Preparation of PbS Quantum Dot Materials by the Sol-Gel Process

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ソル-ゲル法による PbS 量子ドットの作製

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Quantum dot materials based on PbS-doped sodium borosilicate glasses were prepared by the sol-gel process using silicon methoxide (TMOS), boron ethoxide, sodium and lead acetates as starting materials. The chemical state of Pb species in the glasses fully densified at 590°C was identified to be PbS by X-ray photoelectron spectroscopy and electron diffraction. The amount of PbS crystallites in the glasses was 4-13 wt% of mother glasses. The size of the crystallites was 5-15 nm in diameter. The absorption edge of the glasses was near 2500 nm, which was slightly shifted to higher energy from 3200 nm for the bulk PbS crystal.

Key-words: PbS, Quantum dot, Sol-gel process, Soda borosilicate glass

1. Introduction

Nano-sized semiconductor and metal particles such as CdS, CdSe, CdTe, PbS, Au, Ag, etc. dispersed in a dielectric medium has recently been receiving a great deal of attention as quantum dot materials which exhibit a large resonant non-linear susceptibility with picosecond-order response time.¹⁻⁴⁾ The sol-gel process is advantageous over conventional melt-quenching technique in preparing these quantum dot materials when semiconductor particles are easily oxidized or decomposed at high temperatures.

This advantage becomes significant when gel is fully densified into a pore-free glass that is essential for practical device application. Most reports on the preparation of quantum dot materials by the sol-gel process, however, deal with silica gels which can not be densified at low temperatures where the decomposition or oxidation of the semiconductor materials does not occur.⁵⁻⁷⁾

Recently, we succeeded in preparing optically transparent, fully densified glasses of Na₂O-B₂O₃-SiO₂ system containing up to 10 wt% CdS crystallites of 5-10 nm in diameter by the sol-gel process, using TMOS, B(OEt)₃, aqueous NaOAc/Cd(OAc)₂ solution as starting materials.⁸⁾ 10 wt% CdS-doped gel-derived glasses showed a $\chi^{(3)}$ of 1×10^{-6} esu under near resonant conditions, i.e., in the vicinity of 460 nm.

This process of preparing the CdS-doped glasses

can be applied, in principle, to any other sulfide semiconductor dispersed systems provided that the sulfide is stable up to 600°C.

The energy gap of bulk PbS crystal is reported to be 0.286 eV at 4 K and the absorption edge of PbS shifts to higher energy from 3200 nm for the bulk crystal up to 530 nm for the particle smaller than 1.3 nm.⁹⁾ Thus the quantum dot materials with nano-sized PbS having resonant conditions near the wavelength for optical communication should be obtainable by controlling the particle size. The fabrication of such materials with high nonlinearity is of practical importance for the development of optical switching device for communication.

Since PbS decomposes at a temperature above 600°C in ambient laboratory atmosphere, our process based on soda-boro-silicate system is particularly advantageous over other methods in fabricating full dense quantum dot materials of PbS-dispersed system.

In this paper, we report the preparation of PbS-dispersed full dense glasses by the sol-gel process developed for the fabrication of CdS-doped quantum dot materials.

2. Experimental

2.1 Preparation of glasses

The composition of the matrix glass and the procedure for the gel preparation and subsequent treatments were similar to those used in the fabrication of CdS-doped glasses⁸⁾ except that Pb(OAc)₂·3H₂O was used for Cd(OAc)₂·H₂O. That is, the process consisted of: preparation of Pb(OAc)₂ doped wet gel, precipitation of Pb(OAc)₂ microcrystallites in the gel, conversion of Pb(OAc)₂ to PbO by heating the gel in air, conversion of PbO to PbS by exposing the gel to H₂S, and densification of PbS-doped gel.

Precursor solutions with the composition of 6.25Na₂O-18.1B₂O₃-80SiO₂ (in mol) + x PbO ($x=5, 10, 15$ wt%), were prepared from TMOS, B(OEt)₃, and aqueous NaOAc/Pb(OAc)₂ solution. Taken consideration was the loss of Na₂O and B₂O₃ due to extraction when acetone replaces the liquid inside the wet gel for precipitating Pb(OAc)₂ microcrystallites.¹⁰⁾

First, 2.0 g of TMOS was hydrolyzed with 0.489 g

of aqueous hydrochloric acid of pH=2 (molar ratio of TMOS: H₂O=1: 2) for 1h at 20°C by ultrasonic irradiation at 25 kHz. Next, 0.897 g of B(OEt)₃ was added to this silicate solution and mixed for 1h at 20°C for another hour with ultrasonic irradiation. Then, the aqueous solution of freshly dissolved 0.174 g of NaOAc and 0.089 g of Pb(OAc)₂·3H₂O in 0.819 g distilled water ($x=5$ wt%, Sample-A), or 0.174 g of NaOAc and 0.178 g of Pb(OAc)₂·3H₂O in 0.941 g distilled water ($x=10$ wt%, Sample-B), or 0.174 g of NaOAc and 0.267 g of Pb(OAc)₂·3H₂O in 1.237 g distilled water ($x=15$ wt%, Sample-C), was added to the mixture and mixed by ultrasonic agitation for 10–20 min at 0°C. The precursor solution thus obtained was poured into a tightly sealed polypropylene vial of about 33 mm inside diameter. The solution was gelled and aged at room temperature for 6h.

