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Quantum confinement effect in SiO_2 films containing Ge microcrystallites

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SiO_2 thin films embedded with Ge microcrystallites (Ge-SiO_2 films) were prepared by RF-magnetron co-sputtering method from a composite target of Ge and SiO_2. The average size of Ge crystallites can be modulated by the experiment parameters. The optical absorption and non-linear optical properties of Ge-SiO_2 films were measured. The blue shift of the optical absorption edge, the saturated absorption and two-photon absorption under the condition of resonant absorption have been observed, and are discussed according to the quantum confinement effect.

1. Introduction

There has been a great deal of interest in the investigation of optical processes in natural zero-dimensional heterostructure (or self-organized dots) during last decate. Semiconductor crystallites, which are small compared to the bulk exciton Bohr radius, commonly referred to nanometer-scale clusters or quantum dots, exhibit three-dimensional electron and hole confinement [1, 2]. They show discrete, large-molecule-like electronic states that shift to high energy with smaller particle size. The quantum confinement effect on optical properties in glassy thin films embedded with semiconductor microcrystallites is the subject of much current research. The interest arises because of the great potential of these materials for optical device application due to their nonlinear optical property [3–6]. At present, the quantum confinement effect is still insufficiently understood due to the complexity of the system with large uncharacterized distribution of sizes, shapes, stoichiometry, defects, and surface interactions. Germanium is one of the important elemental semiconductors, and its microcrystallites embedded in SiO_2 glassy thin film is a very interesting material. In this paper, we report the quantum confinement effect on the results of optical absorption and optical nonlinear property measurement from different specimen in which the average size of crystallites is different.

2. Experimental technique

The samples were prepared by the RF magnetron sputtering technique on substrates of quartz glass ($\phi 10 \times 0.5$ mm) with a composite target of 99.999% purity SiO_2 plate (50 mm in diameter) attached several Ge (the purity is 99.999%) chips on the surface of it. After vacuum pumping, the co-sputtering was performed with an Ar pressure of 2 Pa and RF power of 200 W at different substrate temperature in the chamber evacuated to 2×10^{-4} Pa before argon gas in a flow of 40SCCM was introduced through a mass flow controller. The thickness of the films was about 500 nm.

XRD measurements were carried out with a Rigaku D/Max-3C diffractometer (Cu k_α x-ray, $\lambda = 0.15406$ nm). Optical absorption (Perkin-Elmer, λ-17) were used to investigate the quantum confinement effect. Sample containing Ge crystallites of 3.2 nm in diameter was used to measure the nonlinear optical properties by use of a Z-scan equipment (Fig. 1) [7]. The experiment condition is as follows: the power of a continuous Gaussian beam (633 nm or 488 nm) with diameter of 1 mm is 30 W. After passing through a lens ($f = 60$ nm), the beam waist is 12 μm in radius and the power density is 10^4 W/cm^2 at the focal plane. For nonlinear optical absorption measurement, the detector (D_2) is used with an open aperture to receive all beams passing through the sample. During experiment procedure the sample is moved from $-Z$ towards the aperture with a step of 1 mm controlled by a computer.

3. Result and discussion

Fig. 2 shows the XRD patterns of films prepared at different substrate temperature (T_s). When T_s is higher than 500°C, three obvious peaks of Ge(111), (220) and (311) appear, which indicates the formation of Ge nanocrystallites (nc-Ge). With the increase of T_s, the XRD peaks become sharper and the full width at half-maximum of each peak decreases. It means that the average size of nc-Ge increases. For the (111) peak, the average size of nc-Ge can be evaluated according to Scherrer formula is about 3.2, 4.8 and 6.5 nm, respectively.

Fig. 3 shows the absorption spectra of films with that of bulk Ge single crystal (curve c) for comparison.

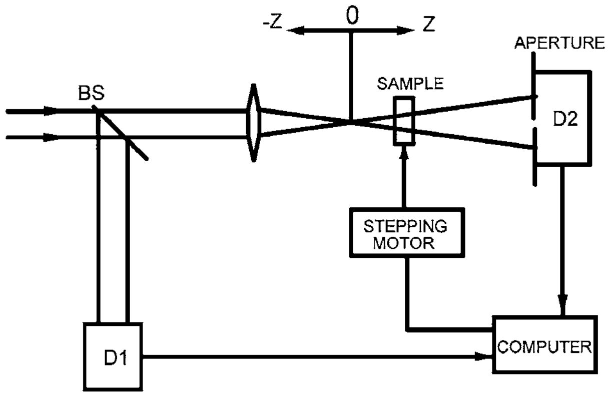

Figure 1 Schematic diagram of Z-scan equipment.

