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Preparation and optical properties of ZnS-microcrystals deposited in silica gels

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Abstract

ZnO doped silica gels were synthesized by the hydrolysis and condensation of complex solution tetraethyl orthosilicate (TEOS) and zinc acetate ($Zn(Ac)_2$) and heating at 500°C in the air. For conversion to ZnS doped gels, they were exposed to H_2S gas at appropriate temperatures. The crystal size of ZnS determined by the width of X-ray diffraction pattern and direct transmission electron micrograph (TEM) grows from 1 to 4 nm with an increase of reaction temperature with H_2S gas. The edge energies of optical absorption shifted to higher energy side compared with that of bulk crystal and reciprocally increased in proportional to the square of the crystal size. The peak energy of fluorescence spectra also shifted to lower energy side with an increase of reaction temperature exposing to the H_2S gas. Thus, the quantum size effect could be found for ZnS microcrystals in the gels.

Keywords: A. Sol–gel process; C. Optical properties; ZnS microcrystal; Fluorescence spectra; Quantum size effect

1. Introduction

The microcrystals dispersed silica gel are widely synthesized, because they have a characteristic property such as optical non-linearlity [1]. The blue shift of optical absorptions is discussed in terms of quantum size effects. However, we are faced with how to control of particle size distribution and dispersivity of the microcrystals. Various methods have been proposed to dope semiconductor microcrystals such as CdS in the matrix [2–8]. The sol–gel process can deposit various pure crystals in the matrix compared to the conventional melting method. II–IV and III–V group semiconductor compounds are selected as dopants because of large optical nonlinearity [9–14]. Nogami et al. succeeded in preparing metal sulfide doped gels by the sol–gel process combined a with proceeding reaction with H_2S gas [15–19]. The structure and size of crystals deposited in the matrix depend on the reaction condition with H_2S gas. Now we prepare the ZnS doped silica gels and investigate quantum size effects from observations of optical absorption and fluorescence spectra.

2. Experimental procedure

2.1. Preparation of porous gels and reaction with H_2S gas

Tetraethyl orthosilicate (TEOS) and zinc acetate ($Zn(Ac)_2$) are used as starting materials. TEOS was first partially hydrolyzed by dropping into a solution of water, ethyl alcohol (EtOH) and hydrochloric acid, whose mol ratios to TEOS were 1, 1 and 0.0027, respectively. After stirring vigorously for 1 h, $Zn(Ac)_2$ dissolved in 5 g methyl alcohol (MeOH) was added and stirred subsequently for 1 h at room temperature. This homogenious solution completely hydrolyzed by adding a solution of H_2O, EtOH, and NH_4OH. In this second hydrolysis reaction, each mol ratio to TEOS was maintained at 4, 1 and 0.011, respectively. After stirring for 1 h, the sol solution was poured into polystyrene containers and left for a few weeks at 40°C under sealed conditions. Then the sol plates were heated at a rate 50°C/h to the desired temperature between 300 and 700°C and kept for 4 h at each temperature. Finally, the dried gels, whose thickness was about 2 mm, were reacted with H_2S gas at the appropriate temperature between room temperature and 250°C.

2.2. Apparatus

Differential thermal analysis (DTA) was employed using a Shimazu DTA-50 equipment with a heating rate

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of 10°C/min. Specific surface area was determined by N_2 gas adsorption using Shibata SA-1100. The pore size distribution was measured by a poresizer (Micromeritix Co., 9303). Optical absorption spectra of ZnS doped gels with 2–3 mm thickness were measured by a double beam spectrophotometer (Hitachi Co., U-2000). The X-ray powder diffraction measurements were performed by a Rigaku diffractometer with CoK_α. The intensities were collected stepwise from 50 to 70° (2θ) in 0.05° step and accumulation time of each point was 10 s. Fluorescence spectra were measured using a He-Cd laser as an exciting line. The direct TEM observation of ZnS microcrystals in gel were made with a JEM-200 CX transmission electron microscope.

3. Results and discussion

3.1. Pore size distribution and surface area of gels before reaction with H_2S gas

Gels firstly obtained are colorless and transparent. Fig. 1 shows a DTA curve of the silica gel containing ZnO. In this figure, an endothermic peak appeared around 100°C due to the removal of water and alcohol trapped in micropores. And an exothermic peak around 400°C is also seen, whose origin may be attributed to burning and oxidation of $Zn(Ac)_2$ and residual alkoxide. The variation of specific surface area of ZnO doped gels with heat treatment temperature is shown in Fig. 2. Specific surface area increases with heat treatment temperature until 500°C and then decrease above 500°C. Thus, the elimination of residual components lead to an increase in specific surface area. Above 500°C, the specific surface area decreases due to contraction of the gel structure. The pore size distribution of the gels heated at 500°C is shown in Fig. 3. One sees that the micropore made by interstices of secondary silica particles are occupied by ZnO.

