

ZnO nanorods and nanopolypods synthesized using microwave assisted wet chemical and thermal evaporation method

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Zinc oxide (ZnO) nanostructures have been grown on glass and silicon substrate by microwave assisted wet-chemical (MAWC) method and thermal evaporation using TGA. The effect of different preparative parameters on the growth of ZnO nanostructures has been studied. The synthesized nanostructures are characterized using UV-Vis spectroscopy, particle size analyzer, XRD, SEM, and EDX. ZnO nanostructures, i.e. nanorods (NRs) obtained using evaporation method are of 200-250 nm in diameter and nanopolypods (NPPs) with pod diameter in the range 150-200 nm and pod length in the range 700-800 nm, whereas from MAWC method, NRs produced are 100-150 nm in diameter and NPPs with pod diameter in the range 150-200 nm and 1.5-2 μm of pod length. XRD studies show that the prepared samples are nanocrystalline in nature with hexagonal wurtzite phase and highly oriented along (002) direction.

Keywords: Zinc oxide, Thermal evaporation, Microwave method, Nanorods, Nanopolypods

1 Introduction

The transition metal oxides have attracted much attention owing to their unique chemical, optical and electronic properties. Among the transition metal oxides, zinc oxide (ZnO) has been recognized as a promising semiconductor material because of its wide bandgap of 3.37 eV and a large exciton binding energy of 60 meV. Besides, it exhibits interesting morphologies and structures such as nanorods¹, nanotubes², nanorings³, nanowires⁴, pencil-like⁵, whisker⁶, tetrapods⁷, nano-needles and nano-flowers⁸. ZnO can be easily formed as nanorod arrays, usable in hybrid devices owing to its high electron transportation. It has attracted attention for wide range of applications including photovoltaic cell⁹. Furthermore, the use of thin film technology has opened the field to the fabrication of high quality ZnO for applications such as UV light emitters^{10,11}, gas sensing elements¹², and even catalysts¹³. With reduction in size, novel electrical, mechanical, chemical and optical properties can be tailored in nanostructured ZnO films. A variety of methods including pulsed laser deposition¹⁴, spray pyrolysis¹⁵, electrodeposition¹⁶ and chemical vapour deposition¹⁷ have been applied to deposit nano-structured ZnO thin films.

We have adopted two unique different methods, which are rarely explored, for the deposition of the ZnO nanostructures viz. microwave assisted wet chemical (MAWC) method and thermogravimetric

analyzer (TGA). MAWC method is an attractive approach for the growth of ZnO nanostructures because of its simplicity, low temperature process, and most importantly suitability for large-scale production on arbitrary substrate. In addition to this the use of microwave radiations enhances the growth rate since it supplies the energy directly to the precursor molecules. Hence the efficiency of this method is high. The need of high vacuum in case of physical methods can be neglected by using inert atmosphere like flow of Ar gas. This is possible with the TGA method. Since the working chamber of TGA is small and the inert atmosphere condition is effective, the proper mixture of the oxygen and Ar can be used to deposit the ZnO nanostructures.

In the present paper, the effect of capping agent on the particle size, operation temperature, reaction atmosphere and microwave radiations in the formation of different ZnO nanostructures has been studied.

2 Experimental Details

2.1 Substrate cleaning

All substrates were thoroughly cleaned by following sequence: Cleaned by labolene detergent and rinsed with double distilled (DD) water. Then boiled with dilute chromic acid for 15 min and thoroughly rinsed with DD water. After that, ultrasonicated for 10 min in acetone, then in methanol and finally all substrates were dried in an oven.

2.2 Microwave assisted wet chemical (MAWC) method

The ZnO NRs and NPPs on glass substrates were grown using MAWC method in place of conventional heating¹⁸. The growth of ZnO NRs was carried out in following two steps.

