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Influences of Microstructure Changes on the Optical Properties of Manganese Doped Zinc Oxide Semiconductor

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Abstract

Polycrystalline zinc oxide (ZnO) doped with bismuth oxide (Bi_2O_3) and manganese oxide (MnO) with 15 nm particle sizes was synthesized via the high energy ball milling (HEBM) technique for 12hours milling time and sintered from 500 to 1300 °C with 100 °C increments. X-Ray Diffraction (XRD) results revealed the formation of ZnOwurtzite structure as the main phase and Bi_2O_3 as the secondary phase. Decreasing particle size by HEBM technique would lead to improved grain growth control due to the well-formed microstructure even at low-sintering temperature and improved grain boundary characteristics. The variation of band gap value was decreased due to the quantum confinement and growth of interface states at the grain boundaries as the grain size increased.

Introduction

Zinc oxide (ZnO) is a very promising material for semiconductor device application due to the direct and wide band gap in the near-UV spectral region. ZnO also has large exciton binding energy so that excitonic emission processes can persist at or even above room temperature, and piezoelectric properties. In semiconductors, electrons are confined to a number of bands of energy, and forbidden from other regions. The term band gap also called energy band gap refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band. Electrons are able to jump from one band to another. However, in order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy either a phonon (heat) or a photon (light) for the transition. In polycrystalline zinc oxide materials, understanding and controlling the microstructure is very important since the optical band gap properties are directly influenced by the microstructure effect.

Nanoscale materials have drawn broad attention and become an active research over the past few decades owing to their interesting versatile properties [1] and due to their potential applications in electronics, optics, and photonics [2-6]. Nanoscale ZnO materials are of great interest nowadays because the properties of the materials change drastically when the particle size reaches the nanometer range. ZnO nanoparticles with controlled size and structure are necessary to study their size-dependent properties because at this nanomaterials range where quantum confinement effect and surface effects may be prominent and study their structure-dependent properties at relatively low temperatures. Ball milling is considered as an effective and simple technique to synthesize nanoparticles at low sintering temperature because of its simplicity and inexpensive equipment. It has been reported that ball milling not only induces morphological and structural changes in the particles, but also changes its electrical [7] and in optical [8] properties.

While a majority of the studies has focused on the optical properties of ZnO semiconductor, to date very few studies have been carried out to understand the microstructure of ZnO nanoparticles. The evolution of the microstructural and optical properties mainly on nano or submicron scales starting materials which are important as well has been neglected in past year. Hence, in this research, a systematic study on microstructure changes to the optical band gap properties in manganese doped-ZnO from low sintering temperature (nanometer size regime) to high sintering temperature (micrometer size regime) was investigated.

Experimental

Samples of the doped-ZnO samples with the composition of ZnO-Bi_2O_3-MnO were prepared by high energy ball milling (HEBM) technique. The high purity powders of ZnO, Bi_2O_3 and MnO were weighed in stoichiometric ratio and milled for 12 hours. Then the milled powder was granulated by monodispere granulation technique where in this technique the milled powder were mixed with polyvinyl alcohol (PVA) until it was fully wet and dried under fluorescent lamp. After drying, the powder was ground and sieve through a 150 nm sieve. The resulting powder was then pressed into disc-shapes samples by uniaxial pressing and sintered at 500, 600, 700, 800, 900, 1000, 1100, 1200 and 1300 °C. The densities of the samples after sintering measured using the Archimedes method and the particles sizes of the milled powder were obtained by transmission electron microscope (TEM). The crystalline phase of the samples was analyzed by using X-ray diffraction (XRD) characterization. The

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microstructure of the samples after sintering was observed by field scanning electron microscope (FESEM) and the average grain size was measured by the intercept method from the cross-sectional surface of the FESEM images of ZnO grains. The UV-Vis Spectrophotometer (UV-3600, Shimadzu) with the wavelength range of 200 to 800 nm was used to measure the optical band-gap energy of the samples. The disc sample was ground into fine powder by using mortar and pestle and the fine powder was sent to the UV-Vis spectrometer for the energy band gap (E_g) value. The acquired diffuse reflectance spectrum from UV-Vis spectrometer is converted to Kubelka-Munk function as follows:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} \qquad (1)$$

where F(R) is the Kubelka-Munk function, k and s are the absorption and scattering coefficients respectively and R is the reflectance. The intercept of the plot between $(F(R)h\nu)^2$ vs hv gives the energy band gap, E_g.