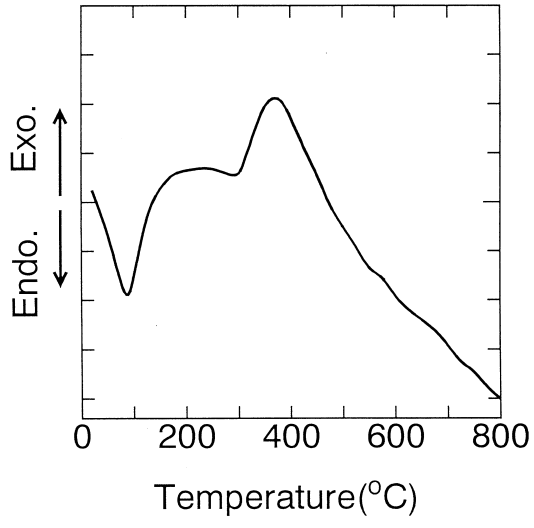

Fig. 1. DTA curve of a dried gel containing ZnO with a heating rate of 10°C/min in air.

3.2. XRD and TEM observation of ZnS doped silica gels and crystal size of ZnS

Fig. 4 shows XRD patterns of the gel heated at 500°C and then reacted with H_2S gas for 1 h at various

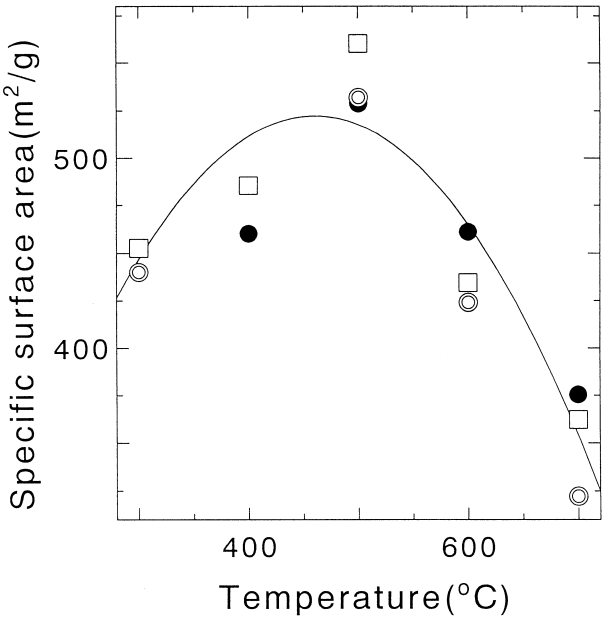

Fig. 2. Specific surface area of the gels containing: ●, 1.5 wt.%; ◎, 3.0 wt.% and □, 6.0 wt.% ZnO heated for 4 h at various temperatures.

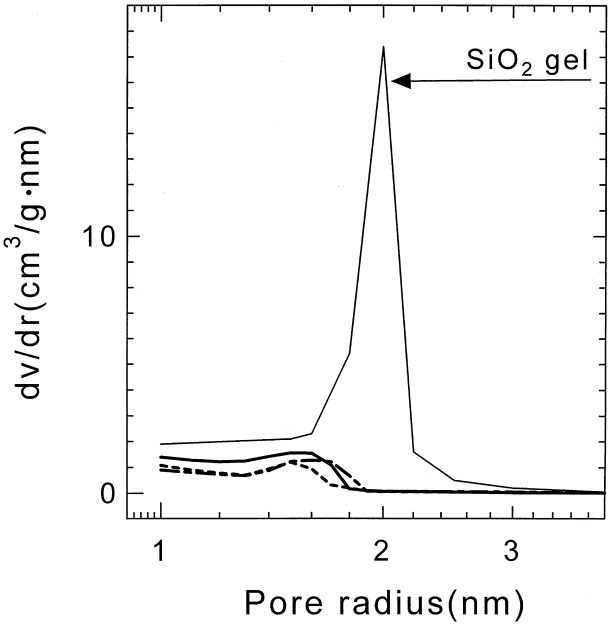

Fig. 3. Pore size distribution calculated from the N_2 adsorption isotherm of gel heated for 4 h at 500°C. (The solid line shown in the figure represents silica gel and the dotted lines represent silica gels containing ZnO.)

