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$_2$SiO$_4$ and SiO$_x$ 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.

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

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...
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 4x10⁻⁷ 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 cm away from the centre of the substrate holder and defined as znso1, znso2 and znso3 and znsoq1, znsoq2 and znsoq3, 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. He²⁺ 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 znsoq1 and znsoq2 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 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 znosi1, znosi2 and znosi3, respectively, which indicates blue shift of band gap in znosi3 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 znosi3 film compared to the znosi1 and znosi2 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 E₁(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 znosi1 film and it decreased in znosi2 and znosi3 films relative to znosi1 film which may be due to variation in Zn concentration indicated by RBS spectra results.

Fig 5. FT-IR spectra of the deposited ZnO/SiOx nanocomposite films.
**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 zno1 film compared to the zno2 and zno3 films. This results in the formation of larger ZnO nanocrystals in the zno1 film compared to zno2 and zno3 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$_2$SiO$_4$ phase is observed between the ZnO and SiO$_2$ phases in the thin films. Blue shift in band edge is observed for smaller ZnO nanocrystals in silica matrix.

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**Reference**


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