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Journal of Crystal Growth 306 (2007) 303-310

www.elsevier.com/locate/jcrysgro

Growth and characterization of ZnO nanocrystalline thin films and nanopowder via low-cost ultrasonic spray pyrolysis

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Received 10 February 2007; received in revised form 3 May 2007; accepted 8 May 2007 Communicated by D.P. Norton Available online 18 May 2007

Abstract

In this paper, we report the preparation and characterization of both the ZnO nanocrystalline thin films and nanopowder by ultrasonic spray pyrolysis technique. ZnO films were grown on polished Si(100) and amorphous glass substrates at different deposition temperature range varying from 200 to 500 °C. Both orientation and the size of the crystallites were found to depend on the substrate and substrate temperature. XRD patterns of the films deposited on glass show strong *c*-axis oriented crystal structure with preferred (002) orientation, while those deposited on Si show predominant (100) orientation. Field emission scanning electron microscopy (FESEM) further confirms the *a*- and *b*-axis orientation in ZnO films on Si substrate. The morphology and crystallite size of the ZnO nanopowder characterized by FESEM and TEM revealed that the powder consisted of the mixture of nanoparticles with particle size of 50–100 nm. The XRD results indicated that the synthesized ZnO powder had the pure wurtzite structure with lattice parameters *a* and *c* of 3.244 and 5.297 nm, respectively. High-temperature XRD studies of ZnO nanopowder showed that the crystallite size increased with increasing temperature with a systematic shift in peak positions towards lower 2θ values due to change in lattice parameters. Temperature dependence of the lattice constants shows linear increase in their values. Diffraction patterns of ZnO nanopowder obtained from TEM were also in agreement with the XRD results. The synthesized powder exhibited the estimated direct band gap (E_g) of 3.43 eV. \mathbb{C} 2007 Elsevier B.V. All rights reserved.

PACS: 61.72.Vv; 81.07.-b; 81.05.Dz

Keywords: A1. Characterization; A1. Crystal morphology; B1. Nanomaterials; B1. Zinc compounds

1. Introduction

Zinc oxide (ZnO) is a wide band gap semiconductor and has been extensively investigated due to its potential utility in various applications such as UV photonics, transparent high-power electronics solar cells, varistors, surface acoustic wave devices, piezoelectric transducers and gas sensing devices [1,2]. The notable properties of ZnO are its direct band gap of $3.37 \,\text{eV}$ at room temperature and high transparency in the $0.4-2\,\mu\text{m}$ optical wavelength range. ZnO also has high exciton bonding energy of 60 meV, which is much higher than the values of other widely used wide band gap materials, such as ZnSe (20 meV) and GaN (21 meV). This large exciton binding energy provides excitonic emission more efficiently even at high temperature. Moreover, ZnO films can be deposited at lower temperature than ZnSe and GaN. ZnO also has high thermal and chemical stability. Due to the various attractive properties and potential applications of ZnO, there have been much attention paid on the fabrication of ZnO films and nanopowder in recent years.

A variety of techniques have been used to fabricate ZnO thin films such as pulsed laser deposition (PLD) [3], sol-gel [4], DC magnetron sputtering [5], laser molecular beam epitaxy (LMBE) [6] and spray pyrolysis [7]. Compared to other vacuum deposition techniques spray pyrolysis still offers the possibility of preparing small as well as large area

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^{0022-0248/} $\$ - see front matter \odot 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jcrysgro.2007.05.023

coating of ZnO thin films and nanopowder at low cost for various technological applications. Unlike physical vapour deposition methods, spray pyrolysis does not require highquality target and nor does it require vacuum at any stage, which is a great advantage if the technique is to be scaled up for the industrial applications. Moreover, in spray pyrolysis technique, the deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameters, thus eliminating the major drawbacks of chemical methods such as sol–gel, which produces films of limited thickness.

Earlier we have reported the successful fabrication of superconducting Josephson junctions devices [8] and HTSC-coated conductors [9] prepared via ultrasonic spray pyrolysis technique. In the present study, we have used the same simple and low cost technique to grow ZnO nanocrystalline thin films and nanopowder. The effect of substrate and substrate temperature on the growth of ZnO thin films has been investigated. The films deposited on glass are found to be *c*-axis oriented, while the films on silicon show preferred a- and b-axis orientation. The majority of work reported about ZnO films is with c-axis orientation, and only rarely with a- and b-axes orientation [20]. However, our experiments suggest that it is also possible to grow ZnO films with a- and b-axes orientation via low-cost spray pyrolysis technique, which have applications in thin film Si solar cells. Further, we have also tried to prepare ZnO nanopowder with particle size in the range 50–100 nm via the simple route of spray pyrolysis and tried to correlate the structural and optical properties of nanopowder with ZnO nanocrystalline thin films.

