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# Preparation of Ge/ZnO nanocomposites by radio frequency alternate sputtering

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## Abstract

Nanocomposite films of Ge/ZnO were prepared on quartz glass substrates by alternate RF sputtering of ZnO and Ge. Formation of nanometer sized Ge particles in the ZnO matrix was observed by transmission electron microscopy. The size of the nanoparticles and their optical properties depended strongly on the temperature of annealing. On increasing the temperature of annealing, the size of the Ge particles reduced and the band gap shifted to the higher energies. The higher energy shift of band gap was attributed to the quantum confinement effect in nanometer size Ge particles. An indirect to direct band gap transition was observed in Ge nanoparticles.

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## 1. Introduction

Nanocomposite materials consisting of very small particles of a guest substance (diameters less than 100 nm) dispersed through a host matrix are of intense current interest for their potential applications in chemical catalysis, electronic and photonic materials [1–5]. Semiconductor nanoparticles, commonly known as quantum dots or QDs, exhibit new quantum phenomena which have potential application in a variety of photonic devices [1–7]. Although, nanoparticles of direct band gap semiconductors like CdS and CdSe have been studied extensively, the recent discovery of

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photoluminescence (PL) from nanoparticles of indirect band gap semiconductors, such as Si or Ge, has generated much interest in these materials [8–15].

In comparison with the electronic properties of Si, Ge has a larger dielectric constant and smaller effective masses for electrons and holes, and the energy difference between indirect gap ( $E_g = 0.66$  eV at 300 K) and the direct gap ( $E_0 = 0.78$  eV) is smaller ( $\Delta E = 0.12$  eV). The effective Bohr radius  $a_B$  for wannier excitons in Ge is calculated to be about 24 nm. These electronic conditions lead to the expectation that it is much easier to change the electronic structure around the band gap of Ge.

By the inspiration of this viewpoint, several workers have prepared nanocrystalline Ge (nc-Ge) with different sizes using different techniques. Venkatasubramaniam et al. [16] have fabricated nanometer-sized planar Ge structure by plasma assisted etching of Ge using a  $CF_4/O$  gas mixture and observed PL near 1.9 eV in it. Paine and co-workers [17–18] have prepared nc-Ge by chemical reduction of an oxide alloy of  $Si_{1-x}Ge_xO_2$  formed by high-pressure oxidation. Fujii et al. [19] and Hayashi et al. [20] have prepared nc-Ge embedded in a gassy  $SiO_2$  matrix by RF co-sputtering technique and observed a very clear blue shift of the optical absorption edge as the average size of the nanocrystallites decreased. Maeda [21] has prepared nc-Ge on Si substrates by depositing Ge oxide films on it by RF co-sputtering and subsequent thermal annealing in argon atmosphere. Maeda and co-workers [22] have also reported the emission of orange PL band (2.18 eV) in nc-Ge embedded in silica matrix and explained the mechanism of PL emission in them through the quantum-confinement model.

Though the nc-Ge was prepared in  $SiO_2$  matrix by several researchers, no effort has been made to prepare nc-Ge embedded in functional matrix material like ZnO. In the present work, we report on the preparation of nc-Ge in ZnO matrix through RF alternate sputtering technique for the first time. Apart from the conventional applications of Ge/ $SiO_2$  nanocomposites, Ge/ZnO nanocomposites might have some special advantage in catalysis and electrolysis applications.

## 2. Experimental details

The composite films were prepared on quartz glass substrates by alternate deposition of ZnO and Ge using an RF magnetron sputtering system. At 45 mTorr argon partial pressure, the films of ZnO and Ge were deposited on the substrates alternately using a 100 W RF power. A ZnO film of about 80 nm was first deposited on the quartz glass by sputtering a ZnO target (5 cm diameter, 99.995%) for 10 min and then a Ge film of about 6 nm was deposited by sputtering a Ge target (5 cm diameter, 99.999%) for 1 min. The process was repeated for six times, and depositing a ZnO layer at last, the deposition process was terminated. The whole process was carried out by changing the substrate position on different targets (i.e. on ZnO and Ge targets) i.e. without bringing the films outside the deposition chamber before completing the deposition process. The total thickness of the structure was about 600 nm.