The aged wet gel was then placed in 10 ml of 10 vol% iso-PrOH/acetone solution at room temperature for 3 days, in order to replace the liquid in the micropores of the gel with the solution and to precipitate Pb(OAc)₂ microcrystallites on the micropore walls. The gel thus treated was dried at 60°C for two weeks.

The monolithic porous dried gels of about 23 mm in diameter and 1.7 mm in thickness were subjected to heat treatment at 400°C for 12h in a silica tube with flowing oxygen gas, in order to decompose and convert Pb(OAc)₂ into PbO. The PbO containing gels after being cooled to room temperature were exposed to dry H₂S gas to convert PbO to PbS at 100°C for 6h in a silica tube previously evacuated of N₂ by a rotary pump. The gels were then heated to 590°C in flowing helium gas for 7h for densification into pore-free glasses.

2.2 Characterization of glasses and measurement of absorption spectra

The Pb contents in the final glass was determined by the measurement with a SEIKO EG & G Type SED 8600 energy dispersive X-ray analyzer (EDX) and the chemical state of Pb species was investigated by X-ray photo spectroscopy (XPS) using Perkin Elmer ESCA-5500MT spectrometer. The spectra of Pb_{4f} and S_{2s} electrons were measured over the ranges 125–150 eV and 217–237 eV using the monochromatic Al K α radiation at 300 W.

Electron micrographs and the electron diffraction pattern of the PbS particles in the densified glasses were obtained by using the JOEL TEM-100CX transmission electron microscope at 100 kV. Samples were fragmented and dispersed in carbon tetrachloride (CCl₄). The solution was then dropped onto a holey carbon film supported by a copper grid.

The measurement of absorption spectra was carried out on the platelet samples of about 100 μ m in thickness over the wavelength from 800 nm to 2500 nm with Near-IR Spectrometer JASCO UVIDECS-590 using air as the reference.

3. Results and discussion

3.1 Composition and crystallite development of Pb species

The Pb contents in the samples determined by EDX were 4.3, 8.5 and 13 wt% in terms of PbS/mother glass, respectively. These values are slightly lower than those in precursor solutions. This reduction in Pb content is due to the extraction loss by syneresis of the liquid from wet gel.¹⁰⁾

Figure 1 shows the XPS spectra of Pb_{4f} and S_{2s} electrons on Sample-C containing 13% of PbS. Both of the peaks at 137.5 eV for Pb_{4f} and at 225.1 eV for S_{2s} are characteristic of PbS and there is no other peak which is assigned to the Pb compound in other state.¹¹⁾ The information on the lead which had been incorporated in glass structure as modifier ions was not obtained. However, its amount, if any, is considered to be small from the processing conditions.

The electron diffraction pattern of Sample-C having PbS content of 13 wt% is shown in Fig. 2. The spots in the figure were identified to be the reflection from the (111), (200), (220), (311), (222), (420), (422) and (600) planes of PbS. The very distinct spots in the diffraction pattern suggest that each particle is a single crystal.

The TEM micrograph of Sample-C is shown in Fig. 3. PbS appears as dark particles with diameters ranging from 5 to 15 nm. Both average size and the range of size distribution are very large compared

Fig. 1. Pb_{4f} and S_{2s} spectra for lead compound in Sample-C.

Fig. 2. Electron diffraction pattern of lead compound in Sample-C.

Fig. 3. TEM micrograph of Sample-C (white bar=100 nm).

Fig. 4. Absorption spectra of glasses with PbS content of; A: 4.3 wt%, B: 8.5 wt%, C: 13 wt%.

with those of CdS microcrystallites i.e., 6 ± 2 nm, prepared by the similar procedure.⁸⁾

3.2 Absorption spectra

The absorption spectra of Samples A–C are shown

in Fig. 4. There is not so distinct difference of the absorption edge among three samples due to broad particle size distributions, although the edge shifted slightly to higher energy from 3200 nm for the bulk PbS crystal. There is an indication of the shoulder in the vicinity of 2200 nm in the spectrum of Sample-C containing 13 wt% of PbS. This is probably attributed to the resonant absorption typical of quantum dot materials.

The wavelength of 2200 nm, where a high non-linear susceptibility is expected, is too long to be immediately applied to the optical communication system. The elaboration of the processing conditions to obtain the PbS microcrystallites of smaller size and narrower size distribution is the next step of the study to prepare the materials fit to the application.

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