2. Experimental procedure

ZnO thin films were prepared from aqueous solution of zinc nitrate $(Zn(NO_3)_2 \cdot 6H_2O)$ dissolved in distilled water to a concentration of 0.1 M. The substrates were first ultrasonically degreased with acetone, ethanol and deionized water. Various parameters such as nozzle to substrate distance, deposition rate and flow rate of air (carrier gas), deposition temperature and concentration were optimized to get good quality films. Specially designed digital substrate heater with temperature controller from excel instruments was used to heat the substrate. The rate of deposition was controlled by the carrier gas flow rate, substrate temperature as well as precursor concentration.

Ultrasonic spray pyrolysis is also an effective technique for preparation of homogeneous particle compositions in single step. The distribution of particle size produced by ultrasonic spray pyrolysis is narrow and controllable from micrometer to nanometer range, the purity of product is high and composition of the powder is easy to control. In the present study, ZnO powder was prepared using the modified ultrasonic spray process. The set-up was composed of three zones. The first was the ultrasonic spray zone, which consists of the mist generating system of liquid source with ultrasonic atomizer and misted dropletcarrying system with air carrier gas. The second was the heating zone in which the misted droplet was pyrolyzed in a preheated reactor. The last and the third zones were for the trapping of produced powder. To prepare ZnO nanopowder zinc nitrate (Zn(NO₃)₂.6H₂O) (purity >99%, Sigma-Aldrich, USA) was used as precursor. The solution was prepared from dissolution of metal nitrate hydrate in pure water to a concentration of 0.1 M. The aqueous zinc nitrate solution was delivered into the reactor by liquid atomization. The atomized droplets containing the precursor were passed through a reactor and nanopowder was collected on a special geometry. The deposition time for nanopowder was 1 h.

The orientation and crystallinity of the powder and films were studied using Bruker AXS C-8 advanced diffractrometer with high-temperature attachment in θ -2 θ geometry. The high-temperature stage allows samples to be measured at tightly controlled temperatures from room temperature to 1600 °C in open air, under vacuum, or in a purge gas. The film thickness was about 2.3 µm as measured from surface profilometer and deposition time for the films was 15 min. The surface topography and microstructure were studied using scanning probe microscope (NT-MDT: NTEGRA Model) and field emission scanning electron microscopy (FESEM). The micrographs and diffraction pattern of nanopowder was studied using transmission electron microscope (Philips EM400). Perkin-Elmer Lambda 25 UV-vis spectrometer was used to study the optical properties of both films and nanopowder.

3. Results and discussions

3.1. ZnO nanocrystalline thin films

ZnO thin films were deposited using ultrasonic spray pyrolysis on Si(100) and amorphous glass (component: CaO:NaO:6SiO₂) substrates at various deposition temperature in the range varying from 200 to 500 °C. The chemical solution was atomized into the stream of the fine droplets via ultrasonic nebulizer operated to an atomizing frequency of 1.7 MHz. Nitrates precursor solution was poured into the vessel from inlet side. The aerosol was generated from the vibration of the transducer. The nebulized spray, which goes up in the column, was deposited on a hot substrate. The average diameter of the misted droplet can be approximately calculated from an expression given by Lang [15]:

$$D_{\rm d} = 0.34 \left(\frac{8\pi\gamma}{\rho f^2}\right)^{1/3},$$

where D_d is the droplet diameter, γ is the solution surface tension (72.9 × 10⁻³ N/m), ρ is the solution density (1030.3 kg/m³), and *f* is the applied ultrasonic frequency (1.7 MHz). The diameter of the misted droplets was calculated using the above parameters and was found to be 2.8 µm.



Fig. 1. XRD pattern of the ZnO thin films deposited on: (a) glass and (b) Si substrate at various deposition temperatures.