Results and Discussion

Microstructure-related analysis

The XRD patterns of the ZnO based varistor ceramics are shown in Figure 1. The XRD pattern reveals the presence of primary phase ZnO and secondary phases of Bi_2O_3. The peaks are (100), (002), (111), (102) and (110) shown in the patterns can be identified as the hexagonal wurtzite structure of ZnO ceramic. The Bi_2O_3 secondary phase was found existed from 700 to 1000 °C sintering temperature due to the liquid-phase sintering and as the temperature increased the formation of Bi-rich phase diminished due to its volatility at higher sintering temperatures [9]. Moreover, there is no secondary phase related to MnO detected at low amount of dopant possibly due to small addition of dopant and below detection limit of XRD equipment [10].From the XRD spectra it was shown that as the sintering temperature increased the diffraction peaks became sharper and stronger, indicating the crystallinity improvement of the samples.

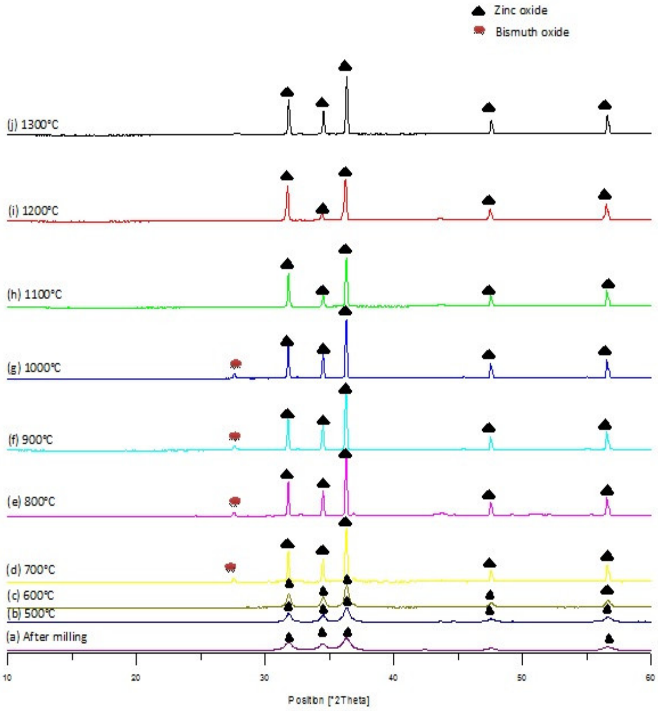
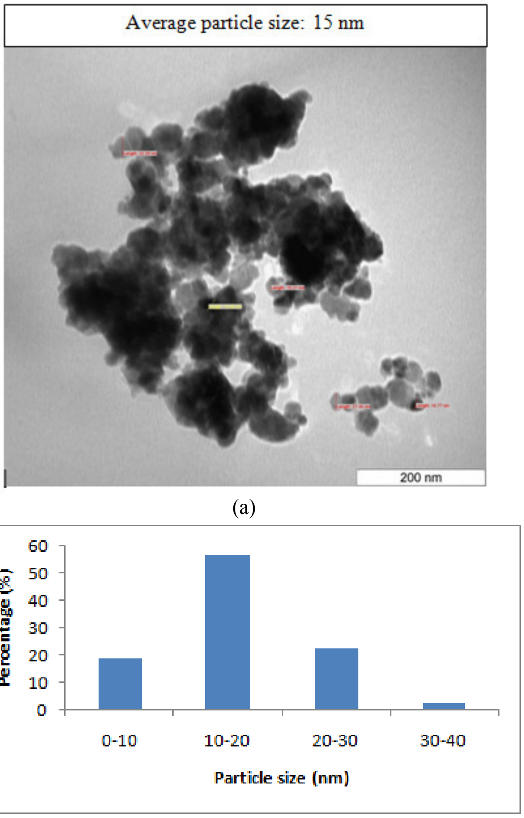


