Preparation and Optical Properties of CdS-Microcrystallites Deposited in Porous Vycor Glass

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多孔質バイコールガラス担持 CdS 微粒子の調製と光学特性

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[Received March 4, 1993; Accepted May 21, 1993]

CdS-microcrystallites were prepared in porous Vycor glass (PVG) by impregnation of PVG with an aqueous solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and subsequent reaction with H_2S gas. The optical absorption edge of the CdS/PVG containing 1.0 wt% cadmium exhibited a blue shift by 0.37 eV compared to bulk CdS, indicating the quantum size effect. The blue shift decreased with increasing diameter of CdS-microcrystallites in PVG. In the photoluminescence spectra of the CdS/PVG, the band-edge emission and the deep-level emission were observed. In accordance with the optical absorption spectra, the blue-shifted band-edge emission was also observed. The deep-level emission was effectively quenched by heating the CdS/PVG up to 300°C in air or by addition of methyl viologen (MV^{2+}) as an electron acceptor, suggesting that the emission arose from electron-hole pair recombination on the surface of CdS-microcrystallites.

Key-words: CdS-microcrystallites, Porous Vycor glass, Optical nonlinearity, Optical absorption, Photoluminescence

1. Introduction

Recently, semiconductor/glass composites with large third-order optical nonlinearity have attracted much interest as materials for optical functional devices, such as optical switches, shutters or waveguides.¹⁾⁻⁴⁾ The large nonlinearity of the composites is interpreted by the quantum size effect. In fact the diameter of semiconductor microcrystallites in the glass matrices was under 10 nm. Thus the microcrystallites are considered as "quantum dots."

CdS-microcrystallites/glass composites have been prepared by various methods such as melt-quenching,⁵⁾⁻⁷⁾ sol-gel,⁸⁾⁻¹⁰⁾ sputtering deposition,¹¹⁾⁻¹³⁾ and precipitation in porous matrices.¹⁴⁾⁻¹⁶⁾ Optical properties of CdS-microcrystallites are known to be different by the preparation methods.

Kuczynski and Thomas have investigated the photophysical properties of CdS deposited in porous Vycor glass (PVG).¹⁴⁾ It is known that PVG has the porous channels and the CdS in PVG must have one dimension much smaller than 4 nm, i.e., the diameter of the cylinders in the PVG. However, they

reported that the spectroscopic properties of CdS in PVG were indicative of bulk CdS material. Therefore, information on the optical properties of CdS-microcrystallites deposited in PVG is not sufficient.

In the present work, by means of optical absorption and emission spectra measurements, we have investigated the optical properties of CdS-microcrystallites deposited in PVG.

2. Experimental

Porous Vycor glass (PVG) used was a product of Corning (No. 7930), the size being about 10 mm × 10 mm in length and 1.0 mm in thickness with the specific surface area of 232 m²·g⁻¹ and the average pore size of 4.4 nm. From the N₂ adsorption isotherm, the surface area and the pore size of the PVG were obtained by using the well-known BET-equation and by the "t-method", respectively.¹⁷⁾

The following gas and chemicals were used without further purification: a gas mixture of 19.6% H₂S and 80.4% N₂ (Nippon Sanso K.K.), and Methyl viologen, 1,1'-dimethyl-4,4'-bipyridinium dichloride (Sigma Chemical Co.), and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Kojundo Chemical Laboratory Co., Ltd., 99.99%).

Figure 1 shows the schematic preparation process of CdS/PVG. First, PVG was cleaned in 30% H₂O₂ solution for over 24 h, then heated at 180°C in air. CdS/PVG was prepared by soaking the cleaned PVG in an aqueous solution of 0.1–1.0 mol·dm⁻³ Cd(NO₃)₂·4H₂O for 70–90 h at room temperature and

Fig. 1. Schematic preparation process of CdS/PVG.

firing the PVG at 400°C for 2 h in air, thereby leaving the cadmium oxide in PVG. Precipitation of CdS in PVG was carried out by heating the PVG with cadmium oxide in the glass tube with flowing the dried gas mixture of 19.6% H₂S and 80.4% N₂ in the temperature range between 50 and 300°C. The cadmium content was 0.2–2.1 wt% determined by ICP emission spectroscopy. The subsequent heat treatment of CdS/PVG was carried out at 100–300°C in air to investigate the origin of photoluminescence of the deposited CdS in PVG. The obtained CdS/PVG samples were yellow or orange in color and are quite transparent for use in optical studies.

