PRAMANA © Indian Academy of Sciences Vol. 75, No. 6
— journal of December 2010
physics pp. 1157–1161

Effect of ZnO doping on the structural and optical properties of $BaWO_4$ thin films prepared using pulsed laser ablation technique

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Abstract. $BaWO_4$ doped with ZnO (2, 3, 5, 7 and 10 wt%) nanostructured films are prepared on quartz substrates by pulsed laser ablation. The films are post annealed at 900°C. GIXRD analysis of the post-annealed films reveal the change of orientation of scheelite tetragonal crystal growth from 1 1 2 reflection plane to 0 0 4 planes when doping concentration is more than 3 wt%. The AFM images show that film with 7 wt% ZnO doping concentration has good ceramic pattern with surface features giving a minimum value of rms surface roughness suitable for optoelectronic device applications. The optical transmittance and band-gap energy of the films are found to decrease considerably on post-annealing which can be due to the increase in grain size of the crystallites on annealing. Thus doping with ZnO improves the surface features of the films and increases the optical band-gap energy.

Keywords. Thin films; X-ray diffraction; optical properties; pulsed laser ablation; nanostructured barium tungstate film.

PACS Nos 78.20.-e; 61.05.cp; 68.55.-a; 81.15.Aa

1. Introduction

Scheelite structured ceramic materials are gaining importance due to their potential applications as laser host materials in quantum electronics and scintillators [1,2], stimulated Raman scattering materials [3] and catalysts [4]. They are direct band-gap dielectric materials, which can act as host materials for rare earth and semiconductor materials [5]. Zinc oxide (ZnO) is a wide band-gap ($E_g = 3.37$, eV) II–VI semiconductor which has potential applications in optoelectronic devices such as short-wavelength lasers and light emitting diodes [6]. This paper reports the preparation of laser ablated ZnO-doped $BaWO_4$ nanostructured films on quartz substrate and the effect of thermal annealing and doping concentration of ZnO on the structural and optical properties of the films are systematically investigated.

2. Experimental methods

$BaWO_4$ thin films doped with 2, 3, 5, 7 and 10 wt% of ZnO are prepared using pulsed laser deposition technique (PLD) and are designated as BWZn-2, BWZn-3, BWZn-5, BWZn-7 and BWZn-10 respectively. The pellets (having 11 mm diameter and 3 mm thickness) are prepared from commercially available $BaWO_4$ and ZnO (Sigma Aldrich, purity 99.9%) powders. The pellets sintered at 900°C for 4 h are used as targets for laser ablation. The deposition of the films are carried out inside a vacuum chamber evacuated down to a base pressure of $\sim 10^{-6}$ mbar, using a Q-switched Nd:YAG laser (Quanta-Ray INDI-series, Spectra Physics) with frequency doubled 532 nm laser radiation with a pulse width of 7 ns and repetition frequency of 10 Hz. The deposition of the film is done for 20 min on quartz substrates (fixed at an on-axis distance of 6 cm from the target) using 140 mJ laser energy. The ablated films are post-annealed for 4 h at 900°C. The crystalline structure and crystallographic orientation of the films are characterized by X-ray diffraction measurements (XPERT PRO Diffractometer) using CuK_{α} radiation of 0.15405 nm wavelength. The surface morphology at nanometer scale is investigated using atomic force microscope (AFM) (Digital Instruments Nanoscope E, Si_3N_4 100μ cantilever, 0.58 N/m force constant) measurements in contact mode. Optical transmission and reflectance spectra of the films are recorded using JASCO V 550 UV-VIS-NIR double beam spectrophotometer in the region 190–900 nm. The thickness of the films is measured using a Dektak 6M Stylus profiler.

3. Results and discussion

GIXRD patterns of films post-annealed at 900°C is shown in figure 1. The presence of sharp, intense peaks suggests the polycrystalline nature of these films. The

Table 1. Structural and optical parameters of as-deposited and post-annealed films.