Figure 1:X-ray diffraction (XRD) patterns of ZnO-Bi_2O_3-MnO samples

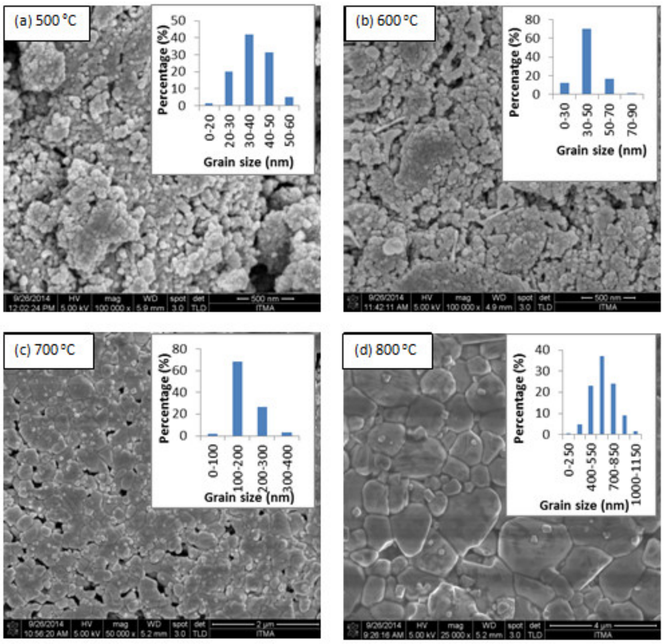
Figure 2 shows the TEM image and particle size distribution of the milled ZnO powder (Fig. 2a) for 12 hours and the average particle size (Fig. 2b) was found to be 15 nm. The optimization control of starting particle size is important in order to control the microstructure of the sample such as grain size, pore size and density because the optical properties are sensitive to these parameters. Hence, the TEM result proved that the nanoparticles powder was successfully obtained from HEBM technique.



(a)

(b)

Figure 2: (a) Transmission emission microscope (TEM) micrograph and (b) particle size distribution of ZnO-Bi_2O_3-MnO powder milled for 12 hours



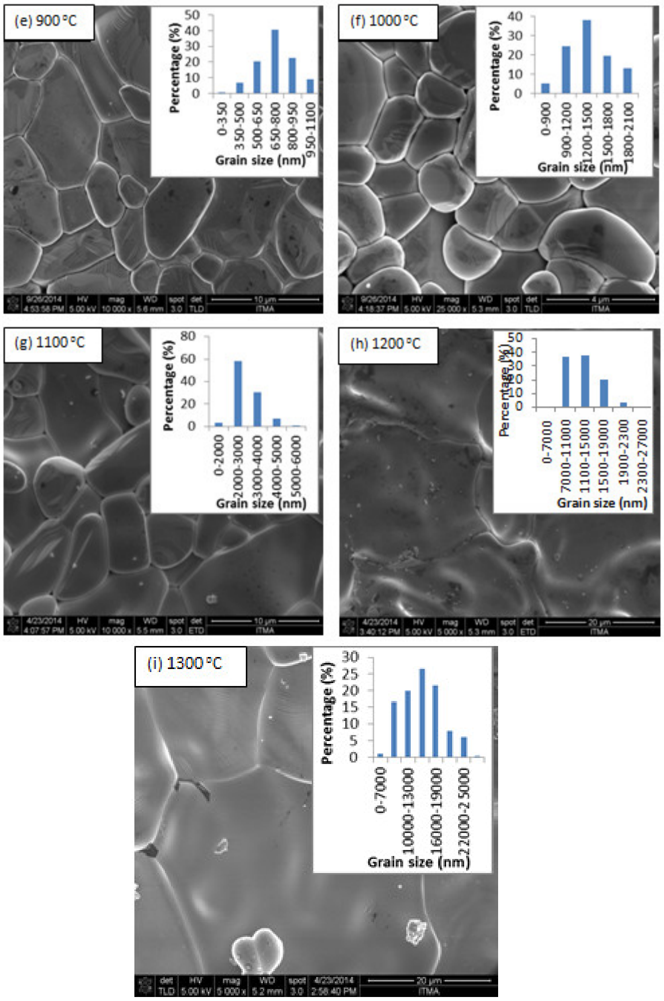


Figure 3: FESEM images and grain size distribution of ZnO-Bi_2O_3-MnO sintered at (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C, (f) 1000 °C, (g) 1100 °C, (h) 1200 °C, (i) 1300 °C.

