2.0 eV indicates that the solubility limit of MnO in ZnO has been reached.

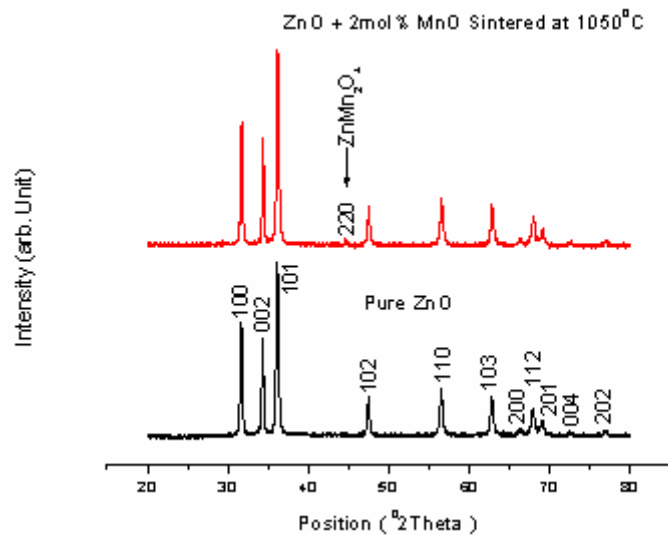


Figure 3: XRD pattern for pure ZnO and doped ZnO with MnO

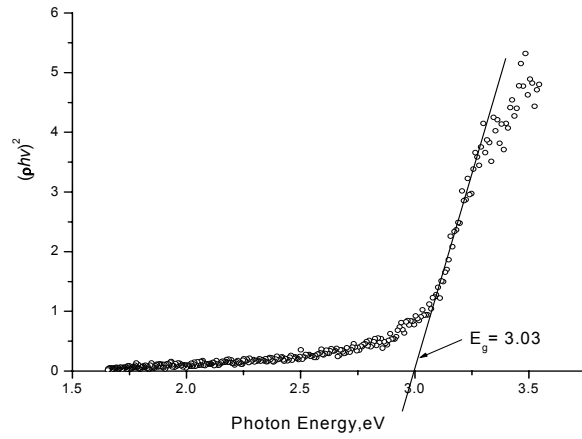


Figure 4: Excitation photon energy dependence of $(\rho h\nu)^2$ for pure ZnO

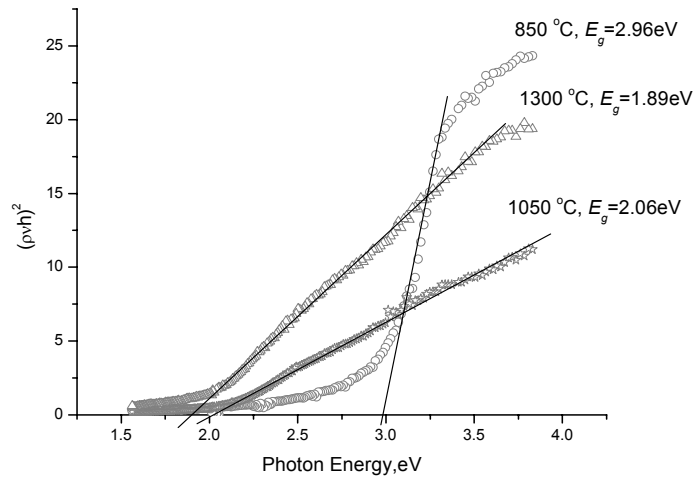


Figure 5: Band-gap energy at different sintering

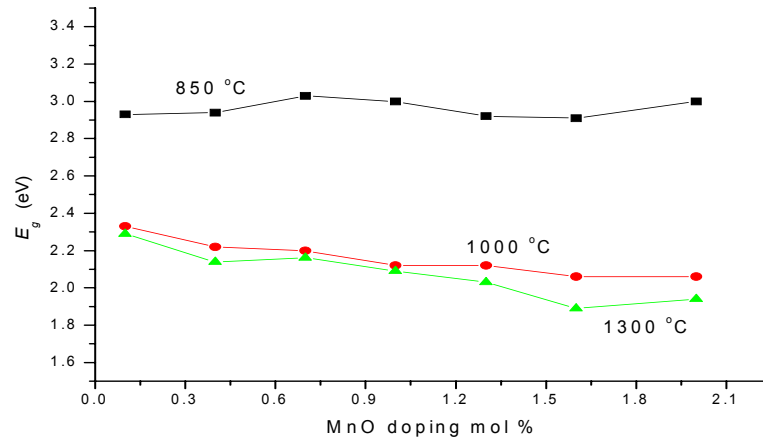


Figure 6: Dependence of energy band gap (E_b) at mol % of MnO at different temperatures.

CONCLUSION

PPE spectroscopy of ZnO doped with different mol % of MnO shows the decrease in band-gap energy at higher temperatures up to certain doping level and XRD results are correlated with this.

ACKNOWLEDGEMENTS

The authors would like to thank the Ministry of Science, Technology and Environment of Malaysia for the financial support of this work under IRPA Grant No. 02-02-04-0132-EA001.

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