Fig. 1 shows the XRD patterns of ZnO films grown by ultrasonic spray pyrolysis on glass and Si substrate at various deposition temperatures. The films deposited on glass at the substrate temperature (T_s) of 200 °C were polycrystalline with no preferred orientation. XRD pattern of the films deposited below $T_s = 300$ °C show (100), (002) and (101) reflections. The crystallinity of the films was found to increase with increase in deposition temperature. The films deposited at $T_s = 300$ °C or above 300 °C were found to be oriented along the *c*-axis. XRD pattern revealed that the film deposited at $T_s = 400$ °C was highly oriented along the *c*-axis and exhibits preferred (002) orientation that is, the *c*-axis of the crystal lattice is normal to the plane of the substrate. ZnO usually grows along the (002) direction due to the low surface free energy of (002) plane [16]. The absence of (002) preferential orientation at low temperature reveals the suppressing effect of low temperature on the (002) direction growth, which is similar to that reported previously [17]. This may be due to the fact that there is no enough energy at low temperatures for atoms to move to low-energy sites, which induces strain in the films. As the temperature increases to $350 \,^{\circ}$ C, there is a significant contribution in the (002) direction. At 400 °C, the (0.0.2) peak begins to dominate the XRD spectra indicating the preferential growth along the (002) direction for ZnO films. The results show that the increase of substrate temperature is in favour to the diffusion of atoms absorbed on the substrate and accelerates the migration of atoms to the energy favorable positions, resulting in the enhancement of the crystallinity and *c*-axis orientation of film, which is indicated by the increase in intensity of (002) reflection and decrease of fullwidth at half-maximum value (FWHM).

On the other hand, the films deposited on Si(100)substrate show different kind of XRD pattern (Fig. 1(b)). It was observed that the films deposited at $T_s = 300$ °C has polycrystalline nature and exhibits (100), (002) and (101) reflections in XRD pattern. When the substrate temperature is increased to $400 \,^{\circ}$ C, the intensity of (002) peak starts to decrease and the intensities of (100) and (101)peaks dramatically strengthen. Thereafter, the intensity of (101) peak increases slowly as the substrate temperature increases further. However, the (100) peak gradually increases with the increase in the temperature in the range 400–450 °C. Finally, the (100) peak dominates when the substrate temperature gradually reaches to 450 °C. XRD pattern revealed that the film deposited on Si substrate at $T_{\rm s} = 450$ °C was highly oriented along the *a*- and *b*-axis. It has been reported [18] that the microstructure of ZnO films evolves from (002) crystal plane growth mode to (100)mode, i.e. (002)-(110)-(100)-(101) crystal plane. This phenomenon can be attributed to the different surface free energies associated with different planes. The substrate temperature activates the ZnO film growth from relative lower surface free energy to higher surface free energy, i.e. 1.6 J/m^2 for (002), 2.0 J/m^2 for (110), and 3.4 J/m^2 for (100), respectively [18,19].

The crystallite size (d) of the samples was calculated using Scherer formula [12]

$$d = \frac{0.9\lambda}{B\,\cos\,\theta_{\rm B}},$$

where λ , $\theta_{\rm B}$ and *B* were the X-ray wavelength (1.54056 Å), Bragg diffraction angle and line width at half-maximum, respectively. The value of crystallite size of the best film deposited on glass at $T_{\rm s} = 400$ °C with preferred *c*-axis orientation was 24.9 nm, while the crystallite size of the best film deposited on silicon at $T_{\rm s} = 450$ °C with preferred *a*- and *b*-axis orientation was found to be 67.9 nm, which was greater than the film deposited on glass. The calculated values of lattice parameters of the films deposited on glass and Si substrates from XRD data were found to be a = 3.183 Å, c = 5.198 Å and a = 3.149 Å, c = 5.143 Å, respectively. For bulk ZnO, the reported value of c is 5.204 Å. The value of lattice parameters of the films deposited on glass was observed to be slightly greater than the films deposited on Si, which evidenced that the lattice parameters were different on different substrate. The crystallite sizes of the films deposited on glass at $T_s = 200, 300, 350$ and 400 °C was found to be 20.8, 21.3, 24.2 and 24.9 nm, respectively. It was observed that the crystallite size increased with increase in deposition temperature.

