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Optical characterization of Ge/ZnO nanocomposites

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Nanoparticles of Ge incorporated in ZnO matrix were synthesized by alternate r.f. sputtering of ZnO and Ge targets on quartz substrates. The composite films were annealed at different temperatures in argon atmosphere and characterized by transmission electron microscopy (TEM) and optical absorption spectroscopy. On increasing the annealing temperature, the size of the Ge particles decreased. Optical absorption of the samples revealed an indirect to direct transition of band gap in the Ge nanoparticles. The direct band gap of nanocrystalline Ge blue shifted on decreasing their average size due to quantum confinement effect in them.

Keywords: Thin film; Nanocomposites; Semiconductor particles

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 electronic and photonic materials. Semiconductor nanoparticles, commonly known as quantum dots or QD's, exhibit new quantum phenomena[1] which have potential application in a variety of photonic devices. Although, nanoparticles of direct band gap semiconductors like CdS and CdSe have been studied extensively, the recent discovery of photoluminescence from nanoparticles of indirect band gap semiconductors, such as Si or Ge, has generated much interest in these materials[2].

Several workers have prepared nanocrystalline Ge (nc-Ge) with different sizes using different techniques. Venkatasubramaniam et al.[3] have fabricated nanometer-sized planar Ge structure by plasma asisted etching of Ge using a CF_4/O_2 gas mixture and observed photoluminescence (PL) near 1.9 eV in it. Paine and co-workers[4,5] 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.[6] and Hayashi et al.[7] have prepared nc-Ge embedded in a gassy SiO_2 matrix by r.f. co-sputtering technique and observed a very clear blue shift of the optical absorption edge as the average size of the nanocrystallites decreased. Maeda and co-workers[8,9] have reported the emission of orange PL band (2.18 eV) in nc-Ge embedded in silica matrix and explained the mecanism 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 and optical characterization of nc-Ge in ZnO matrix through alternate r.f. sputtering technique. Apart from the conventional applications of Ge/SiO_2 nanocomposites, Ge/ZnO nanocomposites might have some special advantages 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 r.f. sputtering apparatus. The ZnO and Ge films were deposited on quartz substrates alternatively using 100W r.f. power at $15x10^{-3}$ argon partial pressure. 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 15 minutes and then a Ge film of about 6 nm was deposited by sputtering a Ge target (5 cm diameter 99.999%) for 1 minute. The process was repeated for 6 times and was terminated by depositing a ZnO layer at last. The whole process was carried out by changing the substrate position on different targets. The total thickness of the structure was about de 600 nm. For the transmission electron microscopic (TEM) observations, the samples were prepared on carbon coated NaCl pallets. A 15 nm layer of ZnO, a 6 nm layer of Ge and another 15 nm layer of ZnO were deposited successively on the carbon coated NaCl pallet. The films were transferred to the copper microgrids by floating them on water. The as-grown samples were annealed at 200, 400 and 600^0C for 15 minutes in argon atmosphere. For TEM observations, a JEOL, JEM2000-FXII electron microscope was used. A Shimadzu UV-Vis 3101PC double beam pectrophotometer was used to study the absorption spectra of the composite films.

3. Results and discussion

Figure 1 shows the typical TEM micrograhs for the as-grown and annealed composite films. Formation of nano-clusters in the matrix is clear from the contrast of the

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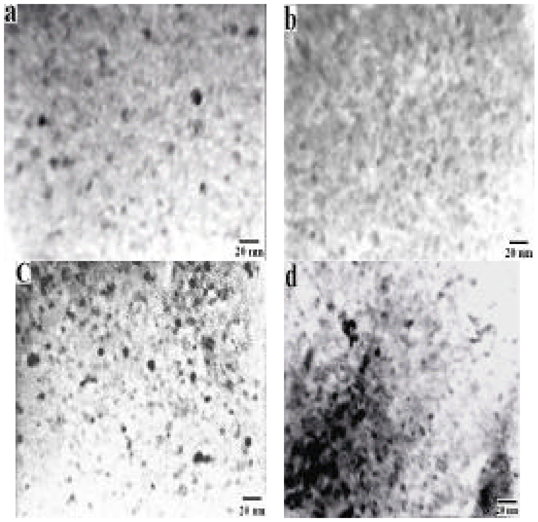

Figure 1. TEM micrographs for the Ge/ZnO composite films a) as-grown, and annealed at b) 200, c) 400 and d) 600 ^{0}C.

