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## Development of uniformly grown ZnO micro-particles structures by simple and cost-effective chemical drop method

M.Prashantha<sup>1</sup>, M.Sekhar Babu<sup>2</sup>, N.Koteeswara Reddy<sup>3\*</sup>, K.Ramesh<sup>1</sup>

<sup>1</sup>Department of Physics, Indian Institute of Science, Bangalore-560012, (INDIA)

<sup>2</sup>Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, (INDIA)

<sup>3</sup>Center for Nanoscience and Engineering, Indian Institute of Science, Bangalore-560012, (INDIA)

E-mail: dr\_nkreddy@rediffmail.com

### ABSTRACT

A simple and cost-effective chemical drop method has been developed and adopted for the synthesis of zinc oxide (ZnO) structures. The depositions were carried out at different substrate temperatures increased from 100 to 250 °C on glass substrates by dropping an equimolar solution consisting of zinc nitrate hexahydrate and hexamethylenetetramine dissolved in deionized-water with a concentration of 5 mM. The structures grown at 200 °C showed nanoparticles (NPs) composed micro-particles (MPs) like surface morphology and exhibited hexagonal crystal structures having a preferential orientation of (002). However, these structures have polycrystalline nature and zinc deficient chemical composition. Raman spectroscopic analyses reveal that the as-deposited ZnO MPs structures at 200 °C have compressive stress and strong polar lattice bonds. The optical studies show that these ZnO structures are highly transparent (92%) in visible region and contain a direct optical band gap of about 3.42 eV. © 2013 Trade Science Inc. - INDIA

### KEYWORDS

ZnO structures;  
Chemical synthesis;  
Drop method;  
Low-cost method;  
Structural and optical properties.

### INTRODUCTION

In recent years, a variety of semiconductor materials have received great centre of attention in the field of materials science particularly due to their unique electrical and optical properties. Among the other materials, direct and wide band gap semiconductor materials have been of great research interest for use in optoelectronic devices including lasers and light emitting diodes etc. Zinc oxide (ZnO) is a direct wide band gap (3.37 eV) semiconductor and has a large exciton binding energy of 60 meV. ZnO has a large number of multifunctional applications in various fields due to its unique

electrical, optical, and mechanical properties<sup>[1]</sup>. For example, ZnO has been widely adopted for piezoelectric transducers, gas sensors, optical waveguides, transparent conductive films, varistors, and solar cells and bulk acoustic wave devices<sup>[2-6]</sup>. The behavior of ZnO majorly depends on its crystallinity, orientation, crystallite size, and morphology<sup>[7-11]</sup>. In order to attain good control over these parameters, there are various chemical as well as physical methods have been realized and also produced significant novel structures. Along with high temperature growth methods, simple and cost-effective low-temperature growth methods including sol-gel<sup>[12]</sup>, evaporative decomposition of solution<sup>[13]</sup>, wet

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chemical synthesis<sup>[14]</sup>, gas-phase reaction<sup>[15]</sup>, hydrothermal synthesis<sup>[16]</sup> etc. have received great attention for the growth of ZnO structures. However, most of these methods employed organic solvents or required rigorous reaction conditions and complicated procedures. In this direction, we have developed a simple and cost-effective method for the synthesis of metal oxide semiconductor structures and successfully adopted for the growth of ZnO structures. In this paper, we have described the methodology of drop method and systematic growth procedure for the development of ZnO structures. The physical properties of as-grown ZnO structures are discussed by analyzing them with advanced analytical techniques and are reported.