2.2.1 Synthesis of ZnO seed layer

Two samples of ZnO sol were prepared, one without capping agent and another with triethanolamine (TEA) as capping agent. In first case (without capping agent), solution of 0.03 M sodium hydroxide (NaOH), (Merck) in methanol (CH₃OH), (Merck) was added slowly to a continuously stirred solution of 0.01M zinc acetate dihydrate (CH₃COO)₂Zn.2H₂O (Merck) in methanol at 60°C. The formed sol is designated as sample S1 hereafter. In second case, 0.24 ml TEA (Merck) was added after a gap of 5 min to a continuously stirred solution of 0.03 M sodium hydroxide and 0.01 M zinc acetate dihydrate (CH₃COO)₂Zn.2H₂O in methanol at 60°C. The formed sol is designated as sample S2 hereafter. For the growth of ZnO nanoparticles, the operation temperature of solution was uniformly maintained at 60°C for 1 h, using 2.54 GHz microwave radiations. The 5 min delay in addition of TEA results into the formation of ZnO and (ZnOH)⁺ cations from the chemical reaction of zinc acetate dihydrate and sodium hydroxide as well as prevented the agglomeration of colloidal particles.

The prepared sol S1 was spin-cast four times on glass substrate at 3000 RPM for 20 s for each time to form uniform ZnO seed layer. Between coatings, the substrates were annealed in open air at 150°-160°C for 15 min to ensure particle adhesion onto the substrate surface.

2.2.2 Growth of ZnO NRs and NPPs

Growth of NRs and NPPs was carried out by suspending the substrates with crystal seed layer upside-down in an aqueous solution containing 0.025 M zinc nitrate hexa-hydrate, Zn(NO₃)₂.6H₂O, (Merck) and 2.58 ml of diethylenetriamine, C₄H₁₃N₃, (Burgoyne Mk) in DD water at 90°C. The required operation temperature was maintained using 2.54 GHz microwave radiations. After 5 h the substrates were removed, rinsed thoroughly with DD water and dried at room temperature. The prepared ZnO film on glass substrate without capping agent is defined as 'F1' and another with capping agent defined as 'F2'.

2.3 Thermal evaporation method

The ZnO NRs and NPPs on silicon substrates were grown via thermal evaporation method using TGA equipment (DuPont 951).

Seed layer is grown by vacuum evaporation (Edwards Coating System, model E 306A) on silicon substrate. For making ZnO seed layer, at room temperature, silicon (100) substrates were placed on the substrate holder. Tungsten boat connected in the resistive circuit of vacuum chamber was filled with commercially available ZnO powder (Merck) as source material. The vacuum was created and maintained at 4×10^{-4} bar. Once the vacuum chamber was stabilized at the desired pressure, a resistive heating of the boat was carried out by passing ~ 20 A current, to increase source material temperature to its vapour point. Upon evaporation the ZnO deposited on the substrate resulting in the formation of uniform ZnO seed layer. These seed layers are used to grow the ZnO nanostructures by thermal evaporation (TGA).

For the growth of ZnO NRs fine zinc metallic powder (Merck) was loaded onto the TGA tungsten boat and Si (100) substrate of 15 mm × 5 mm in size with ZnO seed layer were placed downstream of the quartz tube center. An ultra high pure (UHP) argon (Ar) gas flow of 200 sccm (standard cubic centimeter mass) was supplied as the carrier gas into the reaction chamber. The temperature at the tube center was increased from room temperature to reaction temperature (~750°C) at a rate of 25°C/min and maintained for 90 min. During that period, zinc powder was heated, vaporized, then transported along the Ar gas flow and finally deposited on to the downstream substrate to form the final products¹⁹. The as prepared sample was defined as F3.

While for the growth of ZnO NPPs the tungsten boat of TGA was loaded with fine zinc metallic powder [Merck, ≥ 98%] and Si (100) substrates of 5 mm × 15 mm in size with ZnO seed layer was placed downstream of quartz tube. The temperature of the furnace was raised from room temperature to 610°C at a rate of 25°C/min with Ar gas flow of 100 sccm. At operational temperature, the Ar flow was replaced by a flux of Ar and oxygen in ratio of 10:1 to allow formation ZnO nanostructure. After attaining operation temperature of 610°C, isothermal conditions were maintained for 30 min (Ref. 20). The asprepared sample was defined as F4.

