Quantum Confinement Effect in SiO_2 Thin Films Embedded with Semiconductor Microcrystallites

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Abstract

SiO_2 thin films embedded with Ge microcrystallites (Ge-SiO_2) were prepared by use of r.f. co-sputtering technique from a Ge , SiO_2 composite target. The size of Ge crystallites can been 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 decade. Semiconductor crystallites which are small compared to the bulk exciton Bohr radius, commonly referred to as 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 applications due to their nonlinear optical properties[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 properties measurement from different specimen in which the average size of crystallites is different.

2. Experiment detail

The Ge- SiO_2 thin films of about 500nm in thickness were prepared by the r.f. co-sputtering technique from a Ge, SiO_2 composite target on substrates of quartz glass(Φ 10 × 1.5mm). The average size of Ge crystallites can be modulated effectively by the substrate temperature, and is in the range of 3~10nm, which is evaluated by XRD as well as TEM, according to the substrate temperature.

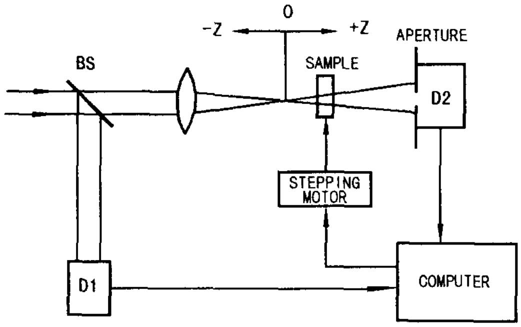

Fig. 1 Schematic diagram of Z-scan equipment

Optical absorption spectra of thin film samples were measured by spectrophotometer in the range of 0.2~0.8 μ m, and compared with that of a bulk Ge single crystal. Sample containing Ge crystallites of 3.2nm 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 continous Gaussian beam (633nm or 488nm) with diameter of 1mm is 30w. After passing through a lens (f=60mm), the beam waist is 12 μ m 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 1mm controlled by a computer.

3. Result and discussion

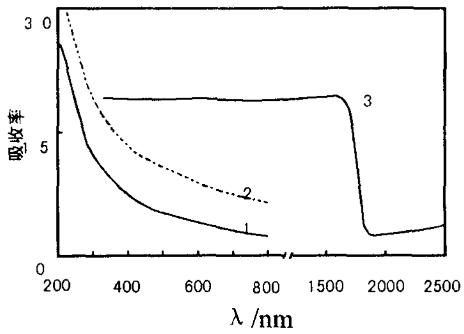

Fig. 2 Optical absorption spectra of Ge-SiO_2 thin films (1,2) and single crystal of Ge (3)

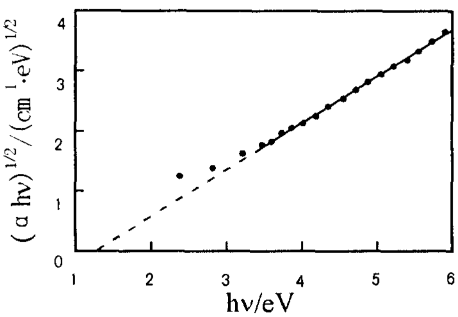

Fig. 3 Typical $(\alpha h\nu)^{1/2}$ vs. hν plot from which the optical band gap is determined

Fig. 2 shows the optical absorption spectra of samples with that of a bulk Ge single crystal (Fig. 2, curve 3) for comparison. Curves 1 and 2 in Fig. 2 are those of films prepared at substrate temperature of 600℃ and 700℃, respectively. As shown in Fig. 2 the films are almost transparent in the visible range, showing obvious absorpion near the 200 ~ 400nm region, and the optical absorption properties which are related to the average grain size of Ge. From the optical absorption spectra, the absorption edges of the films clearly exhibite blue shifts compared with the bulk Ge, which can be seen for all Ge-SiO_2 films, and thus, we could believe that the quantum confinement effect exhibits in the Ge microcrystallittes embedded in SiO_2 . We have tried to obtain the values of optical band gaps from the experiment absorption data by use of $\alpha h\nu \propto (h\nu - Eg)^2$ relation as has been done for Si:H films[8]. A typical plot of $(\alpha h\nu)^{1/2}$ vs. hν is shown in the Fig. 3, which corresponds to curve 1 in Fig.2, where α and hν are the absorption coefficient and the photon energy, respectively. From Fig. 3, we can see the optical band gap for this sample is 1.25ev, which is much larger than that of bulk Ge crystal.

Table 1 Optical band gap and blue shift of optical absorption edge of Ge microcrystals

average diameter (nm)	9.0	6.5	4.8	3.2
optical band gap (ev)	1.25	1.61	2.26	2.95
blue shift ΔE (ev)	0.59	0.95	1.60	2.29

The optical band gaps of the Ge-SiO_2 films are larger than that of bulk Ge crystal. Table 1 shows the blue shifts of samples containing different average size of Ge microcrystallites, from which it can be seen that the blue shift of samples is larger with the smaller of 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 the 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:

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

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

The measurement results of nonlinear absorption of the sample under irradiation of different wavelength are shown in Fig. 4 and Fig. 5. For 633nm irradiation, the absorption is decreasing with the increase of the irradiation intensity (Fig.4). For 488nm 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

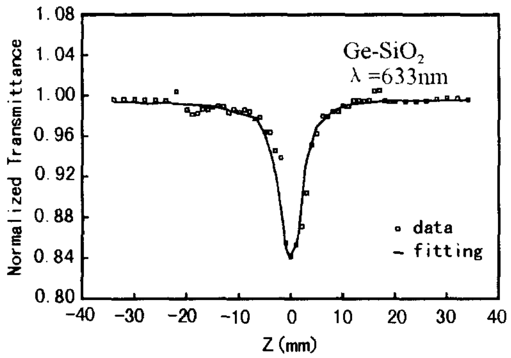

Fig. 4 Z-scan measured data of nonlinear absorption

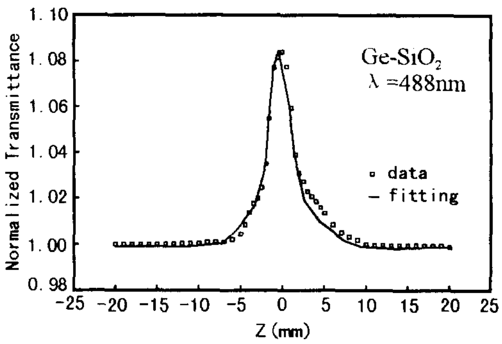

Fig. 5 Z-scan measure data of nonlinear absorption

rise to different nonlinear absorption feature of sample irradiated under beams of different wavelength. The irradiation wavelength is resonated with 1s~1s transition, which satisfies the $\Delta l=0$ selection rule of the transition, in Fig. 5 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. 4, since the optical energy gap of the Ge nanocrystallites of 3.2nm is about 2.95ev, the 1s~1s transition can't be resonated by the irradiation beam of 633nm (1.96ev). But the beam of 633nm satisfies the condition of $Eg<2\ h\nu<2Eg$, so two-photo absorption is permitted. For Fig. 4, 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 biexciton 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 indipendent 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 $Ge\text{-}SiO_2$ thin films were measured to study the quantum confinement effect. From the optical absorption measurement results, the blue shift of the optical absorption edge which increases with the decrease of the particle 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 transiton of Ge particles is possessed of the two-level characteristics. It is discussed according to the quantum confinement effect.

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