### EXPERIMENTAL PROCEDURE

#### Drop method

The schematic diagram of the experimental setup of drop method is given in supporting information (SI-1). A dropper with 1000  $\mu\text{l}$  capacity was used to drop the chemical solution. The solution was dropped onto the hot substrate kept over the heater under the dropper nozzle with a distance of 15 cm. The substrate temperature was automatically controlled using an inbuilt thermocouple. In order to obtain the structures on the substrates with uniform morphology, the substrate was slowly rotated with the help of magnet cum magnetic stirrer. It involves dropping the solution containing the solvable salts of the constituent elements of the desired compound onto a heated substrate. Upon reaching the surface of hot substrate, the dropped droplet undergoes chemical decomposition and forms a single crystallite or a cluster of crystallites of the product. The volatile byproducts and the excess solvents, if any present, escape in the form of vapors. The heated substrate provides the thermal energy necessary for the decomposition and subsequent recombination of the constituent species. This was followed by sintering and re-crystallization of the clusters of crystallites and gives highly crystalline structures. Further, a slow rotation of the substrate provides uniform deposition on the whole substrate. In the present study we have used this method for the growth of ZnO structures using the procedure described below.

#### Growth of ZnO structures

Initially, an aqueous solution was prepared using analytical grade zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , ZN) and hexamethylenetetramine ( $\text{C}_6\text{H}_{12}\text{N}_4$ , HMTA) chemicals using deionized water with an equimolar concentration of 5 mM. The deposition of ZnO structures was carried out on glass substrates at two typical deposition conditions: Initially, the depositions were carried out at different substrate temperatures of 100, 150, 180, 200 and 250  $^\circ\text{C}$  by keeping the quantity of solution as constant at 7-8 drops, whereas in second case the depositions were carried out at different quantities of solution of 3, 6, 9 and 12 drops by fixing the substrate temperature at an optimized value of 200  $^\circ\text{C}$ .

#### Characterization

The powder X-Ray diffraction (XRD) was used for the analysis of structure, crystallinity, and phase purity of the as-deposited ZnO structures. It was operated with 45 kV of voltage and 30 mA of current with  $\text{Cu K}_{\alpha 1}$  radiation with a wavelength of 0.1541 nm and the profile was recorded in the diffraction range of  $2\theta = 20\text{-}70^\circ$ . The surface morphology and chemical composition of the structures were examined using environmental scanning electron microscopy (ESEM) and energy dispersive analysis of X-ray (EDAX) embedded with ESEM by operating at 15 kV. In order to check the individual structure morphology and understand the growth dynamics, a high resolution field emission SEM (FESEM) has been adopted. The vibrational and optical properties of the as-deposited ZnO structures have been studied at room temperature by micro Raman spectrometer with 514.5 nm laser light and UV-Vis spectrophotometer.

### RESULTS AND DISCUSSION

The ZnO structures deposited on the glass substrates at different temperatures as well as with different quantities of solutions are adherent (tape test as well as sonication) to the substrate and appeared light-white in color. While increasing the substrate temperature, the depositions became more uniform and transparent. However, the growth of ZnO structures at higher as well as lower temperatures could not be succeeded due

to anomalous expansion of glass substrate and lack of thermal energy, respectively. For example, upon dropping the solution at higher temperature,  $\geq 250$  °C, the substrates were broken. Thus, the structures deposited in the substrate temperatures range of 150-200 °C and with different quantities of solution were analyzed and the observed properties are reported here.

### Structural properties

The XRD profiles of ZnO structures deposited at three typical substrate temperatures are shown in Figure 1. The structures deposited at the substrate temperature of 150 °C exhibited three clearly distinguishable peaks diffracted at  $2\theta = 32.17$ ,  $34.74$ , and  $36.58^\circ$ . The evaluated d-spacing values of these peaks exactly matches with the standard bulk ZnO data (JCPDS: 36-1451) and reveal that the diffracted peaks belong to (100), (002), and (101) planes of hexagonal ZnO crystal. As compared to other diffraction peaks, the (002) peak is dominant and implies that the as-deposited ZnO structures are preferentially oriented along the  $\langle 001 \rangle$  direction by having (100) and (101) orientations probably as adjacent planes. These results reveal that the as-deposited structures by newly developed drop method are merely consisting ZnO phase and uniquely oriented along the  $\langle 001 \rangle$  direction.

