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# Infrared absorption and evidence of Si<sub>3</sub> nanocluster formation in Si/ZnO composites

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## Abstract

Si nanoclusters embedded in ZnO matrix were prepared by radio-frequency co-sputtering and subsequent annealing of the composite films. Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy techniques were used to characterize the composite films. The average size of the nanoclusters, depending on annealing temperature varied from 3.7 to 34 nm. The nanoclusters in the composites consist of a Si<sub>3</sub> core surrounded by a SiO<sub>x</sub> cap layer. The Si<sub>3</sub> in the clusters remain mainly in its triangular geometrical structure. With the increase of annealing temperature, the vibrational state of Si<sub>3</sub> changes from its excited <sup>3</sup>B<sub>1</sub>(C<sub>2v</sub>) and <sup>3</sup>A'<sub>2</sub>(D<sub>3h</sub>) triplet states to <sup>1</sup>A<sub>1</sub>(C<sub>2v</sub>) singlet ground state and the oxidation state of Si in SiO<sub>x</sub> cap layer increases. © 1999 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

In recent years, the preparation and characterization of low dimensional semiconductor composites have attracted much interest due to their strong photoluminescence (PL) [1,2], modified optical properties [3], and probable applications in devices such as chemical sensors [4]. By incorporating semiconductors in glass matrix in different ways, several optical functional composites have been prepared and the mechanism of the origin of optical functionalities in them are being studied extensively at present. However, the use of functional matrix materials like ZnO, MgO for the preparation of nanocomposites is very recent [5,6], and the influence of such photo-active surrounding host on the embedded low-dimensional dispersoid is not well understood.

We prepared Si nanoclusters in ZnO matrix by r.f. co-sputtering technique and carried out their IR absorption studies. XPS and IR absorption studies showed that the nanoclusters consist of a Si<sub>3</sub> core surrounded by a SiO<sub>x</sub> cap layer. The states of such Si<sub>3</sub> core and the SiO<sub>x</sub> cap layer and their modifications on thermal annealing are studied.

## 2. Experiments

Si/ZnO composite films were prepared on quartz glass substrates by co-sputtering of Si (5 × 5 × 0.3 mm<sup>3</sup> wafers) and ZnO (100 mm diameter) targets with 100 W r.f. power at 10 mTorr Ar pressure. The content of Si in the films varied by changing the number of Si co-targets on the ZnO target, keeping the time of sputtering fixed (60 min). The as-deposited films were annealed at different temperatures (400–800°C) for 5 h in vacuum (2 × 10<sup>-6</sup> Torr). The

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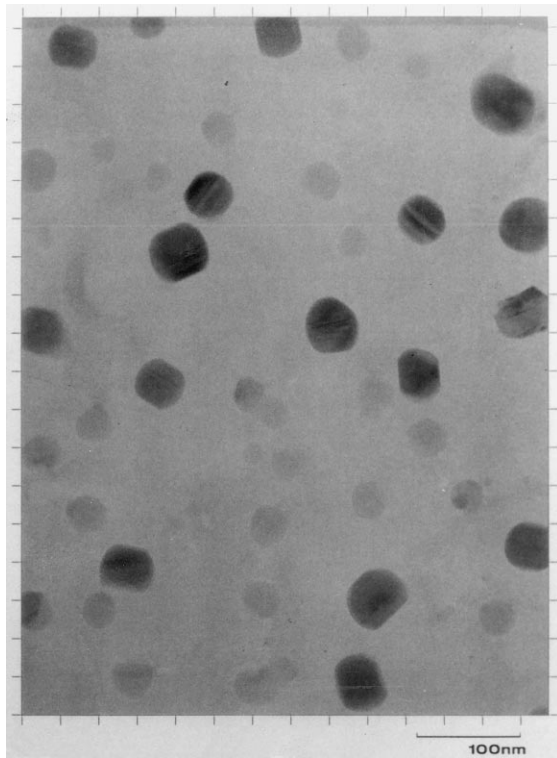


Fig. 1. A typical TEM micrograph of Si/ZnO film prepared with 8 Si co-targets and annealed at 800°C.

chemical state of the individual elements in the films were studied by a Perkin–Elmer (PHI 5600ci) XPS system. For the TEM observations, the composite films of about 25 nm thickness with different Si content were deposited on carbon-coated NaCl substrates. The films after transferring to the copper grids were annealed at different temperatures (400–800°C) in vacuum. A JEOL JEM2000-FXII electron microscope was used for the TEM observations. A Nicolet Magna 750 FTIR spectrometer was used to record the IR absorption spectra in diffuse mode.