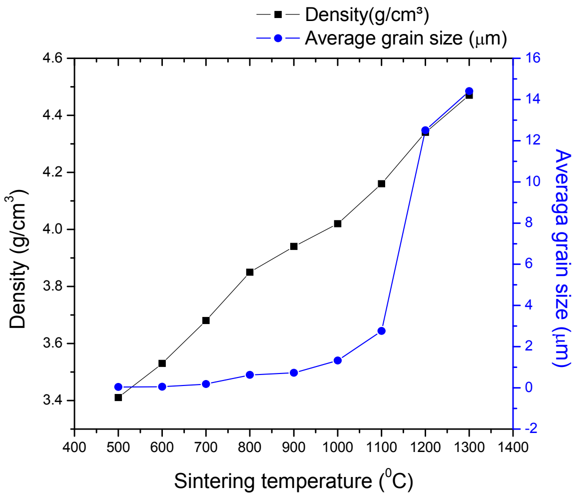


Figure 4: Density and average grain size of ZnO-Bi_2O_3-MnO sintered samples

The evolving microstructure images and grain size distribution of samples sintered are shown in Figures 3. Samples sintered from (a) 500 to (c) 700°C show a rearrangement of particles and particle growth. After sintering at (d) 800 to (i) 1300°C upward, the dumbbell structure occurred through the formation of necks lead to the development of grains. This leads to an increase of the grain size by diffusion during sintering process, where the evolution of grains from very fine size to a larger size would be associated by the evolution of quantum confinement and interface state effect. The variation of grain size and density with the sintering temperature from 500 to 1300 °C of ZnO-Bi_2O_3-MnO samples was observed in Figure 4. The average grain size was increased as the sintering temperature increased and a sudden increased of grain size can be observed at 1200 and 1300 °C. Doped-ZnO with nanometer-sized grains exhibits a much higher energy band gap than samples having micron-sized grain size. The increase of grain size with the sintering temperature is in good agreement with the increase of density. As expected the density of the samples increased as the sintering temperatures increased due to the larger grain size and diminished pores.

Optical properties

The variation of E_g with the photon energy of the doped-ZnO samples were revealing in Figure 5 and the variation in the optical band gap (Eg) with different grain size were shown in Table 1.

Table 1: List of the optical band gap values for Mn-doped ZnO samples and sintered from 500 -1300 °C sintering temperatures

Sintering temperature (°C)	Average grain size (μm)	Energy band gap, E_g
500	0.02	3.20
600	0.03	3.12
700	0.09	3.10
800	0.6	3.00
900	0.91	3.00
1000	1.3	3.00
1100	6.63	2.35
1200	12.1	2.30
1300	13.4	2.20

Obviously, the values of E_g were gradually decreased as the grain size increased for all batches samples. ZnO samples with a grain size in the range of 10–50 nm have demonstrated optical properties caused by quantum confinement [11].An increase in the band gap with decrease in particle size of ZnO is observed which is attributed to the quantum size effect [12]. From Table 1, only at sintering temperature of 500 °C with 40 nm grain size and 600 °C with 50 nm grain size indicate the contribution of quantum confinement effect with the value of the E_g was 3.2 and 3.12 eV. As the grain size increased the quantum confinement effect is no longer exist. Larger grain size contain higher amount of dangling bonds in the interface grain that contributed to the decreased of the E_g. In addition, Mn dopant with large ionic radii segregated at the grain boundaries and contributes to the increased of interface states. Therefore, larger growth of interface at the grain boundaries decreased the value of E_g. This may be associated with quantum confinement for nanograin size and growth of interface state for micron grain size samples. Hence, the variation in the band gap with grain size significantly correlated with the growth of the interface state, indicating that the increase in the sintering temperature induced an increase in the grain size, and caused a reduction in the quantum size effect in the ZnO nanoparticles. An increase of the grain size induced a decrease of the active surface area and affects the concentration of oxygen adsorbed on the grain surface. Therefore, the variation of E_g was contributed by existence of quantum confinement and growth of interface state.