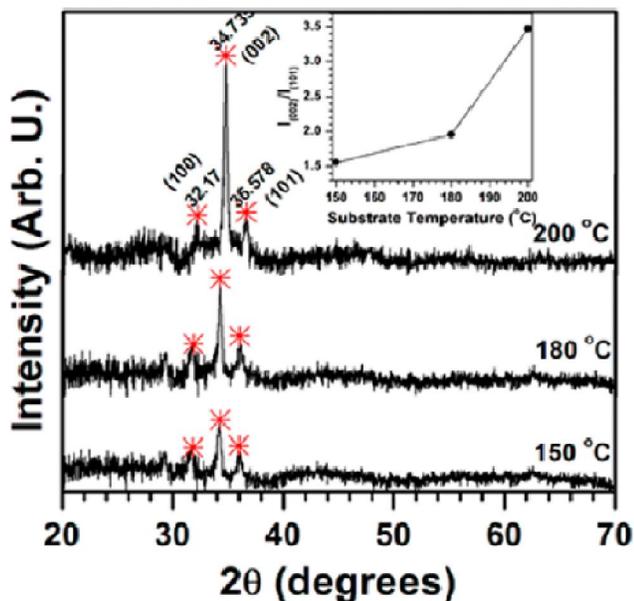


Figure 1 : XRD profiles of ZnO structures deposited at a substrate temperature of 150, 180, and 200 °C with a fixed quantity (7-8 drops) of solution.

Upon increasing the substrate temperature from 150

to 200 °C, the intensity of preferential (002) peak increased and it remained almost the same for other peaks. This indicates that while increasing the substrate temperature, the as-deposited ZnO structures are gradually growing along preferential direction. In order to understand the improvement in the crystalline quality of the as-deposited ZnO structures, the intensity ratio of I (001) and I (101) peaks has been calculated, and its variation with substrate temperature is shown as an inset of Figure 1. It shows that the crystalline quality of ZnO structures preferentially oriented along  $\langle 001 \rangle$  direction is increased with the increase of substrate temperature. Further, the average crystallite size (L) of the ZnO structures along with lattice strain i.e. mean lattice distortion (S) were calculated using the formulae:  $L = K \lambda / (B \cos \theta)$  and  $S = B / (4 \tan \theta)$ , where,  $\lambda$  is the wavelength of the X-ray's, B is the structural broadening, which is the difference in integral profile width between a standard and the unknown sample:  $B = B_{obs} - B_{std}$ . Here,  $B_{obs}$  is found from the analysis of XRD profile with the X'Pert High Scorer software supplied by Philips Analytical B. V., Almelo, the Netherlands. While increasing substrate temperature, the evaluated L value of the ZnO structures oriented along the  $\langle 001 \rangle$  direction is increased from 55 to 260 nm. The changes in the size of ZnO crystallites were clearly observed from the surface analysis of the structures by FESEM. On the other hand, the lattice strain in ZnO structures decreased from 0.37% to 0.16% with the increase of substrate temperature. Elongation of ZnO structures along preferential growth direction gradually relaxes the lattice strain created by glass substrate due its thermal expansion mismatch with ZnO, and as a result, the decrease of lattice strain in ZnO structures with the increase of substrate temperature has been taken place.