temperatures. Two broad peaks are seen on the hallow pattern due to matrix gels. These broad peaks can be assigned to the cubic ZnS. The crystal size can be calculated from the width of the X-ray pattern. The width of the (311) peak ($2\theta = 60°$) is used to determine crystal size, because in this range the background is comparatively flat. After subtracting the contribution of the background intensity, smoothing the date and least square curve fitting with Lorentzian function, the width was determined. Fig. 5 shows the relationship between crystal size and reaction temperature with H_2S gas. It can be found that the crystal size is larger with the increase of reaction temperature and amount of ZnO contents. Transmission electron microscope (TEM) are also used to confirm the

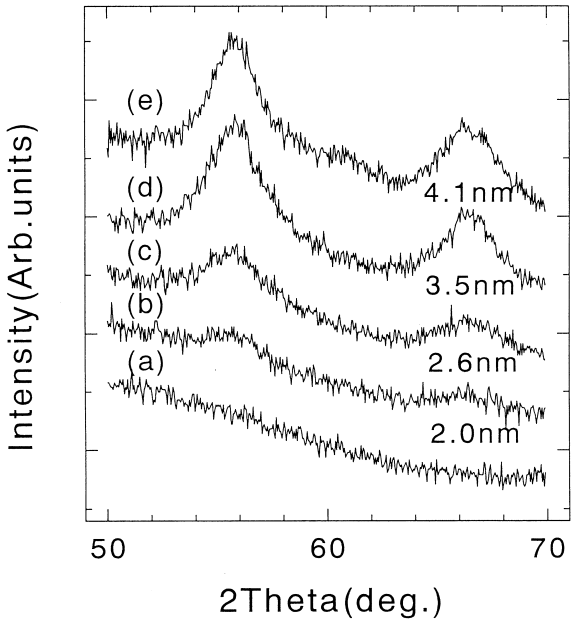

Fig. 4. X-ray diffraction patterns of gel heated (a) for 4 h at 500°C, and gels containing (b) 1.5 wt.%, (c) 3.0 wt.% and (d) and (e) 6.0 wt.% ZnO reacted with H_2S gas for 1 h at (c) (d) 100°C, (b) 150°C or (e) 200°C. (The crystal size shown in the figure was calculated by Scherrer's equation.)

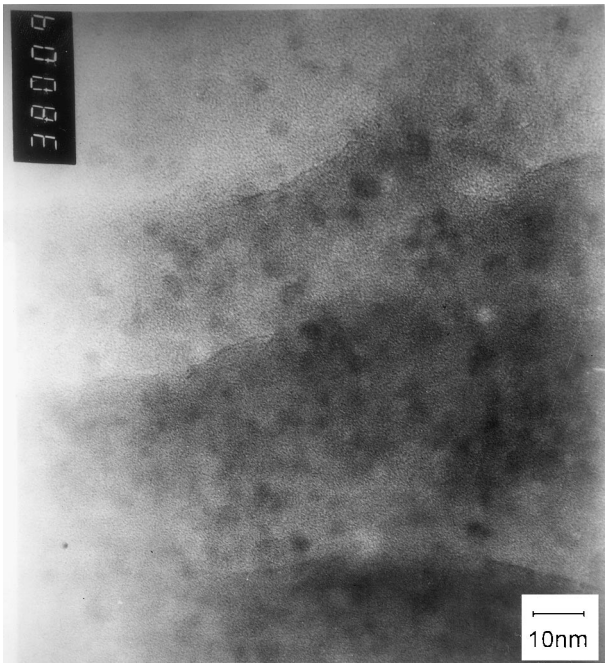

Fig. 6. Transmission electron micrograph of the gel containing 1.5 wt.% ZnO reacted with H_2S gas for 1 h at 250°C after heating at 500°C for 1 h.

