Influence of Microcrystal Size on Third-Order Nonlinear Optical Susceptibility of CdSe Embedded SiO₂ Glass Thin Films Prepared by Rf-Sputtering

Hiroyuki NASU, Akimasa TANAKA, Kenji KAMADA,* Yoshitsugu YAMAMOTO,
Yasuhiro MATSUZAKI and Tadanori HASHIMOTO

Department of Chemistry for Materials, Faculty of Engineering, Mie University, 1515, Kamihama-cho, Tsu-shi, Mie 514-8507
*Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, AIST Kansai,
1-8-31, Midorigaoka, Ikeda-shi, Osaka 563-8577

高周波スパッタリング法により作製した CdSe 含有 SiO₂ ガラス薄膜の三次の 非線形光学効果における微粒子粒径の影響

那須弘行・田中暁優・鎌田賢司*・山本佳嗣・松崎泰拓・橋本忠範

三重大学工学部分子素材工学科, 514-8507 三重県津市上浜町 1515
*産業技術総合研究所関西センター光技術研究部門, 563-8577 大阪府池田市緑丘 1-8-31

CdSe microcrystals with various sizes was successfully embedded in SiO₂ glass matrix by magnetron rf-sputtering technique. The mean size of microcrystals was controllable by changing the relative surface area ratio of the CdSe chips to the matrix in the target, and increased with increasing the relative area. The negative real part of the third-order optical susceptibility was seen for all of the present films, and the magnitude of the absolute value of real part increased with increasing concentration of CdSe. The imaginary part due to two photon absorption also increased with the CdSe concentration. After normalized with respect to the concentration, it was revealed that actual optical third-order nonlinearity of the CdSe microcrystals increased as the mean size decreased, in other words as the quantum confinement effect increased.

[Received May 27, 2002; Accepted July 11, 2002]

Key-words: Third-order optical nonlinearity, Semiconductor microcrystals embedded glass, Z-scan technique, Optical Kerr Effect, Two photon absorption, Quantum size confinement effect

1. Introduction

Since Jain and Rind reported large third-order optical nonlinearity,¹⁾ the semiconductor microcrystals-embedded glasses have been extensively studied. Although there are several ways to prepare semiconductor microcrystals-embedded glasses, such as conventional melt-quenching and sol-gel methods, Rf-sputtering technique has advantages in embedding glasses with various kinds of semiconductor microcrystals, which are even volatile or reactive with atmosphere or matrix substances, and in preparing such composites in the form of films at low temperatures.^{2),3)} When the semiconductor microcrystals with the size below 10 nm are embedded in the dielectric materials, quantum confinement effect comes to appear. Then, the oscillation strength between electrons and holes are drastically increased and the incident electromagnetic wave is concentrated to the particles in the transparent composite films. The optical third-order nonlinearity, thus, is significantly enhanced. Furthermore, because the quantum size confinement effect restricts the spacial location of excited electrons and holes, relaxation takes place quickly as in ps order.

There are two categories for quantum confinement effect.⁴⁾ One is the exciton confinement effect which is for the semiconductors with small exciton Bohr radius (r_B), compared to microcrystal radius (R) or ($R/r_B > 4$), and the other is electron-hole independent confinement effect for the semiconductors with large exciton Bohr radius or ($R/r_B < 2$). For examples, CuCl and CuBr are the former case, and CdSe, GaAs and Si are the latter case. As far, the study on quantum confinement effect has been mainly concentrated to semiconductor microcrystals exhibiting the exciton confinement effect, and there has been revealed much information on the glasses embedded with such microcrystals. In specific, significant influence of the mean size of the

microcrystals has been reported by a group of Nagoya University.⁵⁾ However, for the semiconductor microcrystals which show the electron-hole independent confinement effect, there are only a few experimental works^{6),7)} on the influence of the mean crystal size on the optical third-order nonlinearity, although it has been theoretically predicted.⁵⁾ Therefore, this paper reports the influence of the mean size of CdSe microcrystals in glass matrix (SiO₂ glass) on the optical third-order nonlinearity examined by Z-scan technique using fs pulse laser.