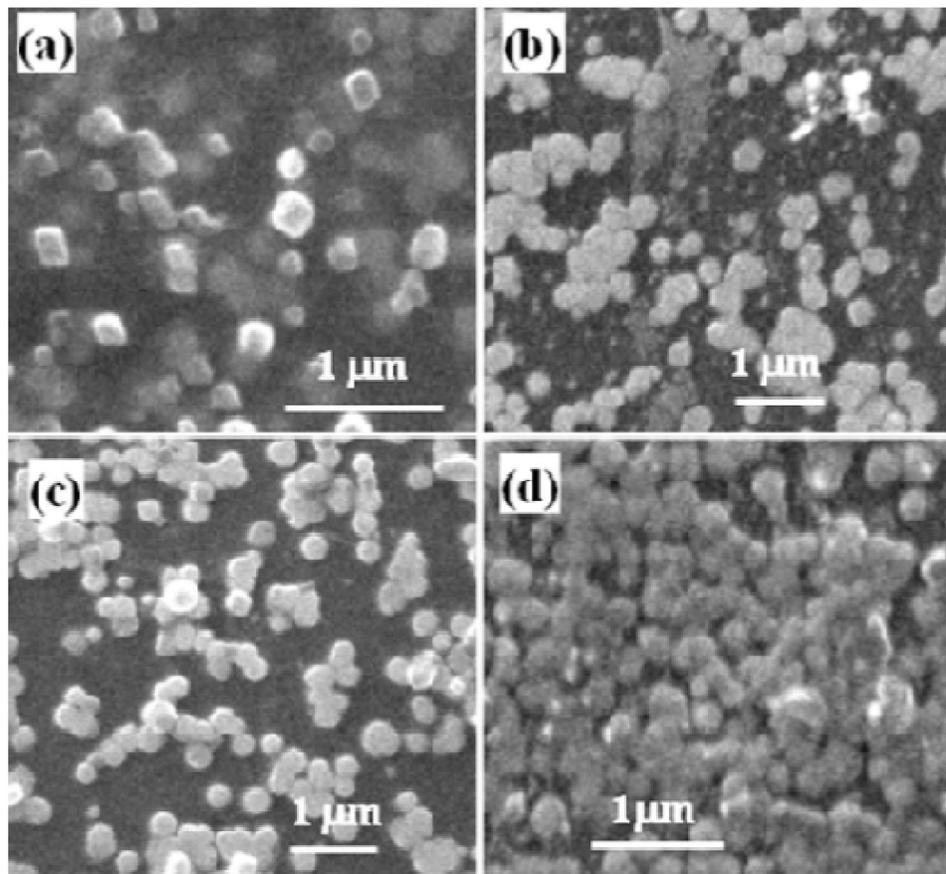
### Surface morphology

The surface morphology of ZnO structures deposited at different substrate temperatures is shown in Figure 2. These ESEM images indicate that all the as-deposited ZnO structures consist of micro-particles (MPs) like surface morphology. The MPs grown at low temperatures ( $\sim 150$  °C) are small in size and lesser in density (Figure 2a). Along with MPs, the structures consist of small amount of blurred material, which could be

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related to partially grown ZnO or non-reacted chemical species. While increasing the substrate temperature, initially the size and density of ZnO MPs are increased and at higher substrate temperatures ( $>200\text{ }^{\circ}\text{C}$ ), the MPs structures become uniform films like structures

(Figure 2d). However, the ZnO MPs grown at a substrate temperature of  $200\text{ }^{\circ}\text{C}$  have uniformly dispersed particles like surface morphology (Figure 2c). These MPs consist of spherical shape morphology and have nearly equal sizes.



**Figure 2 :** ESEM images of ZnO structures deposited at a substrate temperature of (a) 150, (b) 180, (c) 200, and (d) 250 °C with a fixed quantity (7-8 drops) of solution.

The surface morphology of ZnO structures deposited by dropping different quantities of the solution (3, 6, 9 and 12 drops) at a constant substrate temperature of  $200\text{ }^{\circ}\text{C}$  is given in SI-2. These analyses show that as compared to the structures deposited with different quantities of solution, the ZnO structures grown with 9 drops solution have uniformly dispersed MPs. At lower quantities of solution, the density of ZnO MPs is low and their particle sizes are also small, whereas the ZnO structures grown with higher quantities of solution consist of irregular shaped particles with large sizes, and most of them are aggregated. However, while increasing solution quantity the density of MPs is increased upto the quantity of 9 drops and above this, the aggregation of MPs taken place. These results, therefore,

emphasize that the ZnO structures developed by drop method at a substrate temperature of  $200\pm 10\text{ }^{\circ}\text{C}$  with a quantity of  $8\pm 2$  drops solution are consisting of uniformly grown MPs having an average particle size of 250 nm. Thus, the structures grown under these conditions have been used for further analyses, which are described below.