Fig. 2(a) and (b) shows the FESEM images of ZnO film grown on glass and Si, respectively. The films deposited on glass further confirms the *c*-axis orientation with columnar grains running perpendicular to the substrate with average grain size of 120 nm (Fig. 2(a)). However, a- and b-axis orientation with hexagonal columnar grains with approximate grain size of 190 nm, the grain boundaries separating these regions of size approximately 64 nm (Fig. 2(b)) were observed in case of films deposited over the silicon substrate. We found that the films grown over silicon show larger grain size in comparison to the films grown over glass substrate. This behaviour was in agreement with the crystallite size calculated from XRD for both films on silicon and glass, respectively. However, overall particle size shown by FESEM was much higher as compared with that calculated from the XRD results (Table 1). This was because of the fact that the XRD gave the average mean crystallite size while FESEM showed agglomeration of the particles. The XRD and FESEM data can be reconciled by the fact that smaller primary particles have a large surface free energy and would, therefore, tend to agglomerate faster and grow into larger grains.

The surface morphology of the films was also studied using atomic force microscope (NT-MDT: NTEGRA Model) over $3 \mu m \times 3 \mu m$ area in semi-contact mode. Fig. 3 shows the AFM images of the films deposited on the glass and Si substrate. At the growth temperature of 400 °C, ZnO film on glass shows the vertically aligned nanotips-like structure with narrow shafts and sharp ends (Fig. 3(a)). The films deposited on the Si substrate showed the almost similar hexagonal columnar structures as seen in FESEM images. The average grain size was found to be 70 and 125 nm for ZnO films deposited over glass and Si, respectively. Thus, from these studies we concluded that both the nature of substrate and substrate temperature plays an important role in deciding the structural properties of ZnO films.

3.2. ZnO nanopowder

Liquid solution of concentration 0.1 M was prepared from the dissolution of zinc nitrate hydrate in distilled water and was sprayed using an ultrasonic generator operated to an atomizing frequency of 1.7 MHz. The produced droplets were then carried into the chamber by







Fig. 2. FESEM images of best ZnO thin film deposited on: (a) glass (b) Si substrate and (c) ZnO nanopowder.

Table 1 Comparative parameters of ZnO nanocrystalline thin films and nanopowder

Substrate	Deposition temperature	Lattice parameter, a	Lattice parameter, <i>c</i> (Å)	Crystallite size Grain size (nm) (nm))	
	(C)	(A)		XRD	FESEM	AFM	
Glass	400	3.183	5.198	24.9	120	73	
Si	450	3.149	5.143	67.9	190	125	
Nanopowder	Room temperature	3.244	5.297	14.9	63	_	





Fig. 4. High-temperature XRD pattern of the ZnO nanopowder.



Fig. 3. AFM images of best ZnO films deposited on: (a) glass and (b) Si substrate.

air carrier gas and pyrolyzed at a predetermined temperature of 400 $^{\circ}$ C, which was the temperature of second zone. The substrate was kept at room temperature in the third zone to collect the nanopowder.

The results of in situ high-temperature X-ray diffraction in vacuum for ZnO nanoparticles at increasing temperature from 100 to 1000 °C are shown in Fig. 4. ZnO nanopowder mixed with zapon lacquer is applied on a platinum strip, which is used as a sample holder cum heater for hightemperature XRD. It has been observed that the XRD peak broadening decreases with increase of temperature. The observed reflections were (100), (002) and (101)reflections, which were similar to the observed reflections in ZnO bulk. The intensity of these reflections increases with rise in temperature. There is a gradual shift in the peak position towards lower value of 2θ . It is well known that the lattice parameters are temperature dependent, i.e. an increase in temperature leads to expansion of the lattice [10,11]. In case of ZnO nanopowder, it was observed that the particle size and lattice parameters increased with increasing temperature as mentioned in Table 2. No phase change was observed in XRD pattern even after in situ

Table 2 Details of various parameters of ZnO nanopowder at different temperatures

Temperatu (°C)	re Crystallite size (nm)	Lattice parameter, <i>a</i> (Å)	Lattice parameter, <i>c</i> (Å)	No. of unit cells, <i>n</i>
100	15.2	3.244	5.297	12,688
200	16.3	3.245	5.299	15,631
300	17.8	3.247	5.302	20,319
400	19.6	3.249	5.305	27,079
500	19.7	3.250	5.307	27,468
600	20.2	3.252	5.310	29,560
700	21.8	3.253	5.312	37,120
800	24.5	3.256	5.317	52,543
900	30.2	3.259	5.321	98,156
1000	35.7	3.261	5.325	161,823

heating of the powder to $1000 \,^{\circ}$ C. At temperature above 700 $^{\circ}$ C, the reflection due to Zn₂PtO₄ phase was detected (Fig. 4).