X-ray photoelectron spectra (XPS) analyses were performed using a Mg K α X-ray source. Typical operating conditions were as follows: X-ray gun, 13 kV, 10 mA; the pressure in the analytical chamber, less than 4.8×10^{-7} Pa. The measurement of the electron spectra was carried out after in situ scraping of the films surface with a diamond file until no further change in the photoemission spectra was observed. For the calculation of binding energies of each peak, the peak position of the main component in the 1s core level spectrum of carbon was assumed to be 284.6 eV. X-ray diffraction (XRD) measurements were carried out to examine the crystallinity of CdS-microcrystallites in PVG. The optical absorption spectra were measured in the range from 300 to 800 nm by a spectrometer at room temperature. The photoluminescence (PL) measurements were carried out in the temperature range between –261 and 27°C by using a spectrofluorophotometer with filters to eliminate the excitation light. The excitation wavelength was 325 nm. The typical excitation power density was as low as 0.04 W·cm^{–2}. The lifetime measurements for the PL were performed using a N₂ laser with 0.8 ns pulse width at room temperature.

3. Results and discussion

The states of the chemical bond of CdS/PVG have been evaluated by XPS. The Si 2p and O1s electron

spectra of the CdS/PVG containing 1.0 wt% of cadmium are shown in Figs. 2 and 3. The reaction temperature with H₂S was 150°C for 10 min. In the figures, the arrow indicates the standard peak position of Si 2p and O1s of SiO₂.¹⁸⁾ The observed peak position of the CdS/PVG is very close to that of SiO₂. Thus the main component of the PVG was SiO₂. The XRD patterns of the CdS/PVG containing 2.1 wt% of cadmium showed the typical amorphous SiO₂ halo pattern. Because of low CdS concentration in the PVG, the diffraction pattern of CdS could not be observed.

Figure 4 shows the Cd 3d electron spectrum of the CdS/PVG. The examined CdS/PVG was the same as shown in Figs. 2 and 3. In the figure, the arrows indicate the standard peak position for CdS, Cd metal, and CdO.¹⁹⁾ The experimental peak position is close to the standard CdS. In conclusion, the CdS was successfully deposited in porous SiO₂ glass.

Figure 5 shows the absorption spectra measured at room temperature for the CdS/PVG containing 1.0 wt% of cadmium. In the case of CdS/PVG (a), the reaction temperature with H₂S was 50°C for 10 min, (b) 150°C for 10 min, and (c) 300°C for 10 min. The color of the CdS/PVG changes from bright yellow to orange with increasing the reaction temperature with H₂S. In the figure, the band-edge of CdS/PVG shifts to longer wavelength with increasing the reaction temperature. This is because the diameter of the microcrystallites became large. An absorption peak or a shoulder corresponding to the transition from the highest valence subband to the lowest conduction subband cannot be observed. This is due to the wide distribution of size in CdS-microcrystallites.

From the spectra, the power of the absorption coefficient α was plotted against the photon energy $h\nu$. The α^2 varied linearly with $h\nu$ indicating that the direct inter-band transition takes place. The band gap energy, E_g , of the CdS/PVG (a) is clearly blue-shifted by about 0.37 eV compared with that of the

Fig. 2

Fig. 3

Fig. 4

Fig. 2. Si 2p electron spectrum of the CdS/PVG containing 1.0 wt% of cadmium.

Fig. 3. O1s electron spectrum of the CdS/PVG containing 1.0 wt% of cadmium.

Fig. 4. Cd 3d electron spectrum of the CdS/PVG containing 1.0 wt% of cadmium. CdS indicates the peak position of Cd 3d electron spectra of CdS, Cd; Cd 3d of Cd metal, CdO; Cd 3d of CdO.