The ZnO structures grown at a substrate temperature of  $200\text{ }^{\circ}\text{C}$  with 8 drops solution were examined with FESEM and the obtained high magnification image is shown in Figure 3. It reveals that most of the grown ZnO MPs are spherical in shape and composed of thousands of smallest nanoparticles (NPs). The average crystallite size of these MPs is found to be 260 nm, which is nearly consistent with the data obtained in

XRD studies. These results clearly reveal that the as-deposited ZnO MPs are probably formed through the agglomeration of tiny NPs and contain nano gaps between them. Further, these NPs composed MPs are uniformly grown and vertically aligned.

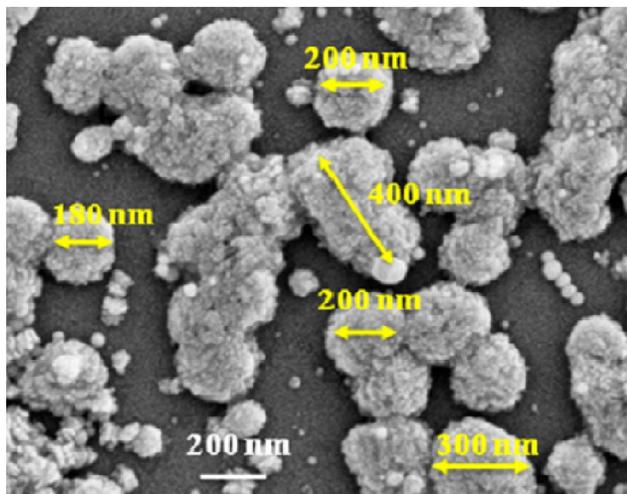


Figure 3 : High magnification FESEM images of ZnO MPs grown at a substrate temperature 200 °C with an optimized quantity (8 drops) of solution.

### Composition

The EDAX profile of ZnO MPs structures grown under optimized substrate temperature and quantity of solution is shown in Figure 4. It reveals that the as-deposited ZnO MP structures have oxygen rich chemical composition since the obtained atomic percent ratio of Zn and O is about 0.6. However, the structures do not show any element other than Zn and O, which reveal the chemical purity of as-deposited structures. Therefore, the as-deposited ZnO MPs structures have pure ZnO composition and however, they are oxygen rich in nature.

### Vibrational and optical properties

The vibrational properties of ZnO MPs structures deposited under optimized conditions were studied using micro Raman spectrometer using a 514.5 nm laser source. The Raman spectrum was recorded in the frequency range of 50-1500  $\text{cm}^{-1}$  with different powers of laser light varied from 3 to 15 mW by keeping the acquisition time as 10 s. The obtained Raman spectrum is shown in Figure 5 and all the peaks are indexed using standard data of bulk ZnO. Based on the group theory, the hexagonal wurtzite structured ZnO belongs to the

space group of  $C_{6v}^4$ , and contains two formula units per primitive cell.