The prepared samples S1-S2 and F1-F4 were characterized at different stages of synthesis and growth. The UV-Vis spectroscopy of all the samples

was done in the range 300-700 nm with the help of photo-spectrometer (Nanodrop-1000 for S1-S2 and Ocean Optics HPX-2000 for F1-F4). Particle size distribution of the samples S1 and S2 was measured using particle sizing system (Nicomp-380ZLS). The structural and morphological study of the samples were carried out using, respectively, Xpert PRO Panalytical Powder X-ray diffractometer (XRD) in the scanning range of 0-80° using Cu K α radiations with wavelength 1.5045 Å and scanning electron microscope (SEM) (JOEL, JSM-6360A and Philips XL-30).

3 Results and Discussion

3.1 Optical analysis

Figure 1 shows UV-visible absorption spectra of samples S1 and S2. It is clear from the figure that the absorbance peak for sample S1 is at 329 nm and for S2 is at 302 nm. The blue shift in the optical absorption can be attributed to the use of TEA as a capping agent. Similar result has been reported by Singh *et al.*²¹. To confirm the blue shift in the optical absorption particle size distribution was recorded on the particle size analyzer and is shown in Fig. 2. Particle size distribution for the sample S1 was observed to be around 942 nm whereas for S2 190 nm as can be seen from Fig. 2. The agglomeration of particles was noticed in case of S1 as evident from Fig. 2a. Thus the blue shift is supported by the size

distribution analysis. Reduction of the particle size from 942 nm to 190 nm was observed in case of S2 because of TEA which prevents the agglomeration.

The UV-Vis optical absorption spectra for sample F1 and F2 are shown in the Fig. 3. The optical absorption edge of both samples was observed at around 373 nm. No significant shift in the optical absorption was observed. Figure 4 shows optical absorption spectra for samples F3 and F4 with absorption edge at around 374 nm for both the samples. These values are found to be less than 380 nm which corresponds to bulk ZnO, indicating nanostructured nature of the grown ZnO thin films.