2. Experimental procedure

The magnetron Rf-sputtering equipment (Hirano Koon, KS-1002) was used to prepare the CdSe microcrystals-embedded SiO₂ glass films. In order to prepare the films, the composite target method was adopted. That is, the CdSe (Kojundo Kagaku, 99.99% purity) chips of 1 mm in diameter were placed on SiO₂ glass plate (Kojundo Kagaku, 99.99% purity). The relative surface area of CdSe chips in the targets was 3.8, 5.2, 6.6, 8.0 or 11.0%. The substrates used were SiO₂ glass for optical measurements including Z-scan, offset Si single crystal for X-ray diffraction (XRD) measurement, and KBr pellet for transmission electron spectroscopy (TEM), respectively. The substrate temperature was 200°C. The sputtering gas used was high purity Ar, input power was kept at 75 W and the distance between target and substrate was 40 mm. The sputtering time was usually 3 h, and for TEM observation it was 80 to 120 s.

The XRD measurement was performed to determine the crystal phase of CdSe. The X-ray source was Ni-filtered CuK α radiation generated at 40 kV and 100 mA. Measurement was carried out in the step-scan mode in the range from $2\theta = 20^\circ$ to 50° , with the step interval of 0.05° and of 2 s.

With respect to chemical state of CdSe microcrystals embedded in SiO₂ glass thin films, X-ray photoelectron spectroscopy (XPS) measurement (Shimadzu ESCA750, ESCA PAC 760) was carried out. The X-ray source used was Mg K α radiation. The peaks measured were Cd 3d_{5/2}, Se 3d, Si 2p and C 1s. The C1s peak (285eV) was used as a reference for calibrating the surface charge effect. In order to estimate the concentration of CdSe in the films, calibration curve of the XPS peak intensity was obtained by using the mixtures of CdSe and SiO₂ powders (10 mol%, 30 mol% and 50 mol%).

The mean size and size distribution of microcrystals were measured by using TEM (Hitachi, H-9000). The KBr pellet on which composite film deposited was soaked into distilled water, and the separated films was put on the copper mesh. The acceleration voltage applied for TEM observation was 300 kV.

The film thickness was measured by scanning electron microscopy (SEM) (Hitachi, S-2300). The typical thickness of the derived films was about 1.5 μ m.

The bandgap energy of microcrystals embedded in SiO₂ film was explored by NIR-Visible-UV spectrometer (Shimadzu, UV-3100). For that purpose, we measured optical spectra from 190 to 1000 nm with scan speed of 200 nm/min.

Z-scan measurements were carried out at AIST Kansai Center. The titanium: sapphire laser generating 116 fs pulses and 10 Hz repetition at 699 nm was used. Real part of $\chi^{(3)}$ ($\text{Re}\chi^{(3)}$) is estimated from the ratio of the incident power dependence of ΔT_{PV} , which is the difference of top and bottom of the Z-scan spectra, of the sample to that of the reference SiO₂ glass. The $\text{Re}\chi^{(3)}$ is related to nonlinear refractive index (γ) as⁸⁾

$$\text{Re}\chi^{(3)} = 2n_0^2\epsilon_0c\gamma \quad (1)$$

where n_0 is linear refractive index, ϵ_0 is dielectric constant of vacuum and c is light velocity. Imaginary part of $\chi^{(3)}$ ($\text{Im}\chi^{(3)}$) was calculated as follows. At first, q_0 was estimated by fitting the experimental transmittance to the following equation

$$T(z, S=1) = \frac{1 - \alpha L_{\text{eff}}}{\sqrt{\pi q(\xi)}} \int_{-\infty}^{\infty} \ln[1 + q(\xi) \exp(-x^2)] dx$$

$$\text{with } q(\xi) = q_0 / (1 + \xi^2) \quad (2)$$

where ξ is the normalized location in z axis with z_R in Rayleigh range, α is linear absorption coefficient, L_{eff} is effective path length, $S=1$ stands for open aperture condition, and q_0 is parameter. The q_0 is related to two photon absorption coefficient (β), incident light intensity (I_0) and effective pass length (L_{eff}) as

$$q_0 = \beta I_0 L_{\text{eff}} \quad (3)$$

Thus, $\text{Im}\chi^{(3)}$ is related to β as,

$$\text{Im}\chi^{(3)} = \frac{n_0^2\epsilon_0c^2}{\omega} \beta \quad (4)$$

where ω is angular frequency. The optical susceptibility $\chi^{(3)}$ is given, as follows⁸⁾

$$|\chi^{(3)}| = \{(\text{Re}\chi^{(3)})^2 + (\text{Im}\chi^{(3)})^2\}^{1/2} \quad (5)$$

3. Results and discussion

Typical XPS spectra are shown in Figs. 1(a), (b) and (c). The peaks of Cd 3d_{5/2}, Se 3d and Si 2p are ascribed to Cd in CdSe, Se in CdSe and Si in SiO₂, respectively. Thus, it is considered that no serious oxidation, decomposition and reaction of CdSe have taken place during sputtering. The CdSe concentration was evaluated from XPS peak intensity ratio Cd/[Cd+Si] normalized with respect to ionization cross section by using calibration curve shown in Fig. 2. The CdSe concentrations thus evaluated are tabulated in Table 1. The CdSe concentration increased with increasing relative surface area of CdSe chips in the composite target.