### 3. Results and discussion

The Si content in the films increased with the increase of Si co-targets. The Si<sub>2p</sub> peak position in the XPS spectra remained in between 101.6 and 102.8 eV. On vacuum annealing, the Si<sub>2p</sub> peak

position shifted towards higher energy with the increase of annealing temperature.

Homogeneously distributed nanoclusters of size ranging from 2 to 4 nm in the matrix are observed in the as-grown composite films. On thermal annealing at 700°C or above, the size of the nanoclusters increased significantly and their number density decreased. In Fig. 1, a typical TEM micrograph of a sample prepared with eight co-targets and annealed at 800°C is shown (average nanocluster size ~34 nm). The increase of cluster size on annealing at and above 700°C is due to aggregation of smaller clusters and to some extent due to the segregation of dispersed Si still remained in the matrix.

IR absorption spectra showed several peaks in the spectral range of 400–1300 cm<sup>-1</sup>. For the analysis of IR spectra we divided the whole spectral range into three regions. The first interval ranges from 400 to 570 cm<sup>-1</sup>, the second interval from 570 to 700 cm<sup>-1</sup> and the last interval from 900 to 1300 cm<sup>-1</sup>. There appeared a broad non-symmetric peak in the first spectra range for all the samples, the position of which varied systematically with the variation of Si content and the temperature of annealing of the films. A computer-simulated decomposition of these complex peaks showed two adjacent bands in them, the position of which vary with the content of Si in the films and also with the temperature of annealing. In Fig. 2, the evolution of the peak with the variation of annealing temperature, and their computer-simulated decomposition are presented for a film prepared with 16 Si co-targets. Both the component peaks moved towards shorter wavelength with the increase of annealing temperature. The peak at the longer wavelength side moved from 485 to 525 cm<sup>-1</sup>, whereas the shorter wavelength peak moved from 512 to 550 cm<sup>-1</sup>. We assign these two sets of bands to the Si–Si stretching asymmetric (SA) and stretching symmetric (SS) vibrations [7] in Si<sub>3</sub> clusters, respectively. A reverse effect is observed on increasing the Si content in the films. With the increase of Si content, the absorption peak in this frequency range shifted towards longer wavelength. In Fig. 3, the IR spectra for the films with different Si content are presented for 450–700 cm<sup>-1</sup> spectral range. The peak in the 450–570 cm<sup>-1</sup> spectral range is not well resolved for the films with lowest Si content (i.e. prepared with four Si co-targets). With the increase of Si content, the

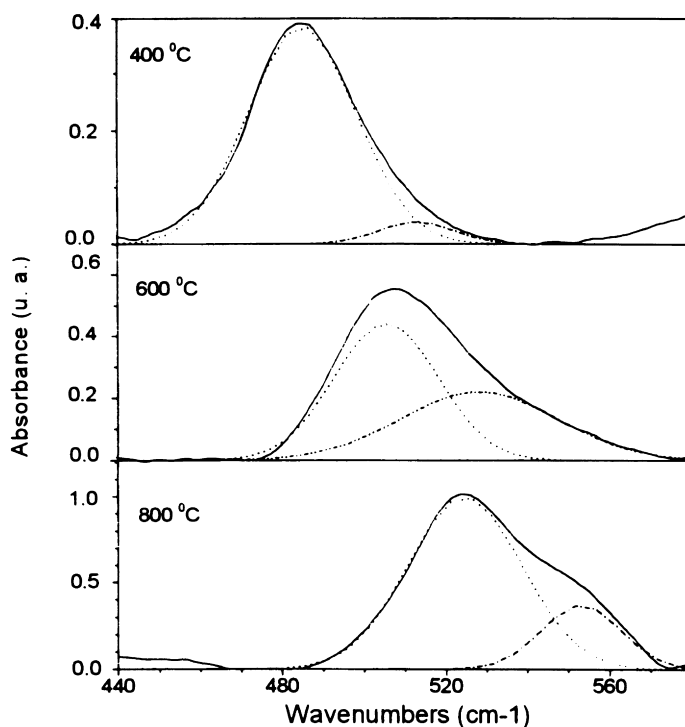


Fig. 2. Evolution of IR absorption peak in the 450–570  $\text{cm}^{-1}$  frequency range and their computer-simulated decomposition, for a film prepared with 16 Si co-targets and annealed at different temperatures.

