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Influence of Zn concentration on the size and optical properties of ZnO nanocrystals in silica matrix grown by RF co-sputter deposition

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ABSTRACT

In the present study we report the influence of variation in amount of Zn on growth and optical properties of thin films of ZnO nanocrystals in silica matrix deposited by rf magnetron co-sputtering with substrate heating at 200° C. RBS studies indicate change in the concentration of Zn in the films while Raman spectroscopy measurements indicate presence of excess zinc with different concentration. The XRD spectra of the thin films shows the formation of strong ZnO phase nanocrystals with different sizes in different films while the UV-VIS spectra shows variation in the band edge energy of the ZnO nanocrystals for these films. FT-IR spectra of the films show the Zn-O, Zn-O-Si and Si-O-Si vibrational features related to ZnO, Zn_2SiO_4 and SiOx phases in the films. The results suggest growth of stable ZnO nanocrystals in silica matrix having better phase and optical quality with increase in the Zn concentration in the thin films, which may be useful in optical applications of ZnO. Copyright © 2013 VBRI press.

Keywords: RF sputtering; ZnO; nanocrystals; phase improvement.

V. V. Siva Kumar is a Scientist at Inter-University Accelerator Centre in Materials Science department. He has registered for Ph.D in Physics from Jawaharlal Nehru University, New Delhi and is working on several projects related to growth of thin films using sputtering process. He has developed dc , rf sputtering systems and a microwave CVD system for growth of thin films. His research interests are growth and characterization of ZnO and Carbon nanostructures, and p-type doping of ZnO.

Sunil Ojha is working as scientist at IUAC Delhi. Currently his major responsibility is operation, maintenance of RBS facility at IUAC. He performed RBS measurements and analysis of data thereafter. Channeling and resonance measurements are also carried out as per requirement.

Fouran Singh did doctorate from University of Paris south XI, Orsay campus and presently working as Sr. Scientist at Inter University Accelerator Centre (IUAC), New Delhi. He has authored/co-authored more than 150+ research articles in reputed International refereed Journals. The published articles are well recognized by the research community, as it is clear from Scopus citation history (h-index 21, i10-index 48, av. Citation per article ~8). His current research interests are in the development of nanocomposites, nanostructures, nanophosphors and thin films for optoelectronic, Plasmonic, display and photovoltaic devices.

Introduction

ZnO (zincite) is a wide band gap (E_g = 3. 37 eV at RT) which has broad range of applications in the field of optoelectronic devices such as lasers and light emitting diodes **[1, 2].** ZnO quantum dots have attracted considerable attention as potential candidates for qubits in quantum information technology **[3, 4].** As photons can mediate an effective coupling between spins in two quantum dots **[5]**, ZnO quantum dots embedded into an optical cavity may be envisioned as spintronic devices working at room temperature **[6]**.

Growth of ZnO in silica/SiO_2 matrix is being actively studied with different growth mechanisms. We have previously reported the growth of ZnO nanocrystals in silica matrix by rf co-sputter deposition and post annealing

[7]. G. Meyer et al. **[6]** have studied the growth of ZnO nanocrystals in SiO_2 matrix by rf sputtering as a $SiO_2/ZnO/SiO_2$ trilayer with an intermediate insitu annealing step. Z. Z. Zhi et al. studied growth of ZnO nanocrystals embedded in SiO_2 matrix thin films on Si (1 0 0) single crystal substrates by plasma enhanced chemical vapour deposition (PECVD) at 230 °C **[8]**. J. K Lee et al. have report the preparation of ZnO nanocrystals embedded in a SiO_2 matrix formed using sequential zinc and oxygen ion implantations and subsequent thermal annealing **[9]**. V. Prankratov et al. studied growth of ZnO nanocrystals embedded in a SiO_2 matrix by growing multilayer structures consisting of ZnO/SiO_2 bilayers using radio frequency magnetron sputtering deposition using ZnO and SiO_2 targets and subsequent heat-treated at different temperatures and in different atmospheres **[10]**.

