PHOTOPYROELECTRIC SPECTROSCOPY OF THE CERAMIC ZnO DOPED WITH Bi_2O_3, Co_3O_4, MnO_2, TiO_2

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Introduction

ZnO is n-type semiconductor material and is widely used in semiconductor devices such as varistor [1]. The exact role of many additives in the electronic structure of ZnO varistors is uncertain. ZnO based varistor is formed with other metal oxides of small amounts such as Bi_2O_3, Co_3O_4, Cr_2O_3 MnO_2, Sb_2O_3 etc. These additives are the main tools that are used to improve the non-linear response. It is necessary to get information of the optical absorption for the investigation of electronic states of the varistor ceramic. Photopyroelectric (PPE) spectroscopy, a powerful non-radiative tool is used to study the variation of optical absorption.

Experimental

ZnO (99.9% purity) was doped with Bi_2O_3 (99.97 % purity), Co_2O_3 (99.7 % purity), MnO_2 (99.99 % purity) TiO_2 (99.9 % purity), according to the scheme $ZnO + 1\ MnO_2 + 0.4\ Co_2O_3 + x\ Bi_2O_3 + x\ TiO_2$ where x = 0.6, 1 mol%. Samples were prepared through solid state route. The dried powder was pressed under a force of 800 kg cm^{-1} to form the disks of 10 mm diameter with 1 mm thickness. Finally the disks were sintered at 1270 ^{o}C for 1, 2, 3 and 4 hours in air at the heating and cooling rate of 6 ^{o}C min^{-1}. 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 to a Polyvinylidene Fluoride (PVDF) PPE sensor using silver conductive grease in between two Perspex plates.

The measurement of PPE signal amplitude by PPE spectrometer has been described elsewhere. 1 kW Xenon arc lamp light beam, kept in the range of 300 to 800 nm, mechanically chopped at 9 Hz. The optical absorption coefficient (α) varies with the excitation light energy $h\nu$ and is given by the expression, $(\alpha h\nu)^2 = C (h\nu - E_g)$, where $h\nu$ is the photon energy, C is constant and E_g is the energy band-gap. PPE signal intensity (α) is directly proportional to α, hence $(\alpha h\nu)^2$ is related to $h\nu$ linearly. From the plot of $(\alpha h\nu)^2$ versus $h\nu$, E_g is obtained by extrapolating the linear fitted region. The PPE spectrum of the sample at room temperature was normalized with respect to the carbon black PPE spectrum, to obtain the true sample spectrum [2]

An empirical relation for absolute measuring temperature (T) and photon energy ($h\nu$), given by the equation:

$$P = P_o e^{\left(\frac{(h\nu - h\nu_o)}{KT} \right)}$$

where k is the Boltzman's constant and P_o, , $_o$ are fitting parameters [4]. $/kT$ is the value which determines the exponential slope, where ($_A$ in A-region and $_B$ in B-region) is the steepness factor. It can be found from the PPE spectrum.

Results and discussion

The main phase observed in the XRD analysis for the combination is ZnO with some other secondary phases as Bi_2O_3 (ref. code 00-018-0244). Some secondary phases Mn_2TiO_4 and $Zn_2Ti_3O_8$, Mn_2TiO_4, Zn_2TiO_4 are found in the ceramic for 3 and 4 hour sintering time when x = 1 mol%.

Relative density of the ceramic decreases slightly from 88.7 % with the increase of the sintering time.for x = 1 mol%. When the doping level is decreased as x = 0.6 mol% of Bi_2O_3 and TiO_2 then the density slightly decreases from 89.4 % with the increase of sintering time indicating the increase of pores with the increase of sintering time. Grain size increased from 41, 46.7 to 77.6, 74 µm with the increase of sintering time for the ceramic at x = 0.6, 1 mol%, respectively. This indicates that the grain size increases due to the grain enhancer Bi_2O_3 and TiO_2 as TiO_2 is a very strong grain enhancer. EDX results shows that the Bi_2O_3 is segregated at the grain boundaries. It was found that the Mn and Co, Ti is present in the grains indicating the substitution in the ZnO lattice.

The energy band-gap (E_g) of the ceramic ZnO, is reduced from 3.2 (pure ZnO) to 2.15 eV for the ceramic at x = 0.6 mol% for 1 hour sintering time Fig. 1. This decrease is due to the interface states produced by the combined effect of 0.4 Co_3O_4, 0.6 Bi_2O_3, 0.6 TiO_2 and $1MnO_2$. No increase or decrease is observed when the sintering time is increased from 1 to 4 hour. The value of E_g is constant at about 2.15 eV for 2, 3, 4 hour sintering time. E_g decreases from 3.2 to 2.17 eV when the amount of additives Bi_2O_3 and TiO_2 is increased from 0.6 to 1 mol%, for 1 hour sintering time. E_g is about constant at 2.15 eV for the 2 to 4 hour sintering time. This decrease is due to the interface states produced by the combined effect of the additives.

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The steepness factor s_A, Fig. 2, slightly increases with the increase of sintering time indicating the decrease in the PPE signal intensity in the ceramics having $0.6\ Bi_2O_3 + 0.6\ TiO_2$ additives. This indicates that the increase in the structural ordering. This structural ordering corresponds to the decrease in the interface states. So this decrease in the interface states is not giving very clear increase in the value of E_g but E_g seems slightly increases. The value of s_A is decreasing very slowly up to 3 hour sintering time and then slightly reduces at the 4 hour sintering time when the additives are increased from 0.6 to 1 mol%. Again the variation in the value of E_g was not observed clearly but E_g decreases due to the growth of interface states.