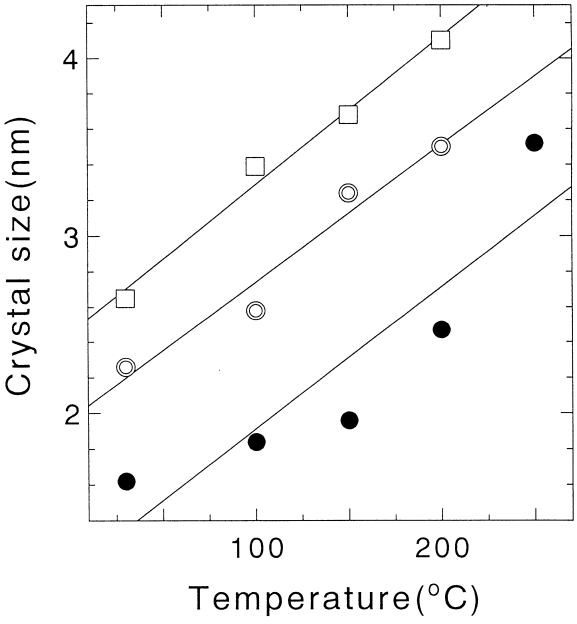

Fig. 5. ZnS crystal size obtained by reaction of the gels containing: ●, 1.5 wt.%; ◎, 3.0 wt.% and □, 6.0 wt.% ZnO with H_2S gas for 1 h at various temperatures.

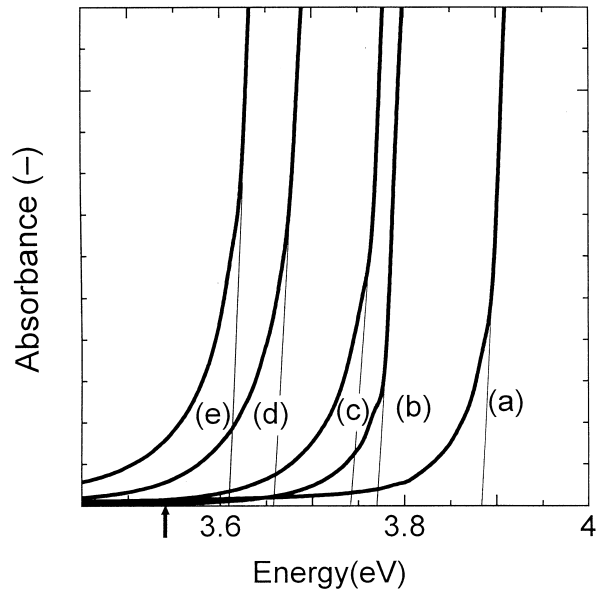

Fig. 7. Optical absorption spectra of gels containing 1.5 wt.% ZnO reacted with H_2S gas at (a) 30°C, (b) 100°C, (c) 150°C, (d) 200°C or (e) 250°C for 1 h. (The arrow shown in the figure represents bulk ZnS absorption edge energy.)

results of XRD. Fig. 6 shows TEM photograph of the gel containing 1.5 wt.% ZnO heated at 500°C for 4 h and followed by reacting with H_2S gas at 250°C for 1 h. Deposited crystals are seen as dark spheres, whose average size is approximately equal to the value determined from XRD patterns.

3.3. Optical absorption and fluorescence spectra of ZnS doped gels [20]

Figs. 7 and 8 show the absorption spectra of gel heated for 4 h at 500°C and subsequently reacted with H_2S gas at various temperatures. By extrapolating the linear part to an abscissa, one can estimate band gap energy (*Eg*). In every case band gap energies are larger than that of the bulk ZnS crystals. The blue shift of absorption edges is also explained by quantum size effect due to confining of carrier. Band gap energy is plotted in Fig. 9 as a function of the inverse square of the crystal size. The linear relationship is apparent for each batch composition, which satisfies the theoretical relationship that band gap energy is reciprocally proportional to the square of the crystal size. The slope differs much among batch composition. This may be mainly ascribed to the difference of dielectric constant in ZnS microcrystals due to the each matrix gels. Thus, it is concluded that ZnS microcrystal deposited in silica gel exhibits the quantum size effect. Relaxation behaviour of exciting carrier in crystal is also observed in fluorescence spectrum. Fig 10 shows the fluorescence spectra of ZnS doped silica gel. The emission peak which attributed to recombination of hole and electron is confirmed at the lower energy range compared to absorption edge energy. Fig. 11 represent peak energy of fluorescence spectra. The peak position is shifted with reaction temperature in accordance with the absorption edge energy. For each sample the width of the spectra are nearly equal. Therefore, it is considered that the crystal size distribution is fairly well homogeneous.