Fig. 5. Optical absorption spectra of the CdS/PVG containing 1.0 wt% of cadmium at room temperature, and the CdS/PVG (a) reacted with H_2S at 50°C, (b) at 150°C, and (c) at 300°C.

bulk CdS (2.41 eV), (b) 0.2 eV, and (c) 0.11 eV. In spherical semiconductor microcrystallites enclosed by an insulating matrix, the blue shift, ΔE_g , is expressed by the following Eq. (1),

$$\Delta E_g = \frac{h^2}{8a^2\mu} \quad (1)$$

where a and μ are the radius of the spherical dots and the reduced effective mass of an electron-hole pair, respectively, and h is Planck's constant. This equation is valid when the radius a is smaller than the Bohr radius of the bulk exciton.²⁰⁾ The diameter of CdS-microcrystallites in the CdS/PVG (a) was about 4.7 nm, (b) 6.4 nm, and (c) 8.6 nm calculated by Eq. (1). It is known that PVG is honeycombed with cylinders which showed a diameter of not more than about 4 nm. Therefore, the CdS deposited in PVG cannot have one of its dimensions greater than 4 nm. However, the diameter of CdS-microcrystallites in the CdS/PVG (a), (b), and (c) by the calculation was greater than 4 nm. It seems that the CdS in the PVG is an elongated structure. The dimension of the CdS-microcrystallites along cylinders became larger with increasing the reaction temperature with H_2S . Because of low CdS concentration in the PVG, the CdS-microcrystallites could not be observed directly by the transmission electron microscope (TEM) observation.

Figure 6 shows photoluminescence (PL) spectra measured at room temperature for various CdS/PVG. In the figure, the CdS/PVG (a), (b), and (c) were the same as those in Fig. 5. The cadmium concentration of the CdS/PVG (d) and (e) were 0.2 and 2.1 wt%, respectively. For the CdS/PVG (b), (d), and (e), the reaction temperature with H_2S was 150°C for 10 min. The emission spectrum for the CdS/PVG (a) consists of a peak at 467 nm and a weak shoulder at 514 nm. The CdS/PVG (d) shows the emission with a peak at 482 nm. In the case of low CdS concentration or low reaction temperature with H_2S , deep-level emission was not observed, suggesting that defects were well suppressed. In accordance with the optical absorption spectrum, the energy of the band-edge emission of CdS/PVG (a) is

Fig. 6. Photoluminescence spectra at room temperature for (a) the CdS/PVG containing 1.0 wt% of cadmium reacted with H_2S at 50°C, (b) at 150°C, (c) at 300°C, (d) the CdS/PVG containing 0.2 wt% of cadmium reacted with H_2S at 150°C, and (e) containing 2.1 wt% of cadmium reacted with H_2S at 150°C.

about 0.25 eV higher than that of the bulk CdS. The shift to higher energy is attributed to a low-dimensional quantum size effect due to confinement of electrons and holes in CdS-microcrystallites. The observed broad emission reflects contributions of wide distribution of CdS-microcrystallites size. The emission is probably due to the recombination of free electron-hole pair or the shallow donor-acceptor pair in the CdS-microcrystallites.²¹⁾ The peak position of emission spectra for the CdS/PVG (d) is 482 nm, (b) 514 nm, and (e) 574 nm. It is clear that the peak shifts to lower energy with increase the concentration of CdS in PVG, suggesting that the long dimension of CdS-microcrystallites along the cylinder became large. The effect of reaction temperature with H_2S on emission spectra has also shown in Fig. 6. In the figure, the peak position of the CdS/PVG (a) is 467 nm, (b) 514 nm, and (c) 539 nm. The peak position also shifts to lower energy with increasing the reaction temperature. Therefore, the diameter of the CdS-microcrystallites was controlled by changing the reaction temperature with H_2S .

In conclusion, the PL spectra of CdS/PVG were largely influenced by the diameter of CdS-microcrystallites in PVG.