intensity of the peak increased sharply and its position shifted from 517 to 485  $\text{cm}^{-1}$ . The absorptions at about 485 and 508  $\text{cm}^{-1}$  correspond to the triplet excited states  ${}^3\text{B}_1(\text{C}_{2v})$  and  ${}^3\text{A}'_2(\text{D}_{3h})$  of  $\text{Si}_3$ , respec-

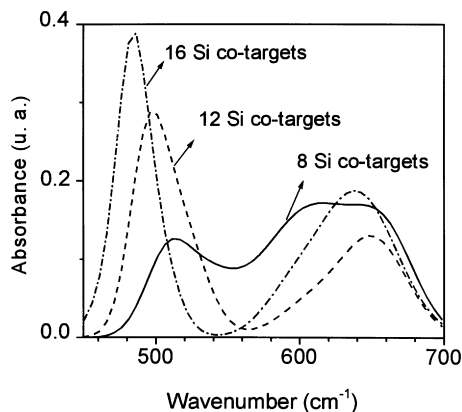


Fig. 3. IR absorption spectra for the films with different Si contents annealed at 400°C.

tively [8]. The peaks appeared at about 525 and 550  $\text{cm}^{-1}$  correspond to the absorption of singlet ground state  ${}^1\text{A}_1(\text{C}_{2v})$  of  $\text{Si}_3$ . So, as the temperature of annealing increased, the configuration of the Si atoms in  $\text{Si}_3$  clusters changed from the triplet to the singlet ground state. The 507 and 532  $\text{cm}^{-1}$  absorptions (Fig. 3) correspond to the most stable triplet  ${}^3\text{A}_1(\text{C}_{2v})$  state of isoscele structure and the second most stable triplet state of linear chain structural form of  $\text{Si}_3$ , respectively [9]. The peaks observed at about 494 and 513  $\text{cm}^{-1}$  might correspond to the vibrations of most stable triplet state of the linear chain structure and the 4th most stable triplet state of  $\text{Si}_3$ , respectively. So, as the Si content in the films increased, the  $\text{Si}_3$  clusters in the films acquired the lesser stable geometrical structures. The peaks appearing at about 585 and 645  $\text{cm}^{-1}$  are the Raman active  $\text{E}_1(\text{LO})$  mode [10] and IR active [11] absorption of ZnO, respectively.

A broad, non-symmetric absorption peak observed in the 900–1300  $\text{cm}^{-1}$  spectral range for all the

samples. Our computer-simulated decomposition showed four components of the emissions in this range. The peaks observed at about 1205 and 1247  $\text{cm}^{-1}$  correspond to the oxygen asymmetric stretch ( $\text{AS}_2$ ) transversal-optical (TO) and the  $\text{AS}_1$  longitudinal-optical (LO) mode of Si–O–Si linkage [12]. The peak observed at about 1135  $\text{cm}^{-1}$  is generally assigned to the out-of-phase oxygen motion associated with  $\text{Si}(\text{O}_4)$  configuration [13]. The position of these three peaks did not change very much from film to film, either with the variation of Si content or with the annealing temperature. However, the position of the other peak varied from 1103 to 1070  $\text{cm}^{-1}$ , with the increase of Si content and with the increase of annealing temperature. This peak is generally assigned to the TO mode of the in-phase asymmetric stretch ( $\text{AS}_1$ ) motion of oxygen atom along a line parallel to the axis through the two Si atoms [12,13]. A shift of this peak position is due to the change of oxygen content in  $\text{SiO}_x$  [13]. On incorporation of Si in ZnO at room temperature, some of the oxygen atoms bonded with Si to form  $\text{SiO}_x$ , and the rest form Si–O dangling bonds around the Si clusters. With the increase of Si content or with the increase of annealing temperature, the oxidation state of Si and the density of dangling bonds changes.

#### 4. Conclusions

Si in ZnO forms clusters that increase in size from 3.7 to 34 nm on annealing. The Si in the clusters are predominantly  $\text{Si}_3$  with triangular geometrical form. Though, the isomers like  $\text{Si}_2$ ,  $\text{Si}_4$  and  $\text{Si}_8$  have some reported [9] absorption peaks very close to 550, 500 and 500  $\text{cm}^{-1}$ , respectively, none of these isomers have absorptions corresponding to all peaks observed in our samples. The nanoclusters of  $\text{Si}_3$  are covered

with a  $\text{SiO}_x$  cap layer. With the increase of Si content in the composites and with the increase of annealing temperature, the structural geometry of the  $\text{Si}_3$  and the composition of the suboxidized silicon cap layer change. A further investigation is required to identify the structural and vibrational modes of Si clusters in ZnO more precisely.

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