For the transmission electron microscopic (TEM) observations, the samples were prepared as follows: A 20 nm layer of ZnO was first deposited on a carbon coated NaCl pallet; then a layer of Ge of about 6 nm thickness was grown on it, and another 20 nm ZnO layer was grown on the Ge layer.

The as-grown samples were annealed at 200°C, 400°C and 600°C for 15 min in argon atmosphere. The crystallinity and chemical state of the films were studied by a Rigaku RAD-C diffractometer with  $\text{CuK}_\alpha$  radiation. A JEOL, JEM2000-FXII electron microscope was used for TEM observation on the samples. A Shimadzu UV-VIS 3100PC double beam spectrophotometer was used to study the absorption spectra of the composite films.

### 3. Results and discussion

Fig. 1 shows the TEM images of the composite films annealed at different temperatures. Formation of nanoparticles is clear from the micrographs. Depending

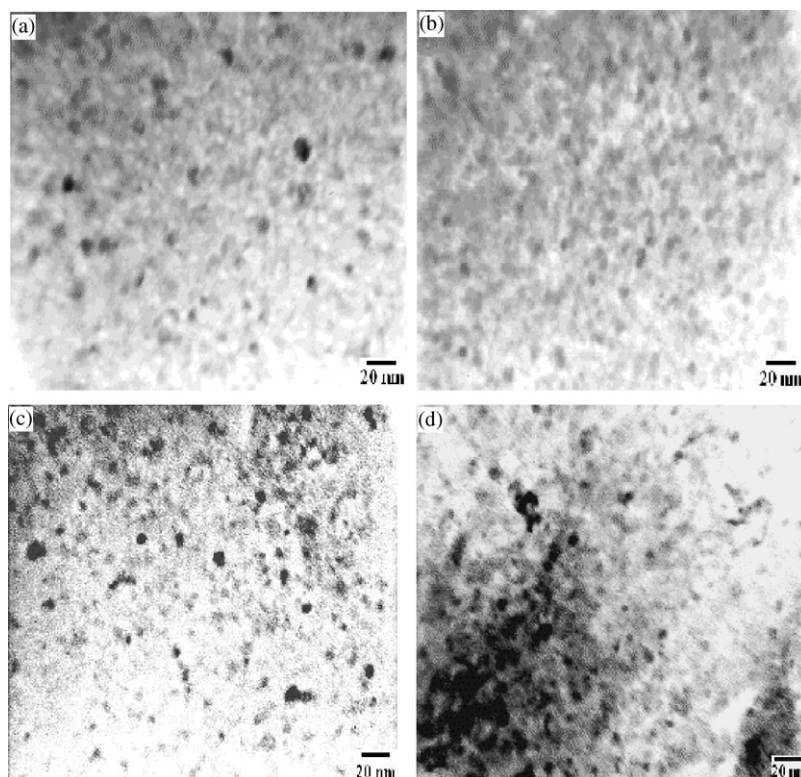


Fig. 1. TEM micrographs of Ge/ZnO composite films: (a) unannealed, (b) annealed at 200°C, (c) annealed at 400°C, and (d) annealed at 600°C.