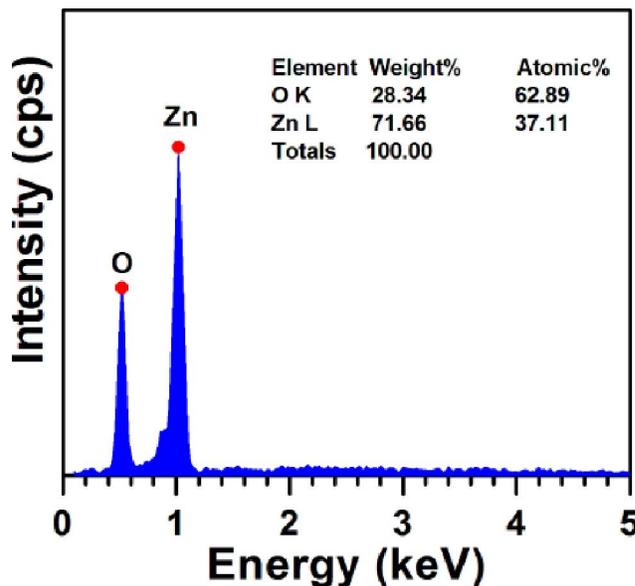


Figure 4 : EDAX profile of ZnO structures grown at a substrate temperature of 200 °C with 8 drops of solution.

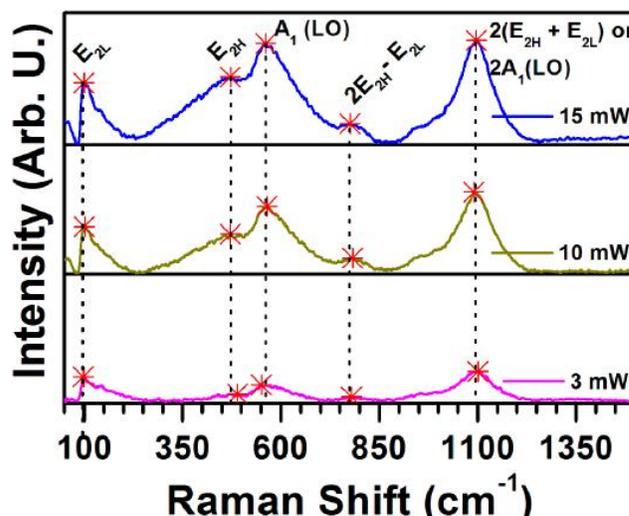


Figure 5: Raman spectra of ZnO MPs structures grown at a substrate temperature of 200 °C with 8 drops of solution, recorded at three typical powers of laser light.

Among its optical phonon (OP) modes, the non-polar modes ( $E_{2L}$  and  $E_{2H}$ ) and polar modes ( $A_1(LO)$ ,  $A_1(TO)$  and  $E_1(TO)$ ), where  $E_{2L}$  and  $E_{2H}$  are low and high frequency  $E_2$  modes, LO-longitudinal and TO-transverse optical phonon modes, are Raman active. The as-deposited NPs composed ZnO MPs on glass substrate exhibited three clearly distinguishable Raman peaks centered at  $105 \pm 2$ ,  $565 \pm 2$  and  $1095 \pm 2 \text{ cm}^{-1}$  along with two weak and broad peaks at  $460 \pm 2$  and  $785 \pm 2 \text{ cm}^{-1}$ . While increasing the power of laser light

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(from 3 to 15 mW), the change in the Raman peak positions is marginal except their sharpness. At higher powers, the obtained Raman spectrum consists of sharp and intense peaks than that of the spectrum recorded with lower powers. The peaks observed at below  $500\text{ cm}^{-1}$  belong to nonpolar modes, whereas at higher frequencies, the peaks belong to either polar modes or overtones of non-polar modes.

As-compared to the bulk ZnO ( $\text{ZnO}_b$ ) data<sup>[1]</sup>, the observed Raman peaks at lower frequencies ( $<550\text{ cm}^{-1}$ ) have slight blue shift (BS) in their positions (consists higher values), whereas the peaks observed at higher wave frequencies ( $>550\text{ cm}^{-1}$ ) have slight red shift (RS) (consists low values). These differences are attributed to surface and size effects of MPs and the presence of strain induced structural defects, respectively<sup>[17,18]</sup>. The first peak observed at  $105\text{ cm}^{-1}$  corresponds to the vibration mode of  $E_{2L}$  has a BS of about  $4\text{ cm}^{-1}$ . The second peak noticed at  $460\text{ cm}^{-1}$  has a BS of  $15\text{ cm}^{-1}$ , which corresponds to the vibration mode of  $E_{2H}$ . These two vibrational modes are associated to oxygen atoms and heavy zinc sublattice, respectively<sup>[1]</sup>. The observed BS in the nonpolar Raman peaks (i.e.  $E_{2L}$  and  $E_{2H}$ ) clearly emphasize that the as-deposited ZnO MPs on glass substrates consist considerable compressive stress<sup>[19,20]</sup>.