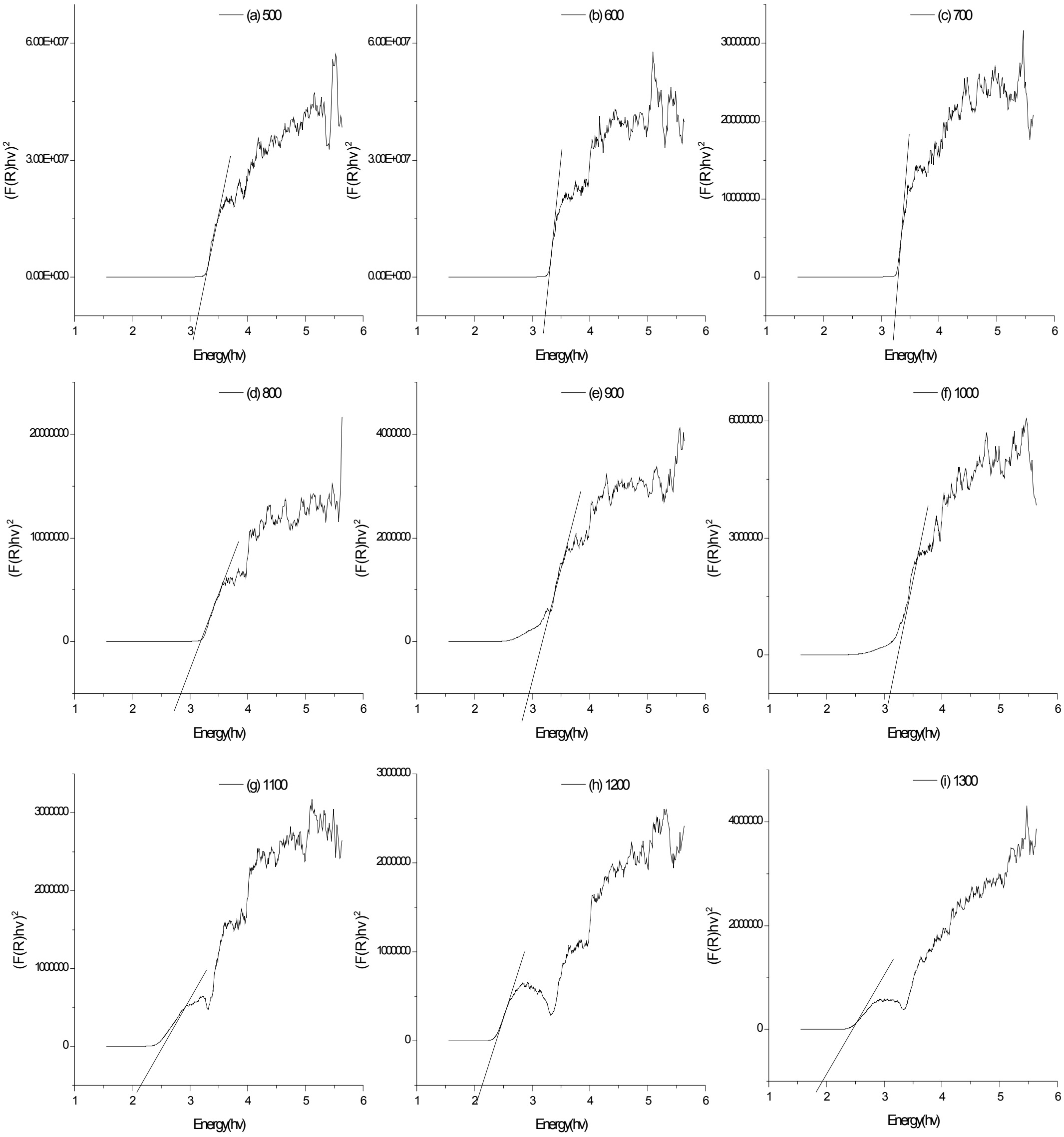


Figure 5: Variation of the energy band gap (E_g) with photon energy of ZnO-Bi_2O_3-MnO samples sintered from 500 until 1300 °C sintering temperature

Conclusion

The influences of microstructural changes on the optical properties of polycrystalline doped-ZnO have been investigated in a range from a relatively low sintering temperature up to high sintering temperature. Nanoparticles ZnO-Bi_2O_3-MnO was successfully prepared using a high energy ball milling (HEBM) for 12 hours. The XRD patterns reveal wurtzite structure for all sintered samples. Microstructural and optical properties showed that phase purity and grain size strongly influenced the energy band gap, E_g. The results strongly suggest that both quantum confinement and interface state effect contributes to the clear decrement of energy band gap as the sintering temperature increased.

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