Growth of ZnO nanocrystals in a host matrix by co-sputter deposition has the advantage of easy control on the amount of material to be dispersed in a host matrix. It will be interesting to study the influence of Zn concentration on the structural and optical properties of ZnO nanocrystals in SiOx matrix grown by co-sputter deposition. In the present work, substrate heating is done during the deposition and variation in the size of ZnO nanocrystals in the deposited thin films was obtained by varying the Zn content in the films using directional sputtering process in a single deposition, which to the best of our knowledge is not reported in the case of synthesis of ZnO nanocrystals in silica matrix by rf magnetron co-sputter deposition.

Experimental

Materials and sample preparation

Thin films were deposited by rf magnetron sputtering using an rf sputtering set-up developed in-house. A composite ZnO/Si target was used for the film deposition on Si and quartz substrates. A 46 mm dia ZnO pellet was made using commercially available powder of ZnO (purity 99.0+ , MERCK, USA) and was pasted to the 4 inch dia Si target (purity 99.999, Goodfellow, USA). The substrates were placed on a grounded anode which is separated by 50 mm from the target. A base vacuum of $4x10^{-5}$ torr was produced in the chamber. The chamber was flushed with argon gas for 20 minutes before the thin films deposition. The films were deposited with an rf power of 200 watts and a process pressure of 10 mtorr (+/- 10 % variation). Before deposition on the substrates, the target was pre-sputtered for 10 minutes with argon ions with the substrates covered by a shutter. The substrate temperature was maintained at 200°C during the thin film deposition. In order to vary the amount of ZnO and silica in the thin films, the substrates were placed in three different locations; at the centre of the substrate holder, 1 cm away from the centre of the substrate holder and 2 cms away from the centre of the substrate holder and defined as znosi1, znosi2 and znosi3 and znoqz1, znoqz2 and znoqz3, respectively. Since the target is a composite ZnO/Si target with a 46 mm dia ZnO target fixed at the centre of the 100 mm dia Si target, due to directional sputtering it is possible that more amount of ZnO will be forming in the thin film formed on the substrates placed at the centre of the substrate holder compared to those placed away from the centre of the substrate holder.

Characterization techniques

Rutherford Backscattering studies were conducted using 2 MeV He ions from a 1.7 MV Pelletron accelerator at IUAC. He^{2+} ions were bombarded perpendicular to the surface and backscattered ions were detected at an angle of 160° to beam direction. Glancing angle X-ray diffraction (XRD) measurements were carried out using a Bruker D8 Advanced AXS diffractometer at a grazing incidence of 2° with Cu Kα (λ = 1.54 Å) radiation. UV-VIS spectra of the films were recorded using a Hitachi spectrophotometer (U – 3300). Micro-Raman spectroscopy measurements were carried out on the films under backward scattering configuration with incident light normal to the sample surface using InVia Raman spectrometer (Renishaw) system consisting of Ar ion laser with 514.4 nm wavelength and RenCam CCD detector, in the range 100 to 2000 cm^{-1}. Fourier transform infrared spectroscopy measurements were performed at room temperature using a Thermo-Nicolet (Nexus 670) spectrometer with a resolution of 4 cm^{-1}.