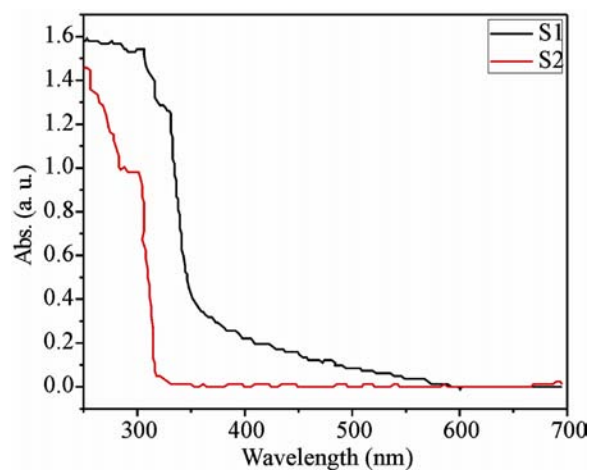


Fig. 1 — Room temperature UV-Vis absorption spectra of the samples S1 and S2

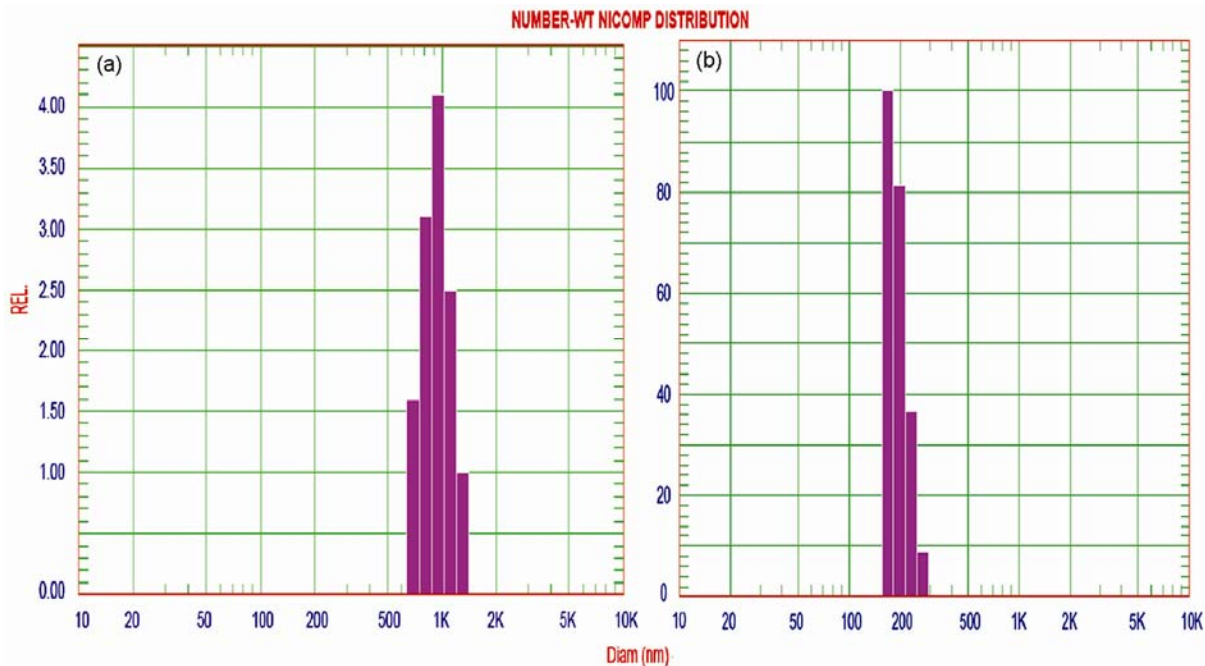


Fig. 2 — Particle size distribution of (a) sample S1, (b) sample S2

3.2 Structural analysis

X-ray diffraction patterns of the samples F1 and F2 are shown in the Fig. 5. Both the samples F1 and F2 are nanocrystalline in nature with hexagonal wurtzite phase²², as can be seen in comparison with the JCPDS card No. 01-075-1526. Both the films are highly oriented along (002) direction as can be seen from the figure.

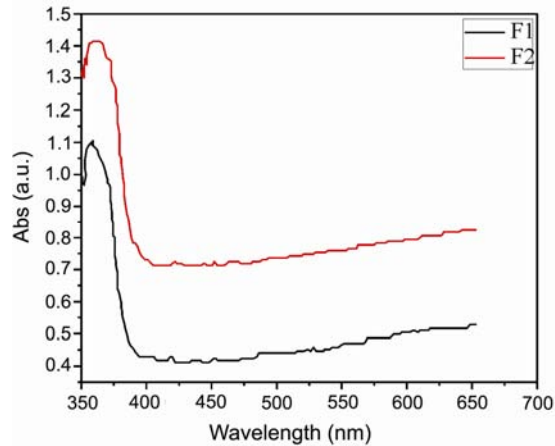


Fig. 3 — Room temperature optical absorption spectra of samples F1 and F2

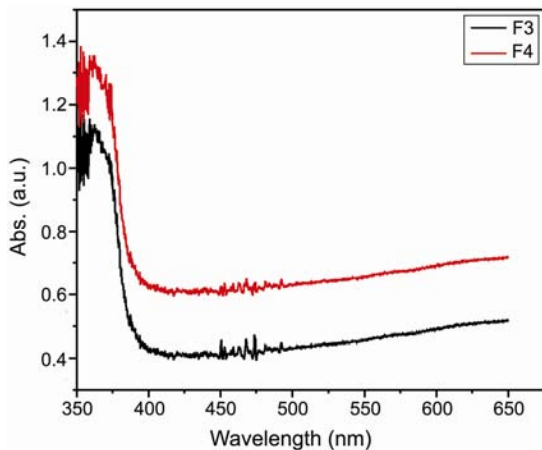


Fig. 4 — Room temperature UV-Vis optical absorption spectra of samples F3 and F4

The crystallite size (T) was calculated for both the samples by Scherrer's formula, using information on broadening of diffraction peak (β), X-ray wavelength (λ) and Incident X ray angle with crystal plane (θ_B), i.e.