The increase of the lattice parameter of ZnO nanopowder with the increase in temperature was calculated using the equation:

$$\frac{1}{d_{101}^2} = \frac{4}{3} \left(\frac{1}{a^2} \right) + \frac{1}{c^2},$$

where *d* is the interplaner distance, *a* and *c* are the lattice parameters (being hexagonal structure $c/a = \sqrt{8/3}$). The XRD spectra were used to calculate the sizes of the ZnO nanoparticles with increase in temperature using Scherrer's formula [12]

$$d = \frac{0.9\lambda}{B\,\cos\,\theta_{\rm B}},$$

where λ , $\theta_{\rm B}$ and *B* are the X-ray wavelength (1.54056 Å), Bragg diffraction angle and line width at half-maximum, respectively. We have also incorporated the instrumental broadening for the size calculations. The XRD results indicated that the synthesized ZnO powders had the pure wurtzite structure with lattice parameters *a* and *c* of 3.244 and 5.297 nm, respectively, which were slightly greater than the value of lattice parameters of ZnO thin films. The reason for this may be attributed to the fact that the structural properties of the ZnO films and nanopowder were different, as nanopowder was polycrystalline while the films were oriented along a preferred orientation.

The lattice parameters (*a* and *c*) and particle size as the function of temperature are shown in Fig. 5 and it was observed that there is a continuous increase in the lattice parameter and particle size with temperature as shown in Table 2. It was found that the size of ZnO nanoparticles was around 15.2 nm at 100 °C, which increased to 35.7 nm when the sample was heated to 1000 °C. According to Ostwald ripening, the increase in the particle size is due to the merging of the smaller particles into larger ones [13] and is a result of potential energy difference between small and large particles and can occur through solid-state



Fig. 5. Variation of particle size and lattice parameter: (a) a and (b) c, with temperature.

diffusion. To examine this let us consider a particle, P of diameter R_0 . The particle P can be changed into n smaller identical unit cells of edges, a and c, without changing its volume,

$$\frac{4}{3}\pi \left(\frac{R_0}{2}\right)^3 = nV, \quad \text{where } V = \frac{3\sqrt{3}}{2}a^2c$$

(for hexagonal structure),

i.e.

$$n = \frac{4}{3}\pi \left(\frac{R_0}{2V}\right)^3.$$

We have observed an increase in the number of unit cells in the particle with an increase in temperature even after incorporating the increase in lattice parameter and is shown in Table 2. This size increment can be attributed to the merging of grain boundaries into neighbouring grains.

The morphology of ZnO nanopowder as revealed by FESEM (Fig. 3(c)) showed nanoparticles of size approximately 50-100 nm. The morphology and structure of powder was further investigated by TEM. Bright field TEM images and the corresponding diffraction pattern for ZnO nanopowder were shown in Fig. 6. The sample was scanned in all zones before the picture was taken. The micrographs revealed that the particles were nearly spherical in shape. The diffraction pattern shows spotty ring pattern without any additional diffraction spots and rings of secondary phases revealing their highly crystalline ZnO wurtzite structure. Three fringe patterns were observed with plane distance of 2.79, 2.58 and 2.44 Å in the electron diffraction pattern which corresponds to 100, 002 and 101 planes of pure wurtzite hexagonal structure of ZnO.

The optical transmission spectra of both ZnO films deposited on the glass substrate and the nanopowder was recorded as a function of wavelength in the range



Fig. 6. TEM images and corresponding diffraction pattern of ZnO nanopowder.



Fig. 7. Transmission spectra of (a) ZnO nanopowder, (b) ZnO thin films deposited on glass at $T_s = 200$ °C, (c) $T_s = 300$ °C, (d) $T_s = 350$ °C and (e) $T_s = 400$ °C.