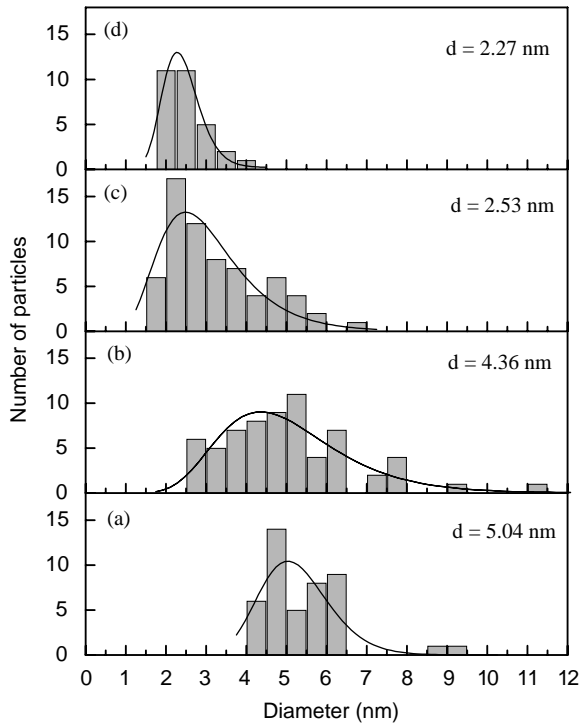


Fig. 2. Size distribution of Ge particles in the composite films: (a) unannealed, (b) annealed at 200°C, (c) annealed at 400°C, and (d) annealed at 600°C.

on the temperature of annealing, nanoparticles of different average size were formed and dispersed homogeneously in the ZnO matrix. Fig. 2 shows the size distribution of the nanoparticles in the composite films annealed at different temperatures. The best fitting of the measured size distributions followed a lognormal distribution. The average size of the nanoparticles decreased with the increase of annealing temperature.

Fig. 3 shows the XRD patterns of the composite films annealed at different temperatures. XRD patterns revealed the oxidized germanium peaks along with the peaks correspond to ZnO. With the increase of annealing temperature, the crystallinity of the ZnO matrix increased gradually and the peaks corresponds to GeO<sub>2</sub> became more intense. On increasing the annealing temperature to 400°C or above some of the oxidized germanium reduced, revealing the peaks correspond to elemental Ge.

Fig. 4 shows the absorption spectra of the composite films annealed at different temperatures. We can observe a steep increase of absorption at lower energies along with the absorption edge of ZnO near 3.27 eV, which correspond to the absorption due to the Ge nanoparticles formed in the ZnO matrix. The absorption coefficient  $\alpha$  of the composite films reaches to the order of  $10^3 \text{ cm}^{-1}$ , which is intermediate of the

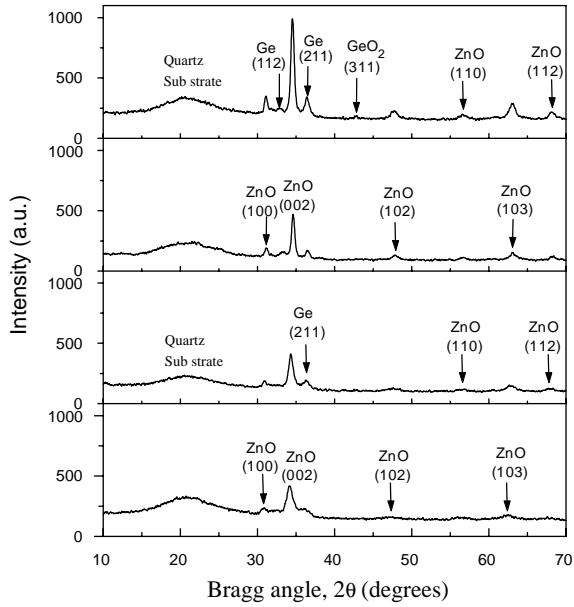


Fig. 3. XRD patterns of Ge/ZnO composite films: (a) unannealed, (b) annealed at 200°C, (c) annealed at 400°C, and (d) annealed at 600°C.