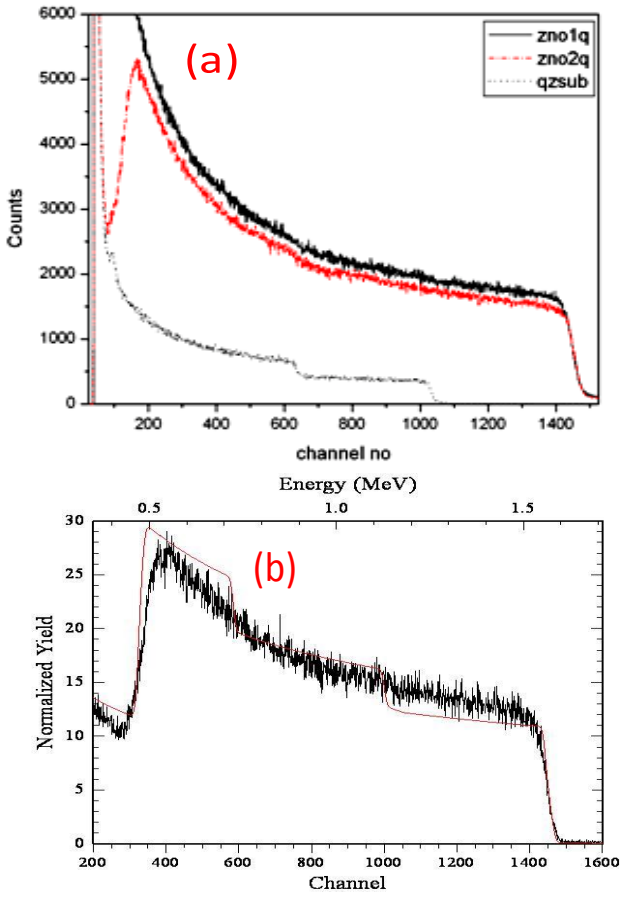

Fig. 1. (a) RBS spectra of the films formed on quartz substrates and the quartz substrate and (b) RBS rump simulated pattern of Znosi2 film.

Results and discussion

Fig 1a shows the RBS spectra for znoqz1 and znoqz2 thin film deposited on quartz substrates, and the quartz substrate (qzsub). The signals from the different elements overlap and the concentration was determined using standard

RUMP program. **Fig 1b** shows a typical RBS RUMP fitted spectrum of the znosi2 film. The fitting of the RBS data shows that the Zn concentration was higher in the films placed at the centre of the substrate holder (0.13 for znosi1) and it decreased in the films placed away from the centre of the substrate holder (0.11 for znosi2 and 0.09 for znosi3).

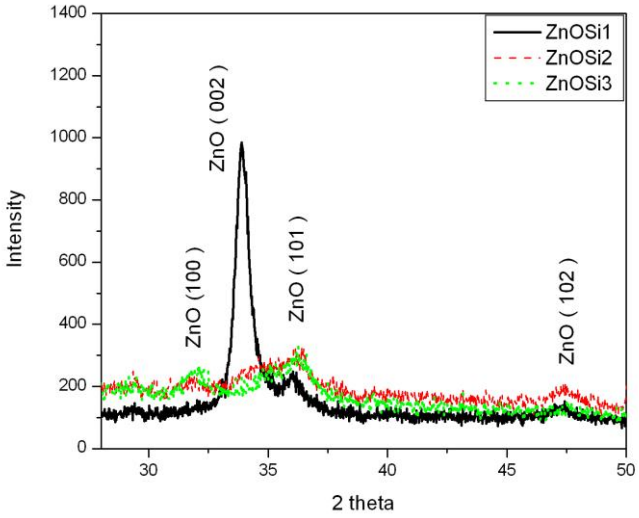

Fig. 2. XRD patterns of deposited ZnO/SiOx films.

The XRD patterns of the ZnO/SiOx films deposited at on Si substrates are shown in **Fig 2**. It can be seen that broad peaks at 2 theta values of 31.4°, 34.4° , 36° and 47.5° are present which correspond to wurtzite phase ZnO (100, 002 and 101 and 102 planes respectively). The XRD pattern of the znosi1 film shows strong ZnO (002) peak compared to the znosi2 and znosi3 films. This shows that highly c-axis oriented ZnO/SiOx nanocomposite films are formed in the film with higher Zn concentration compared to the films with lesser Zn concentration. The size of the ZnO nanocrystals from the XRD pattern for the znosi1 film was 10 nm, calculated using Scherrer's formula. When the Zn content in the film is more, then more Zn atoms will diffuse and get bonded to the growing ZnO nanocrystals and the size of the ZnO nanocrystals will be larger.