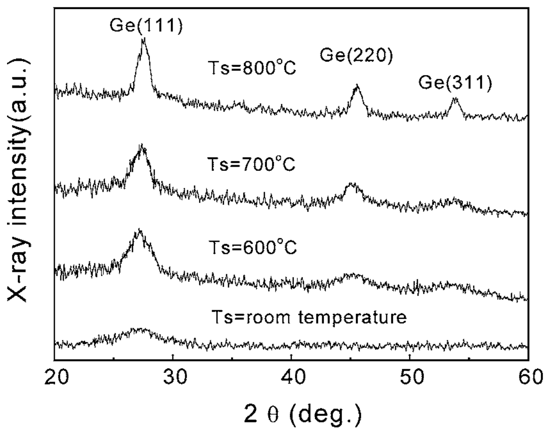

Figure 2 XRD patterns of samples prepared at different T_s.

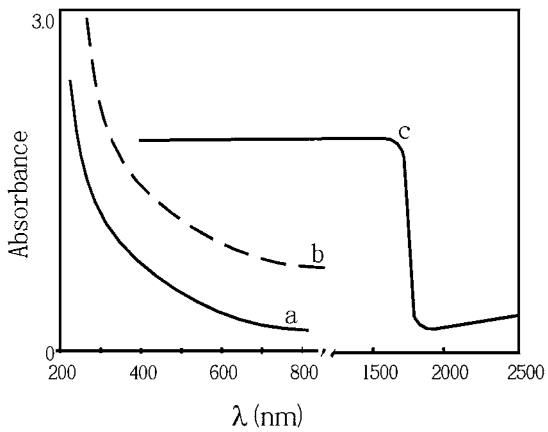

Figure 3 Absorption spectra of films (a, b) and bulk Ge crystal (c).

Curves (a) and (b) in Fig. 2 are those of films prepared at substrate temperature of 600°C and 700°C, respectively. As shown in Fig. 2, the films are almost transparent in the visible range, showing obvious absorption near 200–400 nm region, and the optical absorption properties are related to the average size of Ge. From the optical absorption spectra, the absorption edges of films clearly exhibited blue shifts compared with the bulk Ge, which could be seen for all Ge-SiO_2 films, and thus, we could believe that the quantum confinement effect exhibits in the Ge microcrystallites embedded in SiO_2. We have tried to obtain the values of optical band gaps from the experimental absorption data obtained from the commonly used $\alpha h\nu \propto (h\nu - E_g)^2$ relations has been done for Si : H films [8]. A typical plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for $\lambda = 355$ nm is shown in Fig. 4, which corresponds to curve (a) in Fig. 4, where α and $h\nu$ are the absorption coefficient and the photo energy, respectively. The absorbance data is in accordance with the linear relationship and the optical band gap $E_g = 2.90$ eV is determined by $(\alpha h\nu)^{1/2}$ vs. $h\nu$ measurement. The optical band gaps of the films are larger than that of the bulk Ge crystal by about 0.66 eV at room temperature.

TABLE I Optical band gap and blue shift of optical absorption edge of Ge microcrystallites

Average diameter (nm)	9.0	6.5	4.8	3.2
Optical band gap (eV)	1.25	1.61	2.26	2.90
Blue shift ΔE (eV)	0.59	0.95	1.60	2.24

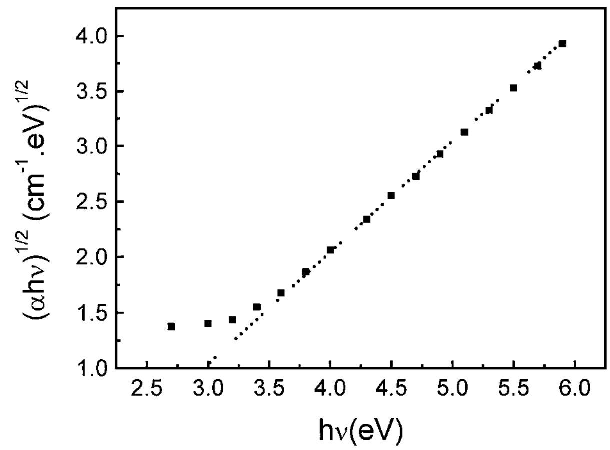

Figure 4 The relation between $(\alpha h\nu)^{1/2}$ and $h\nu$ of the Ge-SiO_2 film.