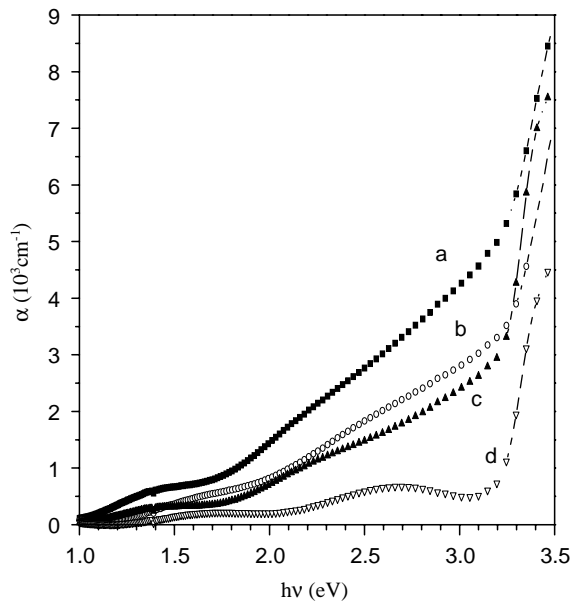


Fig. 4. Variation of absorption co-efficient with photon energy for the Ge/ZnO composite films: (a) unannealed, (b) annealed at 200°C, (c) annealed at 400°C, and (d) annealed at 600°C.

absorption of bulk Ge ( $10\text{--}10^2$ ) [23] and of bulk ZnO ( $10^4$ ). In a small range over the absorption edge, the energy dependence of  $\alpha$  for direct and indirect transitions are

$$\alpha = C_1(h\nu - E_d)^{1/2}, \quad (1)$$

$$\alpha = C_2(h\nu - E_i)^2, \quad (2)$$

respectively. Where  $C_1$  and  $C_2$  are constants,  $h\nu$  is the photon energy, and  $E_d$  and  $E_i$  are the direct and indirect absorption edge. As is well known, the energy band structure of the Ge single crystal has an indirect energy gap ( $\Gamma'_{25} \leftrightarrow L_1$ ) and a direct energy gap ( $\Gamma'_{25} \leftrightarrow \Gamma'_2$ ). So we tried to extract both the energy gaps for Ge particles using the above-mentioned two equations. However, the  $(\alpha h\nu)^2$  vs.  $h\nu$  plots followed better linear fit with the experimental results. In Fig. 5, the  $(\alpha h\nu)^2$  vs.  $h\nu$  plots for the