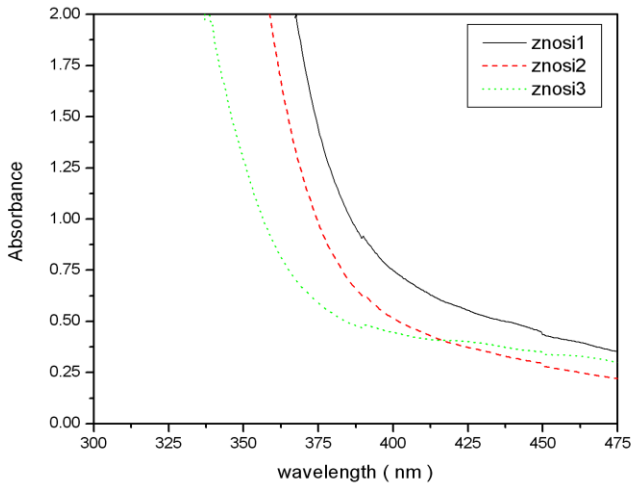

Fig. 3. UV-VIS spectra of the deposited films.

Fig 3 shows the UV-VIS spectra of the films deposited on quartz substrate. It shows sharp absorption feature of ZnO band edge for the films. The band gap estimated from the spectra is 3.18, 3.26 and 3.41 for the films znosio1, znosio2 and znosio3, respectively, which indicates blue shift of band gap in znosio3 film caused by quantum-confinement effects due to smaller size of the ZnO nanocrystals. This shows that the size of the ZnO nanocrystals is smaller in the znosio3 film compared to the znosio1 and znosio2 films which indicate that the size of ZnO nanocrystals increased with increase in the concentration of Zn in the films, which is in agreement with the XRD measurements.

Fig 4 shows Raman spectra of the films deposited on Si substrates. The sharp peaks observed at around 300 and 520 cm^{-1} and the broad peak around 970 cm-1 in the Raman spectra are attributed to Si substrate while the Raman mode at around 580 cm^{-1} is assigned to E_1(LO) mode for ZnO**[11,12,13]**. The observation of the E1 (LO) mode peak here indicates the presence of excess zinc **[14]** in the ZnO nanocrystals grown in silica matrix. The intensity of the E1 (LO) mode peak is higher for znosio1 film and it decreased in znosio2 and znosio3 films relative to znosio1 film which may be due to variation in Zn concentration indicated by RBS spectra results.

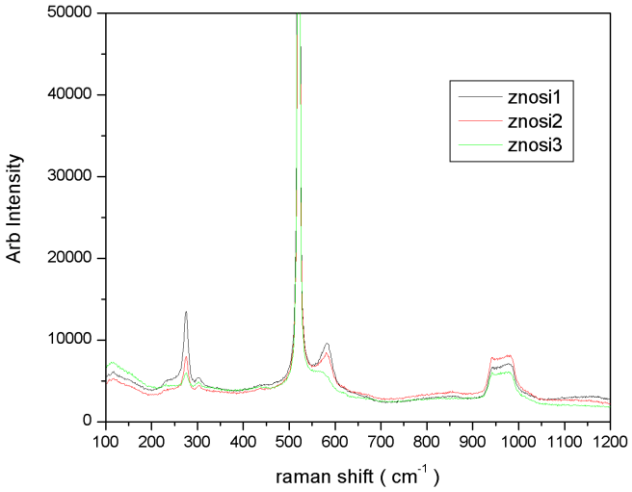

Fig. 4. Raman spectra of the deposited films.