$$T = \frac{0.9\lambda}{\beta \cos \theta_B} \quad \dots(1)$$

The average crystallite size for both samples are given in the Table 1.

3.3 Morphological studies

Figures 6 and. 7 show the SEM micrographs of the samples F1 and F2, respectively. From the Figs 6a

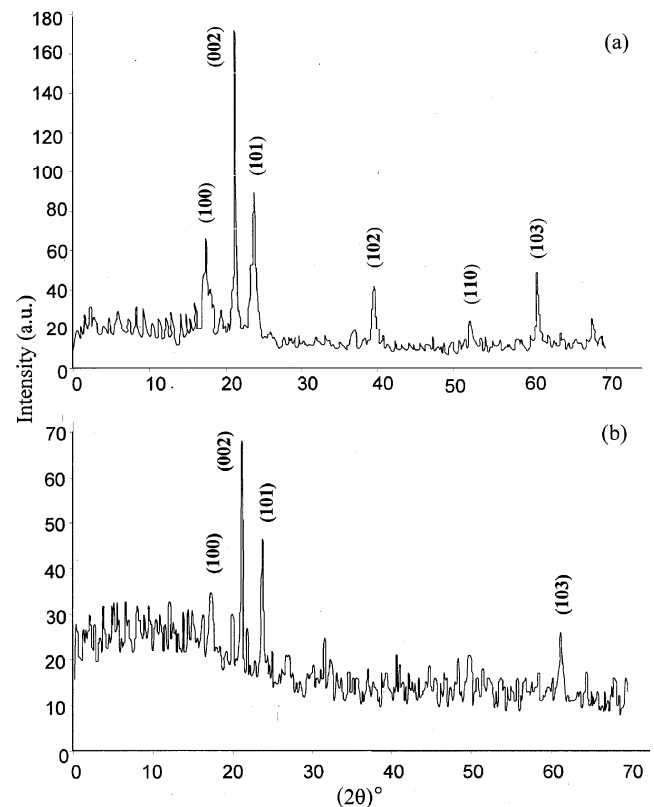


Fig. 5 — XRD pattern of (a) sample F1, and (b) sample F2

Table 1 — Various parameters of the grown ZnO nanostructures

Sample name	Absorption edge (nm)	Particle size (nm)	Diameter (nm)	Length (μm)	Morphology	Crystallite size (T)(nm)
S1	329	942	NA	NA	NA	NA
S2	302	190	NA	NA	NA	NA
F1	373	NA	100-150	NA	Nanorods	35-105
F2	370	NA	100-150	NA	Nanorods	35-141
			150-200	1.5-2	Nanopoly pods	
F3	374	NA	200-250	NA	Nanoparticles	NA
F4	374	NA	150-200	0.7-0.8	Nanopoly pods	NA