The optical band gaps of the Ge-SiO_2 films are larger than that of bulk Ge crystal. Table I shows the blue shift of samples containing different average size of Ge microcrystallites, from which it can be seen that the larger the blue shift of the samples the smaller of the average size of Ge microcrystallites embedded in SiO_2 thin films. As we know, due to the quantum confinement effect, the energy band of microcrystallites embedded in insulating matrix becomes discrete, the energy gap increases with decrease of particle size [9, 10], and the blue shift of optical absorption edge can be expressed qualitatively as:

$$\Delta E_g = \frac{h^2}{8\mu R^2} - \frac{1.78e^2}{\varepsilon R} + \text{smaller term}$$

where R is the radius of the particles, ε is the dielectric constant of the surrounding materials, $1/\mu = 1/m_e + 1/m_n$. Our results agree with that of the equation qualitatively. It is confirmed that the quantum confinement effect exist in the samples of Ge embedded films.

The measurement results of nonlinear absorption of the sample under irradiation of the different wavelength are shown in Fig. 5a and b. For 633 nm irradiation, the absorption is decreasing with the increase of the irradiation intensity (Fig. 5a). For 488 nm irradiation, the absorption is increasing with the increase of the irradiation intensity. It is obvious that there exist two absorption transitions. Different absorption transition gives rise to different nonlinear absorption feature of the sample irradiation under beams of the different wavelength. The irradiation wavelength is resonated with

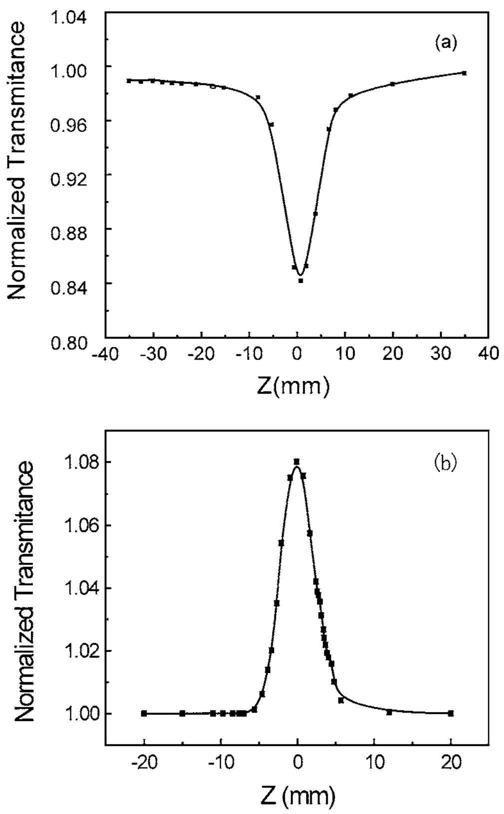

Figure 5 Z-scan measure data of nonlinear absorption (a) $\lambda = 633$ nm, (b) $\lambda = 488$ nm.

1s–1s transition, which satisfies $\Delta l = 0$ selection rule of the transition, in Fig. 5b and the resonant absorption occurs. For the weak irradiation, the irradiation intensity has no influence on the resonant absorption coefficient. But with the increasing of the irradiation intensity, the saturated absorption of the transition of the two-level occurs and the absorption coefficient decrease with the increase of the irradiation intensity. For Fig. 5a, since the optical energy gap of the Ge nanocrystallites of 3.2 nm is about 2.90 eV, the 1s–1s transition can't be resonated by the irradiation beam of 633 nm (1.96 eV). But the beam of 633 nm satisfies the condition of $E_g < 2h\nu < 2E_g$, so two-photo absorption is permitted. For Fig. 5a, the irradiation beam may be resonated with the 1s–1p transition, which satisfies the $\Delta l = 1$ selection rule of the two-photon absorption, it exhibits the two-photon absorption features. Under the quasi-resonance condition in the present experiment, two electrons and two holes are born as soon as two photons absorbed, that is, the confined biexcition which is the sequence of the two-photon absorption comes into existence.

The nonlinear optical absorption behavior of samples illustrates that the absorption transition must obey the corresponding selection rules, which are established on the hypothesis that the electrons and holes are regarded as two independent particles with no interaction between them. In this case, we have a two-level system in which electrons and holes are independent of each other. The experiment gives the evidence that the hypothesis is reasonable and the quantum states of electron and hole are dependent on the quantum confinement effect. The Coulomb interaction effect, which is weaker than the quantum confinement effect, is negligible.

4. Conclusion

In summary, optical absorption and nonlinear optical absorption of Ge-SiO_2 thin films were measured to study the quantum confinement effect. From the optical absorption measurement results, the blue shift of the optical absorption edge that increase with the decrease of the particles size is obtained. From the nonlinear optical absorption measurement, it is observed that under the condition of resonant transition, the phenomenon of the saturated absorption and two-photon absorption show that the nonlinear behavior of absorption transition of Ge particles is possessed of the two-level characteristics. It is discussed according to the quantum confinement effect.

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