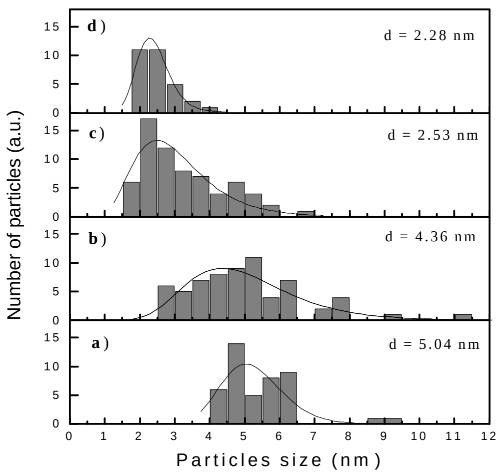

Figure 2. Size distribution of the Ge particles in the composite films annealed at different temperatures. The solid lines are log-normal functions.

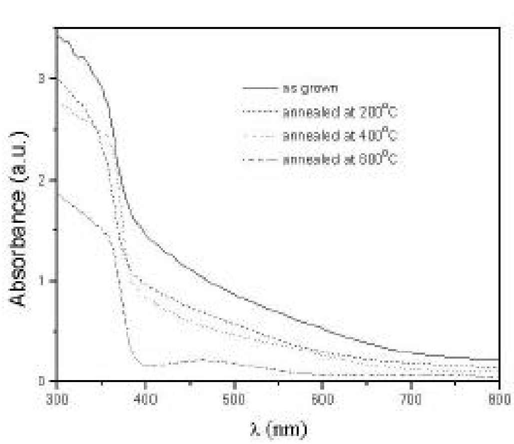

Figure 3. Optical absorption spectra of the Ge/ZnO composite films annealed at different temperatures.

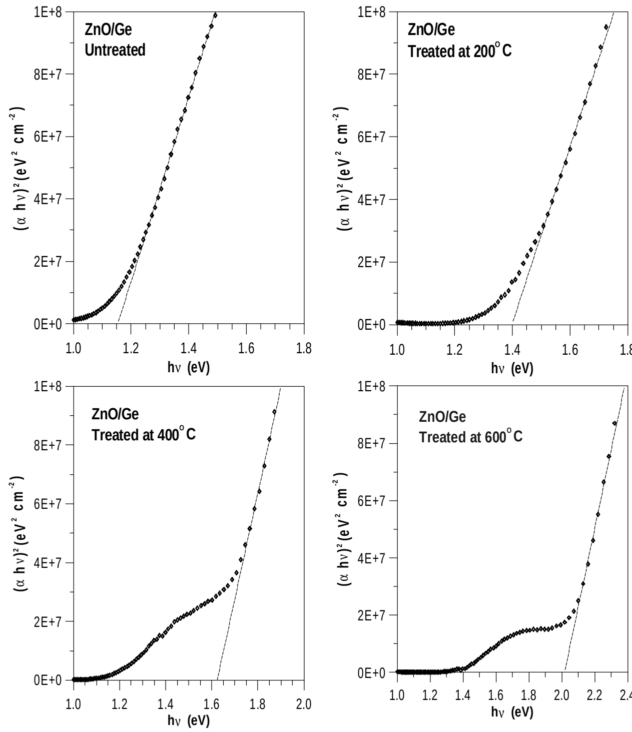

Figure 4. $(\alpha h\nu)^2$ vs. hν plots for the Ge nanoparticles formed in the ZnO matrix and annealed at different temperatures.

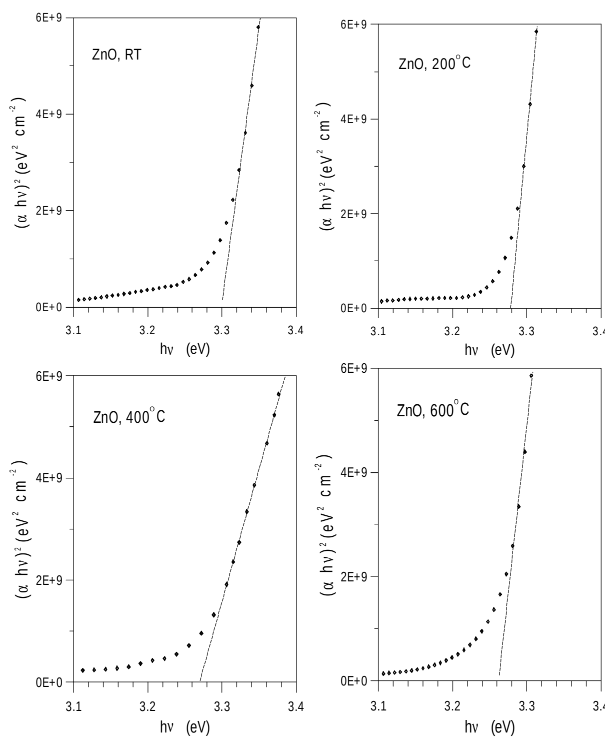

Figure 5. $(\alpha h\nu)^2$ vs. hν plots for the ZnO matrix annealed at different temperatures.