Films	Thickness (nm)	Grain size of annealed films (nm)	R.m.s. roughness of the annealed films (nm)	Average optical transmittance (%)		Band-gap energy (eV)	
				As-deposited	Annealed at 900°C	As-deposited (eV)	Annealed at 900°C (eV)
BWZn-2	190	20.	74	64	60	5.26	3.82
BWZn-3	193	22	57	66	73	5.15	3.61
BWZn-5	195	23	63	75	55	5.1	3.8
BWZn-7	200	53	23	93	77	5.33	4.1
BWZn-10	200	61	48	67	63	5.31	4.61

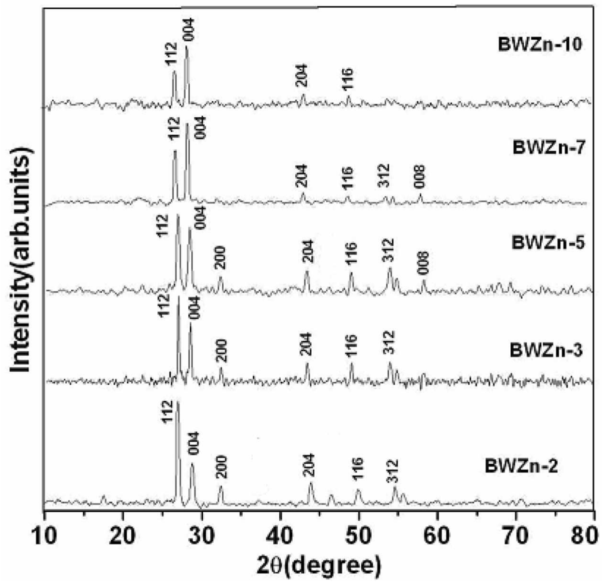

Figure 1. XRD pattern of ZnO-doped WO_4 films post-annealed at $T_{\mathrm{ANN}} = 900°\mathrm{C}$.

peaks are observed at 26.44°, 28.05°, 31.89°, 42.99°, 48° and 53.55° 2θ values corresponding to (1 1 2), (0 0 4), (2 0 0), (2 0 4), (1 1 6) and (3 1 2) lattice reflection planes of scheelite tetragonal phase of $BaWO_4$ [7]. The orientation of crystallites changes from (1 1 2) reflection plane to (0 0 4) plane when doping increases above 3%. The average size of crystallites in the films is determined using the Debye–Scherrer equation [8],

$$D_{hkl} = \frac{0.9\lambda}{\beta_{hkl}\cos(\theta_{hkl})}, \tag{1}$$

where λ is the X-ray wavelength, θ_{hkl} is the Bragg diffraction angle and β_{hkl} is the full-width at half-maximum (FWHM) in radian of the main peak in the X-ray diffraction pattern. The grain size in BWZn films post-annealed at 900°C is found to increase with increase in doping concentration of ZnO (table 1).

The 2D-AFM images of (scan area = 5 μm^2) the annealed BWZn films are shown in figures 2a–e. BWZn-7 film exhibits uniformly distributed grains of equal sizes with well-defined grain boundaries and minimum r.m.s. surface roughness. The r.m.s. surface roughness of the films are obtained using WSxM software of Nano Tech Electronica and are given in table 1.

The transmittance spectra of the as-deposited films are shown in figure 3. The average transmittance in the wavelength range 350–900 nm for the as-deposited BWZn-2 film is 64%. As ZnO doping concentration increases, the average transmittance increases up to 93% for ZnO doping concentration of 7 wt% and thereafter it decreases. The post-annealed films show lesser values for the average transmittance compared to that of the as-deposited counterparts. The average transmittance in