350–900 nm and is shown in Fig. 7. It was observed that the value of transmittance increases from 55% to 86% with the increase of the deposition temperature from 200 to 400 °C of the films deposited on the glass substrate. The transmittance of the film deposited at 400 °C was found to be 86% in the visible range, while 60% in case of ZnO nanopowder. The lower value of transmittance in case of ZnO nanopowder could be due to light scattering at the rough surface. The optical absorption at absorption edge corresponds to the transition from valence band to conduction band, while the absorption in the visible region was related to some local energy levels caused by some intrinsic defects. Higher transmittance in visible region indicates that the film had less defects and better crystallinity. It was concluded from results that the transmittance in visible region increased with deposition temperature indicating that less defects and better crystal structure could be obtained at higher substrate temperature, which was in good agreement with the XRD analysis. The films higher deposition temperature, deposited at i.e. $T_{\rm s} = 400 \,^{\circ}{\rm C}$ were highly transparent in the visible range. In order to calculate the direct band gap, we have used the Tauc relationship [14] as follows:

$$\alpha h v = A(h v - E_g)^n,$$

where α is the absorption coefficient, A is a constant, h is the Planck's constant, v is the photon frequency, E_g is the optical band gap and n is 1/2 for direct semiconductor. An extrapolation of the linear region of a plot of $(\alpha hv)^2$ on the y-axis versus photon energy (hv) on the x-axis gave the value of the optical band gap E_g . Since $E_g = hv$ when $(\alpha hv)^2 = 0$. Here the direct band gap of the ZnO films was evaluated by extrapolating the straight line part of the



Fig. 8. Optical band gap of (a) ZnO nanopowder, (b) ZnO thin films deposited on glass at $T_s = 200$ °C, (c) $T_s = 300$ °C, (d) $T_s = 350$ °C and (e) $T_s = 400$ °C.

Table 3 Various parameters of ZnO nanocrystalline thin films deposited on glass substrate

Deposition temperature (°C)	Crystallite size (XRD) (nm)	Optical bandgap (eV)
200	20.8	3.17
300	21.3	3.18
350	24.2	3.20
400	24.9	3.25

curves $(\alpha hv)^{1/n} = 0$ as shown in Fig. 8(b)–(e). The calculated values of band gap E_g was found to be 3.17, 3.18, 3.20 and 3.25 eV for the films deposited at 200, 300, 350 and 400 °C, respectively (Table 3). It was evident from Fig. 8 that the band gap increased with the increase in the deposition temperature, which could be due to lesser defects and better crystal structure obtained at higher deposition temperature. While in case of ZnO nanopowder the band gap of the films. This reflects that in case of ZnO powder the absorption edge of transmittance shifts to longer wavelength region and there is increase in the optical absorption in the UV region.

4. Conclusion

In summary, we have used modified ultrasonic spray pyrolysis technique to prepare ZnO nanocrystalline thin films and nanopowder. The technique is simple and inexpensive method allowing the large area deposition at low temperature with acceptable film qualities. The nature of substrate was found to have a strong influence on the properties of ZnO thin films. XRD patterns of the films deposited on glass show strong c-axis oriented crystal structure with preferred (002) orientation, while those deposited on Si show predominant (100) orientation. AFM and FESEM studies further confirms the a- and b-axis orientation in ZnO films on Si substrate with hexagonal columnar like grains and *c*-axis orientation in case of glass substrate with grains perpendicular to the substrate. The films with a- and b-axis orientation are preferred for thin film Si solar cell applications. Optical studies showed that the transmittance and the band gap of the films deposited on glass increased with increase in the deposition temperature, which could be due to lesser defects and better crystal structure obtained at higher deposition temperature.

From the XRD and TEM analysis of ZnO nanopowder, it was confirmed that the resultant particles were of pure ZnO with hexagonal (wurtzite) structure. High-temperature XRD also confirmed that the ZnO nanoparticles were stable not only at room temperature but as well at high temperature, i.e. 1000 °C. A linear increase in lattice parameters with temperature along with increase in the size of the grains was observed. An increment in crystallite size with increase in temperature was attributed to the merging of grain boundaries into neighbouring grains.

Acknowledgements

We are thankful to Dr. A.K. Gupta, NPL, New Delhi and Prof. Pushsn Ayyub, TIFR, for fruitful discussions. The financial support provided by DST, India under the scheme Nanoscience and Technology Initiatives (NSTI) with reference no. DST 238 and DRDO under the scheme ARM(RD-17) 2035/1008/D(R&D) with reference no. ARMREB/MAA/2004/54 is highly acknowledged. One of the author Preetam Singh is thankful to CSIR for award of senior research fellowship.

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