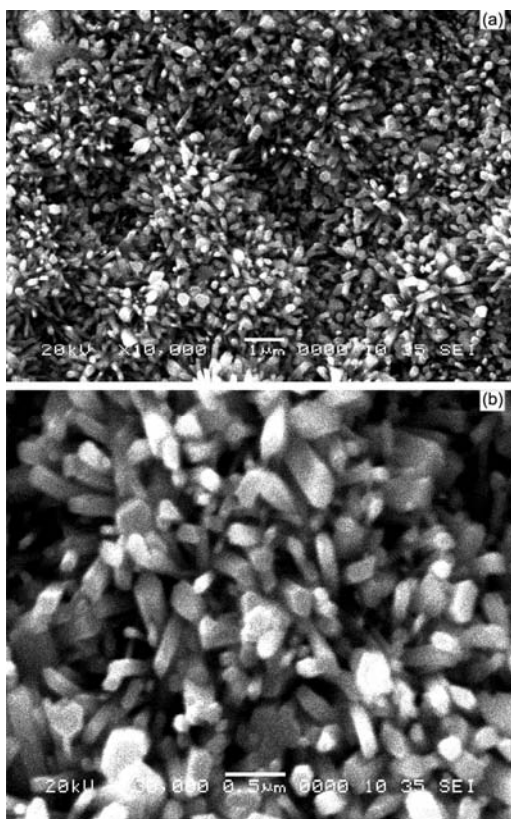


Fig. 6 — SEM images of sample F1 at different magnification; (a) 10,000x and (b) 30,000x

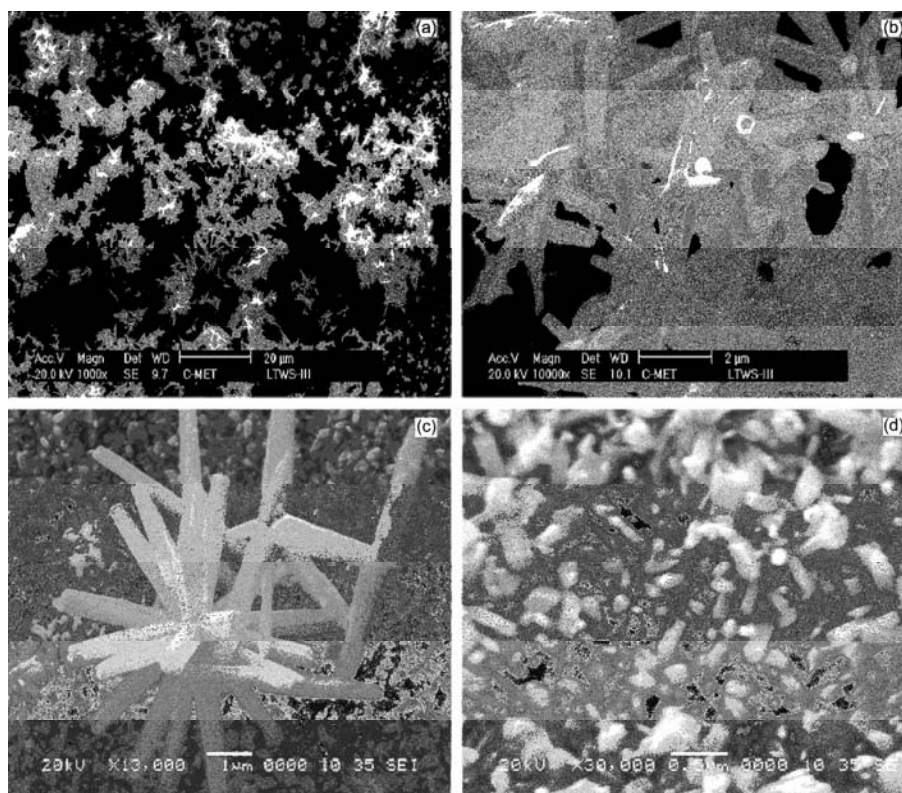


Fig. 7 — SEM images of the sample F2 at different magnification; (a) 1000x, (b) 10,000x, (c) 13,000x and (d) 30,000x

and 6b one can see the growth of uniform and densely packed array of ZnO NRs with diameter 100-150 nm. Figures 7a to 7c show the growth (evolution) of ZnO NPPs over uniform and densely packed array of NRs (Fig. 7d). The NPPs are of pod diameter about 150-200 nm and pod length 1.5-2 μm . The formation of NPPs in sample F2 may be attributed to the addition of TEA as capping agent.

Figures 8 and 9 show SEM images of samples F3 and F4, respectively with different magnification (a, b). Figure 8 shows formation of ZnO nanoparticles with diameter 200-250 nm and Fig. 9 shows formation of ZnO NPPs with diameter 150-200 nm and pod length 700-800 nm. The formation of NPPs is due to high zinc vapour pressure and oxygen concentration during thermal evaporation process²⁰.