Generally, an exponential absorption tail at B-region, for crystalline semiconductors can be characterized as,

$$\left(\sigma_B \Big/ kT \right)^{-1} = A \left\langle U^2 \right\rangle_T C_o$$

Where C_o is the exponential-tail parameter of the order of unity and $A\left\langle U^2 \right\rangle_T$ is the thermal average of displacement of the atoms from their equilibrium positions, then $A\left\langle U^2 \right\rangle_T$ expresses the energy of the displacement of atoms. The steepness factor σ_B increases, Fig. 3, slightly with the sintering time indicating the decrease in the average thermal displacement of atoms for the combination $0.6\ Bi_2O_3 + 0.6\ TiO_2$. This indicates the decrease in the structural ordering and correspondingly, the value of E_g slightly increases, Fig. 1. The steepness factor σ_B decreases, Fig. 3, with the sintering time indicating the increase in the average thermal displacement of atoms for the combination $1\ Bi_2O_3 + 1\ TiO_2$. This indicates the decrease in the structural ordering and correspondingly, the value of E_g decreases due to the decrease in the growth of interface states.

References

[1] D.C. Look (2001). *Recent advances in ZnO materials and devices.* Materials Science and Engineering B **80**, 383-87

[2] A. Minamide, M. Shimaguchi, Y. Tokunaga (1998). *Study on Photopyroelectric Signal of Optically Opaque Material Measured by PVD Film Sensor.* Jpn. J. Appl Phys. **37**, 3144-47

[3] S. Qing,. and T. Toyoda,. (1999). Photoacoustic studies of annealed CdSxSe1-x (x = 0.26) Nan crystals in a glass materials. Jpn. J. Appl. Phys., **38**: 3163-67
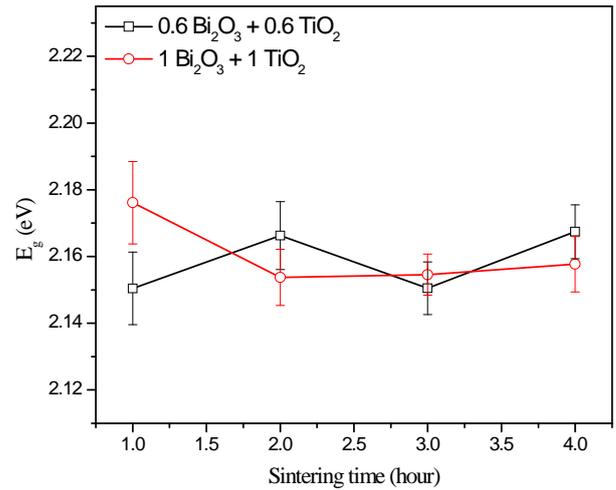
[4] S. Yamazaki,. (1987), Philos. Mag. **B56**, 79
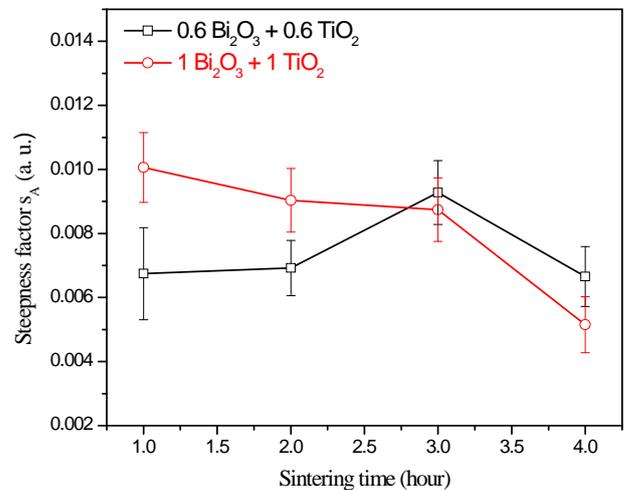
Fig. 1: Variation of E_g with sintering time
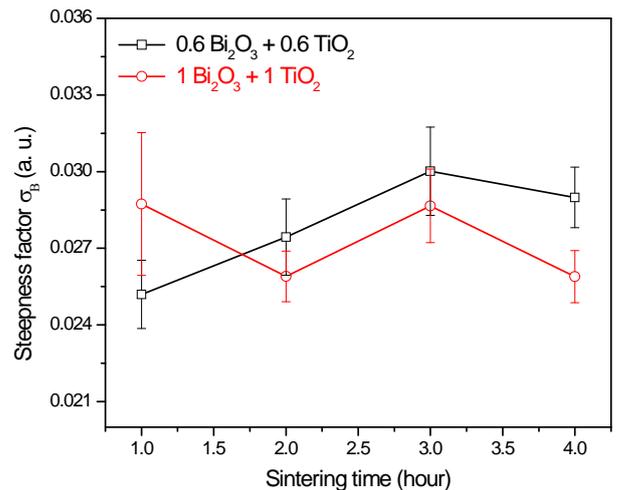

Fig. 2: Effect of sintering time on s_A

Fig. 3: Effect of sintering time σ_B