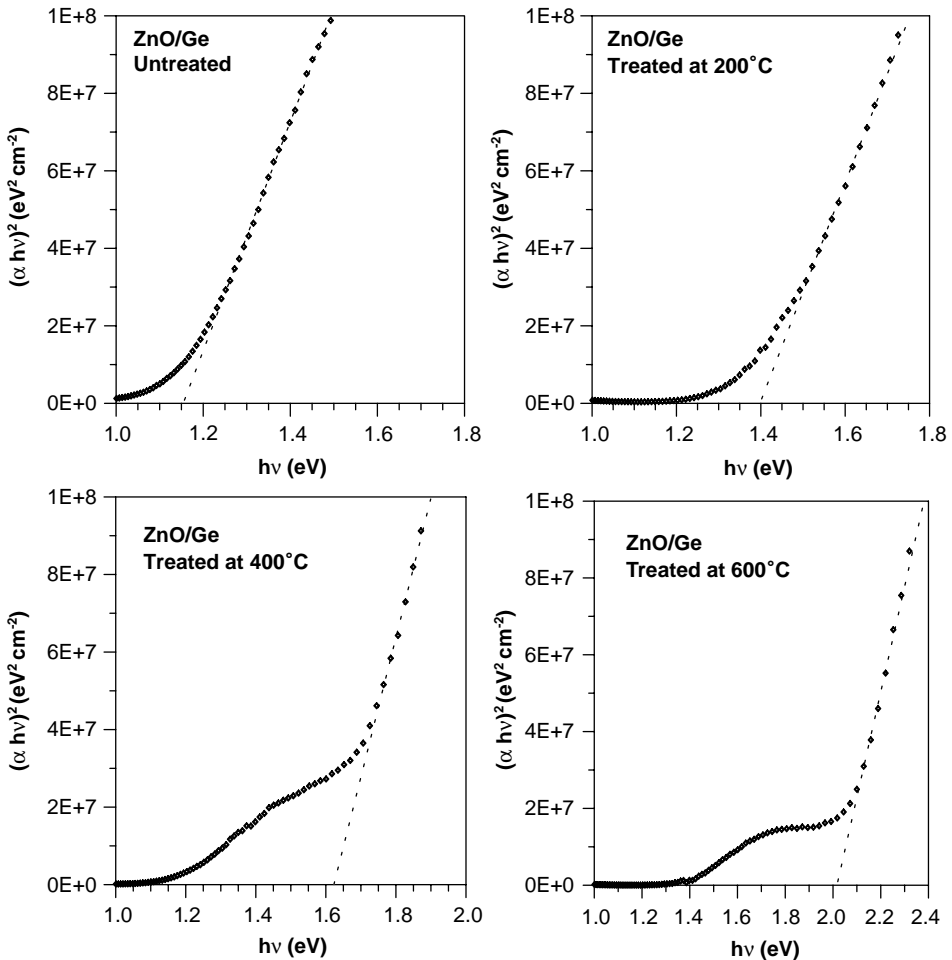


Fig. 5. The  $(\alpha h\nu)^2$  vs.  $h\nu$  plots for the composite films annealed at different temperatures.

Table 1

The band gap values of nc-Ge (annealed at different temperatures) embedded in ZnO matrix estimated from the absorption spectra

Sample	Annealing temp. (°C)	Band gap $E_0$ (eV)
Ge/ZnO	As-deposited	1.160
	200	1.400
	400	1.625
	600	2.025

Table 1

composite films annealed at different temperatures are presented. Well agreement of the absorption spectra with the Eq. (1), rather than with Eq. (2) suggests that the direct transition occurs in Ge QDs, indicating an indirect to direct band gap transition in small nc-Ge as suggested by Rossetti et al. [24]. From the  $(\alpha h\nu)^2$  vs.  $h\nu$  plots the direct band gaps of the nanoparticles were estimated and presented in Table 1. We can observe a significant increase in the band gap value with the decrease of particle size of the Ge nanoparticles. The direct band gap value varied from 1.16 to 2.02 eV for the variation of average particle size from 5.04 to 2.27 nm. Hayashi et al. [20] for their nc-Ge embedded in SiO<sub>2</sub> matrix have made a similar observation.

Theoretically [25–27], the energy band of nc-semiconductors embedded in insulating matrix becomes discrete and the energy gap increases with the decrease of average diameter of the particles. According to the theory [25–27], the blue shift of band gap (with respect to the bulk band gap value) is proportional to  $R^{-2}$  in the strong confinement region (i.e.  $R/a_B < 2.5$ , where  $R$  is the radius of the nanoparticle). However, our experimentally obtained blue shift of the band gap is not proportional to  $R^{-2}$  and is considerably lower than the expected theoretical shift, which might be due to the complicated band structure of the Ge single crystal. As has been mentioned earlier, Ge single crystal has an indirect energy gap ( $\Gamma'_{25} \leftrightarrow L_1$ ) and a direct energy gap ( $\Gamma'_{25} \leftrightarrow \Gamma'_2$ ), which are very close. The lowest electron discrete level of nc-Ge in an infinite well should be determined by the quantization of states near  $L_1$  and  $\Gamma'_2$ . So, the simple calculation of blue shift based on the effective mass equation near the conduction band edge may not be valid for the case of strong confinement ( $R \ll a_B$ ) as argued by Hayashi et al. [20].

#### 4. Conclusions

Ge nanoparticles embedded in ZnO matrix were successfully grown by alternate RF sputtering of ZnO and Ge. XRD spectra revealed that Ge incorporated in ZnO matrix remains in partially oxidized state. The average size of the nanoparticles decreased on increasing the annealing temperature. Annealing the films at 400°C or higher temperatures reduces the oxidation state of Ge. The optical absorption spectra revealed an indirect to direct conversion of band gap in small Ge particles. Observed blue shifts of the band gap in small Ge particles are due to the quantum

confinement effect in them, though the extent of the variation is not in agreement with the theoretically calculated value due to the complicated band structure of Ge single crystal.

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