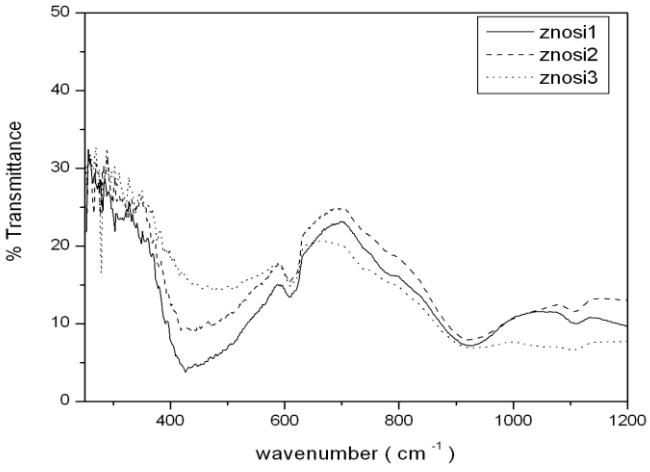

Fig. 5. FT-IR spectra of the deposited ZnO/SiOx nanocomposite films.

Fig 5 shows the FT-IR spectra of the deposited films. The spectra show the vibrational features of Zn-O, Zn-O-Si and Si-O-Si bonds. The assignment of the vibrational features is as follows-: the band at 1080 cm^{-1} is the Si-O-Si stretching vibration **[15]**; the band at 910 cm^{-1} is the Zn-O-Si bending vibration and the band at 411 cm^{-1} is the stretching vibration of Zn-O bond in ZnO lattice **[16]**. The intensity of the Zn-O vibrational band decreased in the znosi2 and znosi3 films relative to znosi1 film. This suggests that more ZnO formed in the znosi1 film with higher Zn concentration compared to the znosio2 and znosio3 films with lower Zn concentration, for the same substrate temperature.

The Zn-O-Si bonds present in the films corresponds to the formation of amorphous Zn_2SiO_4 phase in the films around the ZnO phase. Formation of crystalline Zn_2SiO_4 phase in the nanocomposite films was previously observed with post deposition annealing at higher temperatures **[7]**. Also the intensity of the Si-O-Si vibrational band is less compared to the Zn-O-Si bands which suggests that more amount of Si gets attached in the Zn-O-Si bonds. These results suggest that in the deposited thin films, ZnO nanocrystals are formed which are surrounded by Zn-O-Si bonds linking to the SiOx matrix.

Mechanism

We have previously reported on the growth of ZnO nanocrystals in silica matrix by rf co-sputter deposition and post annealing the films for growth of ZnO nanocrystals in size upto 26 nm **[7]**. Also other studies have been reported on the growth of ZnO nanocrystals in silica where change in average crystalline size of ZnO is brought out by post deposition annealing **[8-10]**. In the present work we show a method of growing thin films having good crystalline quality ZnO nanocrystals in silica matrix and simultaneously bringing variation in the size of the ZnO nanocrystals in the films in a single deposition by varying the amount of Zn in the films using directional sputtering process. During the sputter deposition process, Si atoms will get sputtered from the Si target (100 mm dia) and Zn and O atoms will get sputtered from the ZnO pellet (46 mm dia) pasted at the centre of the Si target. More Zn and less Si atoms will reach the substrate placed at the centre of the substrate holder and more Si and less Zn atoms will reach the substrate placed away from the centre of the substrate holder. During the film growth, Zn-O, Zn-O-Si and Si-O-Si bonds are formed in the films and relatively more amount of Zn will diffuse and bond with the growing ZnO nanocrystals in the znosi1 film compared to the znosi2 and znosi3 films. This results in the formation of larger ZnO nanocrystals in the znosi1 film compared to znosi2 and znosi3 films, and hence the variation in size of the ZnO nanocrystals in the different films.

Conclusion

We have studied the influence of Zn concentration on the growth and properties of ZnO nanocrystals in silica matrix. Highly c-axis oriented ZnO nanocrystals with larger size are formed in silica matrix in the film with higher Zn concentration compared to the films with lesser Zn concentration. Amorphous Zn_2SiO_4 phase is observed between the ZnO and SiO_2 phases in the thin films. Blue shift in band edge is observed for smaller ZnO nonocrystals in silica matrix.

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