3.4 Elemental analysis

Figure 10 shows typical EDAX spectrum of the sample F2. It shows that zinc and oxygen elements in NRs are present almost in stoichiometric ratio (51.8: 48.85). The silicon and calcium peaks in the EDAX spectrum arose from glass substrate. Figure 11 shows the typical EDAX spectrum of sample F4. It is clear from the figure that zinc and oxygen are in stoichiometric ratio. The silicon from the substrate

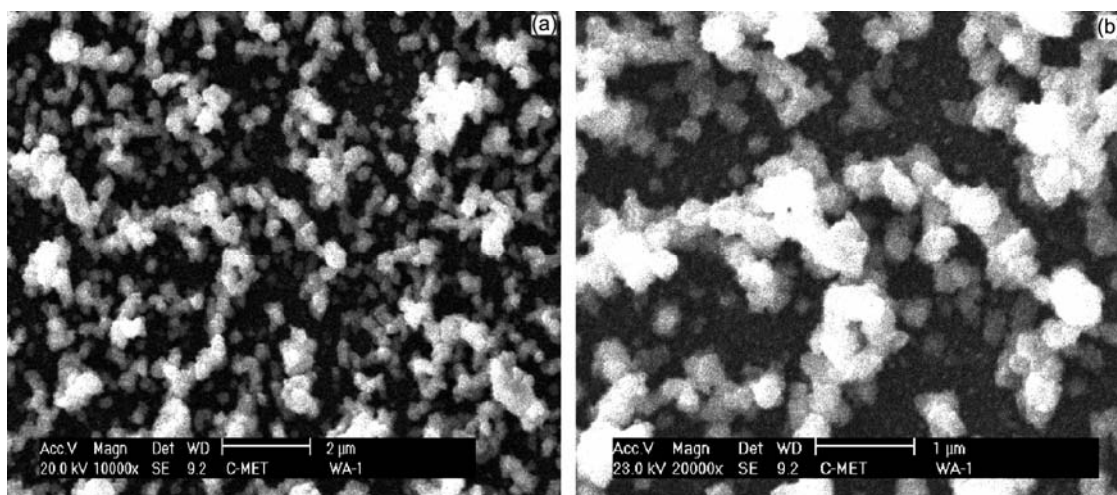


Fig. 8 — SEM images of sample F3 at different magnification; (a) 10,000x and (b) 20,000x