Figure 3 depicts XRD patterns of the present films. Three broad peaks observed at about 25.4°, 42.0° and 49.7° are ascribed to wurtzite and/or zinc-blende crystal phases of CdSe. The peak intensity was increased as the CdSe concentration of the film increased.

Figure 4 shows a typical TEM picture of CdSe microcrystals embedded in SiO₂ glass matrix. The lattice images of dispersed crystal are seen in the obscure glass matrix. The mean sizes and size distribution of microcrystals were estimated on each TEM pictures by assuming that all microcrystal shape was spherical, and they are shown in Fig. 5. The mean diameter of the microcrystals

Fig. 1. Typical XPS spectra of (a) Cd 3d_{5/2}, (b) Se 3d and (c) Si 2p for the CdSe embedded SiO₂ glass films.

Fig. 2. Calibration curve for the determination of CdSe concentration based on XPS.

Table 1. CdSe Concentration of CdSe Embedded SiO₂ Thin Films

Sample	relative surface area(%)	CdSe concentration (mol %)
No.1	3.8	5.2
No.2	5.2	12
No.3	6.6	25
No.4	8.0	37
No.5	11.0	46

Fig. 3. Typical XRD patterns for CdSe microcrystal embedded SiO₂ glass films.

were 4.2 nm, 4.8 nm, 5.1 nm and 5.6 nm for the films No. 1 to No. 4, respectively.

The mean size of the microcrystals calculated by XRD

Fig. 4. Typical TEM picture of CdSe microcrystal embedded SiO₂ glass films.

Fig. 5. Microcrystals size distribution in the films.

patterns and XPS measurement of the present films imply the no dependence of the mean size and concentration of CdSe microcrystals on the substrate and sputtering duration.

With respect to optical absorption characteristics, $(\alpha h\nu)^2$ of the present films is shown as a function of incident light wavelength in Fig. 6, where α is absorption coefficient. The absorption edge, and its blue shift from that of the bulk (1.74 eV) are tabulated in Table 2, for the present films. From Fig. 6 and Table 2, it is evident that the band gap and the amount of blue shift increase with the decrease of the mean size of embedded CdSe microcrystals, which means that the quantum confinement effect appear in the films. The quantum effect came to be stronger when microcrystal size decreased, and a relatively large blue shift as 0.61 eV was observed for the film containing the small amount of CdSe (5.2%).

Figures 7(a)–(e) show Z-scan measurement results ob-

Fig. 6. $(\alpha h\nu)^2$ versus photon energy plots for the composite films No. 1 to No. 5.

Table 2. Optical Absorption Characteristics of CdSe Embedded SiO₂ Thin films

Sample	concentration (CdSe mol%)	Absorption edge (nm)	Band gap (eV)	Blue shift (eV)
No.1	5.2	520	2.35	0.61
No.2	12	545	2.29	0.48
No.3	25	625	2.11	0.37
No.4	37	670	1.90	0.16
No.5	46	705	1.85	0.11

tained with closed aperture and open aperture at different incident light powers for the samples with CdSe concentrations of 5.2% (No. 1), 12% (No. 2), 25% (No. 3), 37% (No. 4) and 46% (No. 5), respectively. Figure 7 (f) is substrate SiO₂ glass plate.

For the films No. 1 to No. 3, the transmittance measured with closed aperture depends on the input power, while no input power dependence is seen for No. 4 and No. 5. The Z-scan signals of No. 4 and No. 5 seem to result from the thermal effect and/or resonant effect, since the band gaps of the two samples are close to 699 nm.

With respect to the shape of the transmittance spectrum obtained with closed aperture, transmittance changes through valley to peak with the sample position (Z) when CdSe concentration is low. But, the valley and peak are reversed when CdSe concentration is increased. After eliminating the influence of the substrate, transmittance of all the samples changes through peak to valley, which means that the sign of the real part nonlinearity of the films is negative.