Among the other peaks at higher frequencies ( $>550\text{ cm}^{-1}$ ), the peak observed at  $565\text{ cm}^{-1}$  is dominant and has a RS of about  $14\text{ cm}^{-1}$ , which belongs to the polar  $A_1(\text{LO})$  or  $E_{2H}+E_{2L}$  phonon mode<sup>[18]</sup> and probably at-

tributed to the strain present within MPs (observed in XRD studies) or interstitial defects<sup>[21]</sup>. Alim et al. also observed similar peak at  $565\text{ cm}^{-1}$  from the Raman spectrum of chemically produced ZnO NPs exclusively with  $325\text{ nm}$  laser light<sup>[18]</sup>. These observations further reveal that the as-deposited ZnO MPs have strong polar lattice bonds. Moreover, the absence of polar  $E_1(\text{LO})$  peak, probably at around  $590\text{ cm}^{-1}$  and presence of  $A_1(\text{LO})$  or  $E_{2H}+E_{2L}$  mode implies that the ZnO MPs probably consist of the lattice vibrations parallel to their growth direction<sup>[1]</sup>.

The other peaks observed at higher frequencies, i.e.  $785$  and  $1095\text{ cm}^{-1}$  can be attributed to second-order multiple phonon scattering process (i.e. overtones). These multiple phonon peaks belong to  $2E_{2H}-E_{2L}$  and  $2A_1(\text{LO})$  or  $2(E_{2H}+E_{2L})$  with RS of about  $30$  and  $60\text{ cm}^{-1}$ , respectively. Sato-Berru et al.<sup>[22]</sup> also observed similar  $2A_1(\text{LO})$  peak from the Raman spectrum of ZnO NPs grown by chemical precipitation method. As compared to the bulk material, the observed RS in LO phonon frequencies strongly reveal the presence of point defects in the as-deposited ZnO MP structures<sup>[1]</sup>. However, the presence of  $A_1(\text{LO})$  and  $E_2$  vibrational modes as active and absence of other modes as forbidden emphasizes that most of the ZnO MPs deposited by the drop method are highly oriented along the (002) planes. This is in accordance with the results observed in XRD studies. Full width at half maximum (FWHM) of  $A_1(\text{LO})$  and  $2A_1(\text{LO})$  peaks is found to be  $55$  ( $6.82\text{ meV}$ ) and  $111$  ( $13.8\text{ meV}$ )  $\text{cm}^{-1}$ ,