Figure 7 shows the PL decay curves of the CdS/PVG (e) shown in Fig. 6 obtained by N_2 laser excitation at room temperature. In the figure, curve (a) shows the decay curve of PL emission at 405 nm and curve (b) at 615 nm. The decay time was estimated to be 450 ns at 615 nm by assuming an exponential function. In this experiment, the decay time at 405 nm was under the instrumental response (1 ns).

Fig. 7. Decay curves of PL emission (a) monitored at 405 nm and (b) at 615 nm for the CdS/PVG (e) shown in Fig. 6.

Fig. 8. Temperature dependence of the PL emission intensity at 615 nm for the CdS/PVG (e) shown in Fig. 6.

Thus the decay time at 615 nm was at least three orders of magnitude larger than that at 405 nm. The temperature dependence of the emission intensity at 615 nm for the CdS/PVG (e) is shown in Fig. 8. The intensity increases with decreasing the temperature. The intensity at -261°C was about 65 times larger than that at 27°C . This is because that the probability of non-radiative transition became lower with decreasing the temperature.

Figure 9 shows the PL emission spectra of CdS/PVG containing 1.2 wt% of cadmium. After the reaction with H_2S at 150°C for 10 min, the CdS/PVG was heat-treated at different temperature in air for 30 min. The non-heat-treated CdS/PVG indicated as R.T. in the figure shows the broad emission with a peak at 540 nm. The peak position shifts to longer wavelength (582 nm) when the CdS/PVG heat-treated at 100°C . On the other hand, in the spectrum for the CdS/PVG heat-treated at 200°C , the blue-shifted band-edge emission at 490 nm can be observed. When the heat treatment temperature increased up to 300°C , the emission could not be observed and the yellowish color of the CdS/PVG was discharged. The intensity of the emission around 500–600 nm decreased with increasing the heat treatment temperature. Thus the CdS in the PVG is easily evaporated by heating the CdS/PVG in air.

Figure 10 shows the effect of MV^{2+} on the PL

Fig. 9. Heat treatment temperature dependence of the PL emission of CdS/PVG containing 1.0 wt% of cadmium reacted with H_2S at 150°C .

Fig. 10. PL emission spectra at room temperature for the CdS/PVG containing 1.2 wt% of cadmium reacted with H_2S at 150°C in the absence and presence of water, and of MV^{2+} .

emission of the CdS/PVG containing 1.2 wt% of cadmium at room temperature. The photogenerated electron-hole pairs of the semiconductor may undergo redox reactions with adsorbed species by reduction of an electron acceptor such as methyl viologen, MV^{2+} . The standard reduction potential of MV^{2+} is -0.446 V vs. NHE, therefore MV^{2+} could quench the PL emission from surface site by electron transfer from the conduction band electrons of CdS-microcrystallites to the adsorbed MV^{2+} .²²⁾ In the figure, it is obvious that water shows no effect on the emission spectrum. On the other hand, the PL emission around 580 nm is quenched easily within 10 min

by addition of $0.005 \text{ mol} \cdot \text{dm}^{-3} \text{ MV}^{2+}$. However the blue-shifted band-edge emission at 490 nm cannot be quenched by MV^{2+} . This again confirmed the emission at 580 nm was due to a surface state of CdS-microcrystallites. In this experiment, the quantitative analysis such as the Stern-Volmer plot for MV^{2+} could not be obtained because of low concentration of CdS deposited in PVG as porous supports.

4. Conclusions

(1) In the optical absorption spectra, the CdS/PVG containing 1.0 at% of cadmium exhibited a blue shift by about 0.37 eV in comparison with that of the bulk CdS. The blue shift of the CdS/PVG decreased with increasing the diameter of CdS-microcrystallites in PVG.

(2) The photoluminescence spectra of the CdS/PVG with 1.2 at% of cadmium exhibited blue-shifted band-edge emission and the deep level emission. The blue-shifted band-edge emission seems to be a low-dimensional quantum size effect. The deep-level emission was effectively quenched by addition of methyl viologen, suggesting that the emission arose from the surface of CdS-microcrystallites in PVG.

Acknowledgements The authors would like to thank Drs. T. Nitta and K. Kanai for their continuous encouragement.

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