The evaluated $\text{Re}\chi^{(3)}$ and $\text{Im}\chi^{(3)}$ are tabulated in Table 3. The absolute value of $\text{Re}\chi^{(3)}$, thus, increased with increasing CdSe concentration and/or mean size. Two photon $\text{Re}\chi^{(3)}$, thus, increased with increasing CdSe concentration and/or mean size. Two photon absorption was observed in all present films. In No. 4 and No. 5 films, The absorption saturation is seen to overlap with two photon absorption, and thus the $|\chi^{(3)}|$ cannot be obtained from these two samples.

According to Nakamura,⁵⁾ it is theoretically predicted that $|\chi^{(3)}|$ is proportional to inverse of cubic microcrystal radius (R^{-3}). To apply this relation, it is necessary to separate the influence of microcrystal size of CdSe from that of concentration. Therefore, we normalized $|\chi^{(3)}|$ by dividing CdSe concentration. Figure 8 shows normalized $|\chi^{(3)}|$ plots for No. 1, No. 2 and No. 3 against R^{-3} . The experimental data well fit the theoretical line. Thus, it is noted that the stronger the confinement effect due to smaller crystal size $|\chi^{(3)}|$ is for electron-hole independent confinement. The influence of matrix is neglected in the present work, since matrix of all films is SiO₂ glass. The influence of matrix for third-order optical nonlinearity should be the next target to the investigation.

4. Conclusion

CdSe microcrystals with various mean sizes were successfully embedded in the SiO₂ glass thin films by rf-sputtering using the composite target consisting of CdSe chips and SiO₂ glass plate. The size of CdSe microcrystals was controlled by changing the relative surface area of CdSe chips in the target. Since the Bohr radius of exciton of CdSe is large, the quantum size confinement should be due to electron-hole independent confinement. The quantum size effect was confirmed in the present CdSe embedded SiO₂ glass thin films on the basis of the blue shift of the absorption edge.

From Z-scan measurements, the real part of $\chi^{(3)}$ of the films was found to be negative and increased with increasing CdSe concentration. The two photon absorption was seen in all films. After normalized with respect to the concentration, it was revealed that $|\chi^{(3)}|$ of embedded CdSe microcrystals is proportional to R^{-3} (R : crystal radius) as theoretically predicted. Therefore, it is noted that strong quantum confinement effect enhances the third-order optical nonlinearity for electron-hole independent system. This dependence is different from that for exciton confinement effect.⁵⁾

Fig. 7. Z-scan results for (a) No. 1, (b) No. 2, (c) No. 3, (d) No. 4, (e) No. 5 and (f) SiO₂ substrate.

Table 3. $\text{Re}\chi^{(3)}$ and $\text{Im}\chi^{(3)}$ of CdSe Embedded SiO₂ thin Films

Sample	concentration (CdSe mol%)	$\text{Re}\chi^{(3)}$ (10^{-12} esu)	$\text{Im}\chi^{(3)}$ (10^{-12} esu)
No.1	5.2	-5.4	0.98
No.2	12	-8.4	1.3
No.3	25	-15	1.3
No.4	37	-15	
No.5	46	-29

Fig. 8. Normalized $|\chi^{(3)}|$ plots as a function of R^{-3} .

References

- 1) Jain, R. K. and Lind, R. C., *J. Opt. Soc. Am.*, **73**, 647-53 (1983).
- 2) Tsunetomo, K., Nasu, H., Kitayama, H., Kawabuchi, A., Osaka, Y. and Takiyama, K., *Jpn. J. Appl. Phys.*, **28**, 1928-33 (1989).
- 3) Hayashi, R., Yamamoto, M., Tsunetomo, K., Kohno, K., Osaka, Y. and Nasu, H., *Jpn. J. Appl. Phys.*, **29**, 756-59 (1990).
- 4) Efros, Al. L. and Efros, A. L., *Sov. Phys. JETP*, **16**, 772-76 (1981).
- 5) Nakamura, A., *New Glass*, **14**, 3-9 (1999) [in Japanese].
- 6) Nomura, S. and Kobayashi, T., *Solid State Commun.*, **78**, 677-80 (1991).
- 7) Tokisaki, T., Akiyama, H., Takaya, T. and Nakamura, A., *J. Cryst. Growth*, **117**, 603-07 (1992).
- 8) Sheik-Bahae, M., Said, A. A., Wei, T., Hagan, D. J. and Van Stryl, E. W., *IEEE J. Quantum Electron.*, **26**, 760-69 (1990).