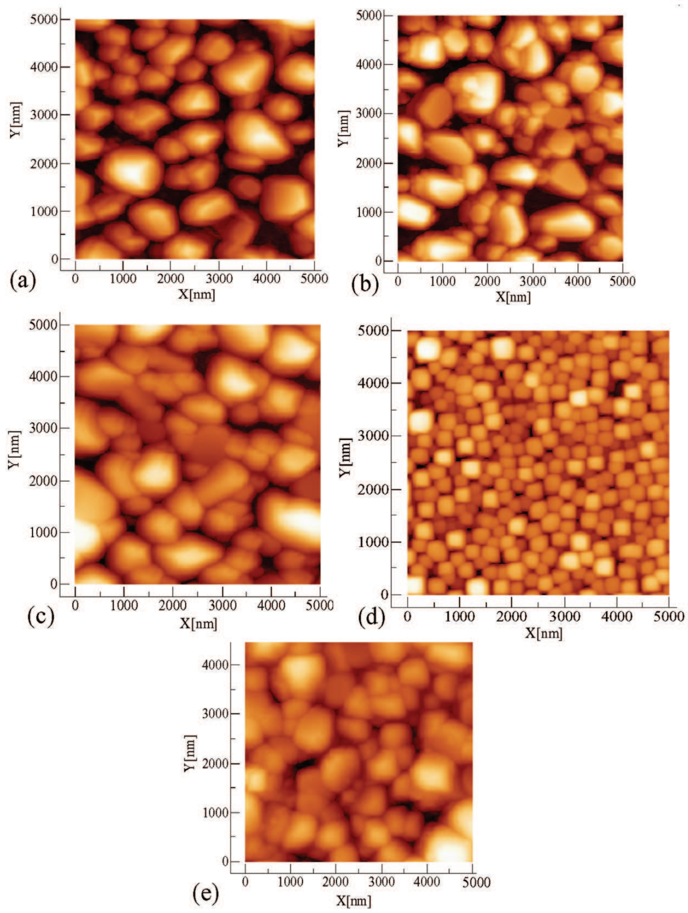

Figure 2. AFM images of (**a**) BWZn-2, (**b**) BWZn-3, (**c**) BWZn-5, (**d**) BWZn-7 and (**e**) BWZn-10.

the wavelength range 350–900 nm for the post-annealed films varies between 60 and 77%.

The optical band-gap energies of the films are calculated using Tauc plots (figure 4) and are given in table 1. The band-gap energies are found to be greater than that of the undoped as-deposited $BaWO_4$ film. The higher values of band-gap energies observed for doped films can be due to Burstein–Moss shift [9].

4. Conclusion

ZnO-doped $BaWO_4$ thin films are prepared on quartz substrates using pulsed laser deposition method. The XRD analysis shows that the as-deposited films are amorphous in nature whereas the films post-annealed at 900°C are polycrystalline in

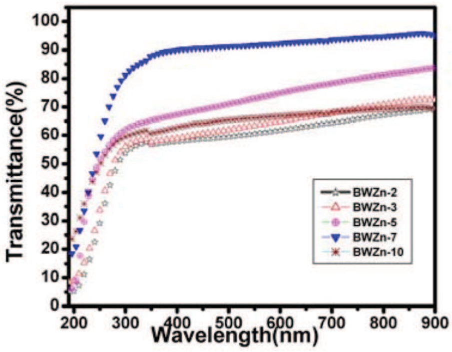

Figure 3. Transmittance spectra of the as-deposited BWZn films.

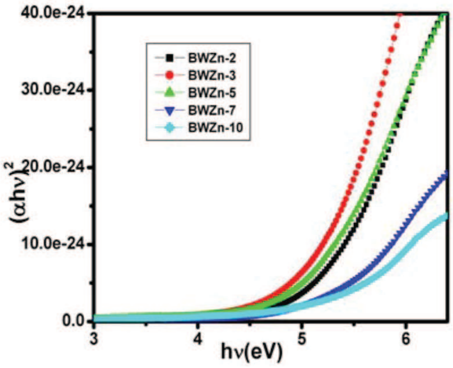

Figure 4. Tauc plots for the as-deposited BWZn films.

nature with scheelite tetragonal structure. AFM images show that the surface features of the films depend strongly on the ZnO doping concentration and all the films are porous in nature. The optical band-gap energies obtained for the as-deposited and post-annealed films are found to be higher than that for the bulk value. The higher values of band-gap energies observed for the ZnO-doped films compared to undoped $BaWO_4$ films can be due to Burstein Moss shift.

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