micrographs. Depending on the temperature of annealing, nanoparticles of different average size were formed and dispersed homogeneously in the ZnO matrix. Figure 2 shows the size distributions of the nano-clusters formed in the composite films as determined from the TEM micrographs. Depending on the temperature of annealing, the average size of the nanoparticles varied from 5.04 to 2.28 nm. With the increase of annealing temperature the average size of the nanoparticles decreased. So, the diameter of Ge particles in the ZnO matrix could be controlled by adjusting the temperature annealing.

Figure 3 shows the room temperature optical absorption spectra for the Ge/ZnO composite filmes annealed at different temperatures. We can clearly observe two absorption slopes for each spectrum in between 700-400 and 400-350 nm spectral ranges. We attribute the absorption in the former region to the absorption in nc-Ge particles and the latter to the ZnO matrix. The absorption in both the regions fitted well with the $(\alpha h\nu)^2$ vs. hν plots indicating direct optical transition in both nc-Ge and ZnO. In figures 4 and 5, the $(\alpha h\nu)^2$ vs. hν plots for 700-400 and 450-350 nm (i.e. for nc-Ge and ZnO) regions are presented.

From those figures, the direct band gap (E_g^d) for nc-Ge and ZnO are calculated and presented in Table 1. From the table, we can observe that the band gap of ZnO varied from 3.30 to 3.26 eV for increasing the annealing temperature up to 600^0C. Such a variation of band gap of ZnO can be attributed to the increased crystallinity of the matrix on annealing. On the other hand, the band gap of nc-Ge increased from 1.150 to 2.025 eV on annealing. Such an increase in band gap value is due to the reduction of particle size value (ref. Figure 2) of the Ge particles and can be attributed to the quantum confinement of electrons and holes in them. Good fitting of the optical absorption datas with $(\alpha h\nu)^2$ vs. hν plots indicates an indirect to direct transition of optical band gap in nanocrystalline Ge.

Table 1. Band gap variation of Ge nanoparticles and ZnO (matrix) on annealing.

Sample	**Temperatura of annealing** (°C)	E_g^d (eV)
	RT	3.30
ZnO	200	3.28
	400	3.27
	600	3.26
	RT	1.150
ZnO/Ge	200	1.400
	400	1.625
	600	2.025

4. Conclusion

Ge/ZnO composite films were grown by alternate r.f. sputtering technique. The size and density of the nanoparticles depended on the temperature of annealing. The size of the nanoparticles decreased with the increase of temperature. Observed blue shifts of the band gap value in Ge nanoparticles are due to the quantum confinement effect in them. An indirect to direct optical transition occurs in Ge nanoparticles.

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References

[1] X.C. Sheng, Optical Properties of Semiconductors (Scientific, Beijing, 1992).
[2] Frank W. Wise, Acc. Chem. Res., **33** 773-780 (2000).
[3] R. Venkatasubramaniam, D.P. Malta, M.L. Timmons, and J.A, Hutchby, Appl. Phys.Lett. **59** (1991) 1603.
[4] D.C. Paine, C. Caragianis, and Y. Shigesato, Appl. Phys. Lett. **60** (1992) 2886.
[5] D.C. Panie, C. Caragianis, T.Y. Kim, and Y. Shigesato, Appl. Phys. Lett. **62** (1993) 2842.
[6] M. Fujii, S. Hayashi, and K. Yamamoto, Jpn. J Appl. Phys. **30** (1991) 687.
[7] R. Hayashi, M. Yamamoto, K. Tsunetomo, Y. Osaka, and H. Masu, Jpn. J Appl. Phys. **29** (1990) 756.
[8] Y. Maeda, Phys. Rev. **B51** (1995) 1658.
[9] Y. Maeda, N. Tsukamoto, Y. Yazawa, Y. Kanemitsu, and Y. Masumoto, Appl. Phys. Lett. **59** (1991) 3168.