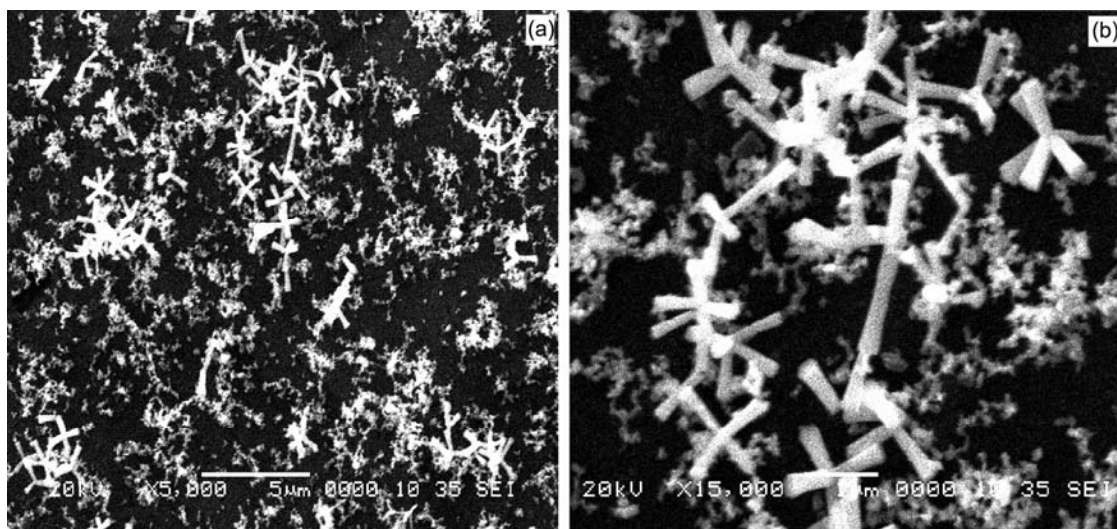


Fig. 9 — SEM images of sample F4 at different magnification; (a) 5000x, and (b) 15,000x

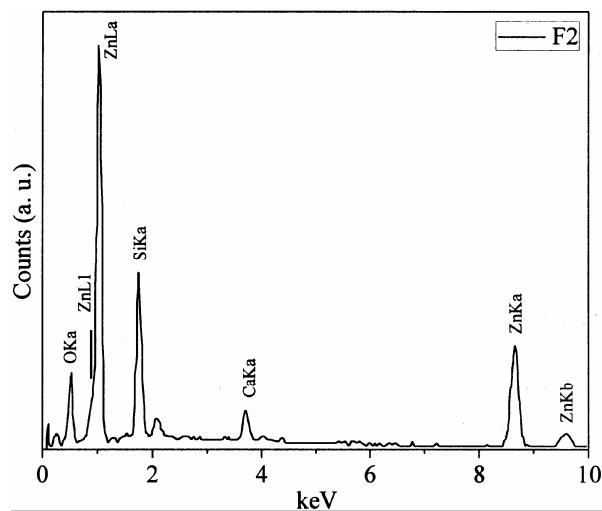


Fig. 10 — EDAX spectrum of sample F2

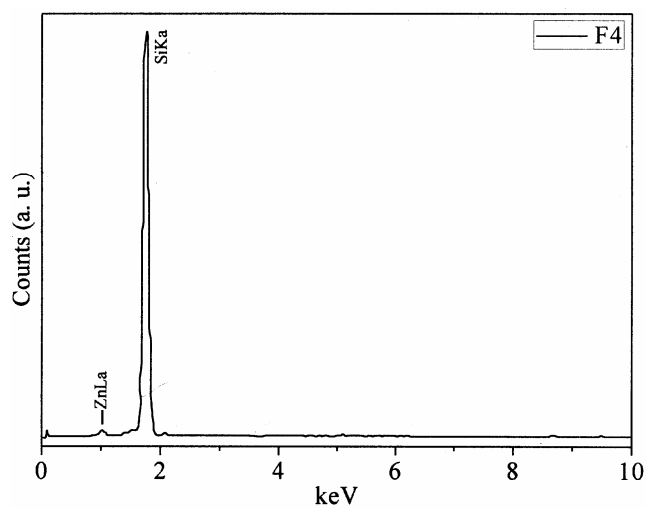


Fig. 11 — EDAX spectrum of sample F4

dominated the ZnO film composition as can be seen from Fig. 11.

All the results of ZnO nanostructures produced by using both physical and chemical methods are presented in the Table 1.

4 Conclusions

In this paper both physical and chemical methods were explored successfully for the growth of different ZnO nanostructures. Using physical method, growth of ZnO nanorods and nanopolypods on silicon (100) substrates were achieved by using TGA equipment. While with microwave assisted wet chemical method, at low temperature, uniform growth of ZnO nanorods with diameter 100-150 nm were achieved and use of triethanolamine as capping agent resulted in the additional growth of ZnO nanopolypods with pod diameter about 150-2000 nm and pod length about 1.5-2 μm on glass substrates. Use of capping agent in chemical synthesis showed nearly five time reduction of particle size and hence blue shift in UV-Vis absorption edge. The EDS of all the samples show presence of zinc and oxygen as main elements in NPPs and NRs. XRD analysis showed the nanocrystalline nature with hexagonal wurtzite phase of the samples and planes highly oriented along (002) direction.

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