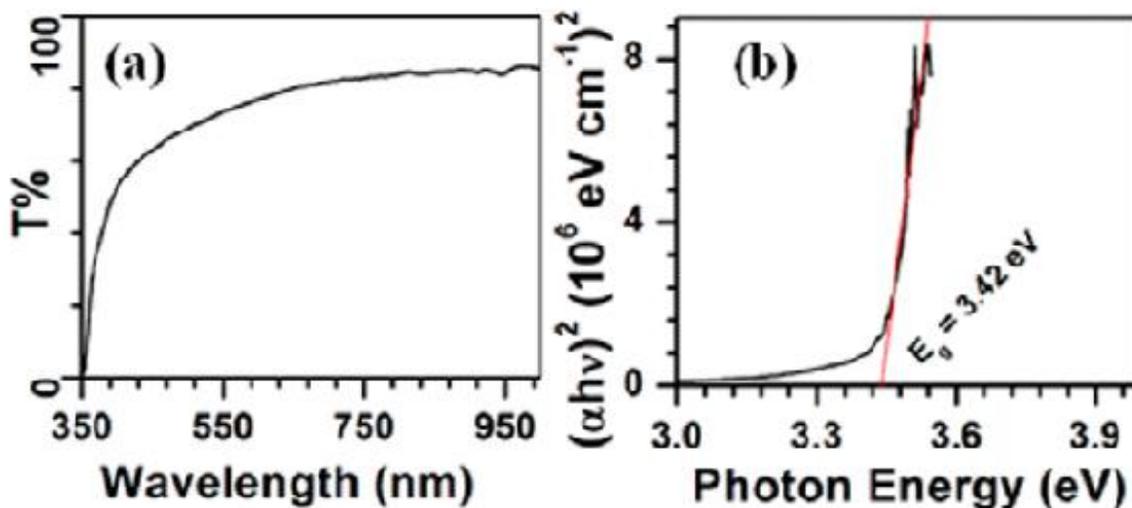


Figure 6: (a) Transmittance (T%) vs. wavelength and (b)  $(\alpha h\nu)^2$  vs. photon energy plots of ZnO structures grown at a substrate temperature of  $200\text{ }^\circ\text{C}$  with 8 drops of solution.

respectively (see SI-3). The intensity ratio of  $A_1$  (LO) and  $2A_1$  (LO) peaks (i.e.  $I_{A_1}/I_{2A_1}$ ) is about 1.78, which is lower than that of its bulk (2.01)<sup>[23,24]</sup>.

The light transmittance of as-deposited ZnO MPs as a function of incident photon wavelength is shown in Figure 6a. At higher wavelengths, the structures exhibited a high transmittance of 92%, and while decreasing wavelength, it gradually decreased. However, at certain wavelength (~375 nm), the decrease in transmittance is sharp, which is treated as fundamental absorption edge (FAE) of the ZnO MPs. This sharp fall in transmittance clearly indicates that the carrier transition between the top of the valance band and bottom of the conduction band is direct, which is also confirmed by plotting the absorbance vs. incident photon energy (see SI-4). Therefore, the direct energy band gap of structures were evaluated from  $(\alpha h\nu)^2$  vs. the photon energy plot by extrapolating its linear part to  $(\alpha h\nu)^2 = 0$ . The  $(\alpha h\nu)^2$  vs. the photon energy plot of the present structures is shown in Figure 6b, and its optical band gap ( $E_g$ ) is found to be ~3.42 eV. This value is slightly higher than that of its bulk data (3.3 eV)<sup>[25]</sup> and could be attributed to two factors: i) presence of smallest NPs (see Figure 3) and ii) existence of compressive stress.

## CONCLUSIONS

A new and novel synthetic drop method, which is a simple and cost-effective, has been designed and adopted for the synthesis of ZnO structures. The ZnO micro-crystalline particles like structures have been synthesized and examined their physical properties using advanced analytical techniques. The observed results from these investigations are summarized below.

The as-deposited structures have pure ZnO phase, which are grown along  $\langle 001 \rangle$  direction and consist slightly oxygen rich chemical composition. The crystalline quality of the structures is increased with the increase of substrate temperature. The ZnO structures grown at a substrate temperature of 200 °C have uniformly dispersed MPs like surface morphology as compared to the structures grown at other temperatures. Further, most of these ZnO MPs are spherical in shape and composed of thousand of smallest NPs. Raman analyses show that the as-deposited ZnO MPs on glass substrates have a considerable compressive stress and

consists of strong polar lattice bonds. These structures exhibited a high transmittance of 92% and have a direct optical band gap of about ~3.42 eV. These results, therefore, emphasize that the ZnO MPs like structures developed by drop method at a substrate temperature of 200 °C with an average quantity of 8 drops solution are consisting of uniformly grown NPs composed MPs.

These interesting outcomes motivated us to adopt this cost-effective methodology for the development of uniformly grown ZnO NP films on conductive substrates, which is in progress. These results will also motivate the scientists to adopt this method for the development of various MO structures and thereby low-cost devices.

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