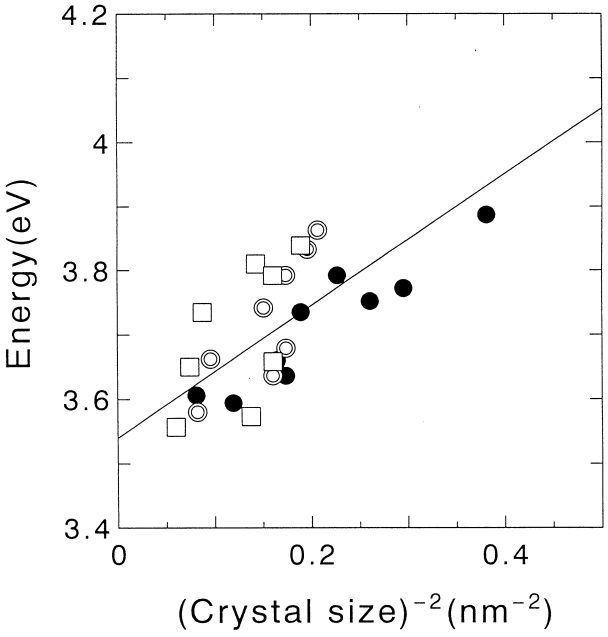

Fig. 9. The relationship between the absorption edge energy and the reciprocal square of ZnS crystal size. (The marks shown in the figure represent the gels containing (●) 1.5 wt.%, (◎) 3.0 wt.% and (□) 6.0 wt.% ZnO reacted with H_2S gas for 1 h at various temperatures.)

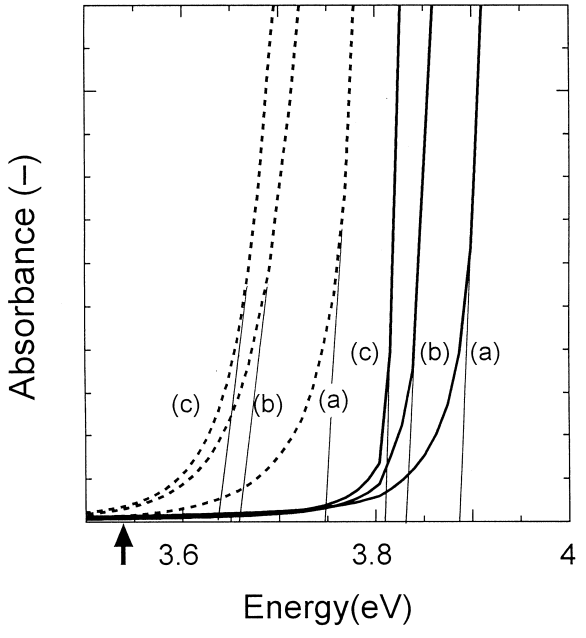

Fig. 8. Optical absorption spectra of gels containing (a) 1.5 wt.%, (b) 3.0 wt.%, or (c) 6.0 wt.% ZnO reacted with H_2S gas at (solid line) 30°C or (dotted line) 150°C for 1 h. (The arrow shown in the figure represents bulk ZnS absorption edge energy.)

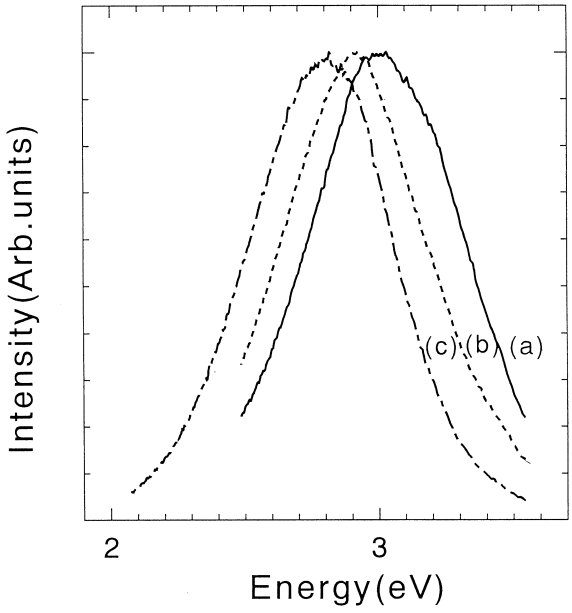

Fig. 10. Fluorescence spectra of gels containing 1.5 wt.% ZnO, measured at 295 K, after being reacted with H_2S gas for 1 h at (a) 30°C, (b) 100°C and (c) 150°C.

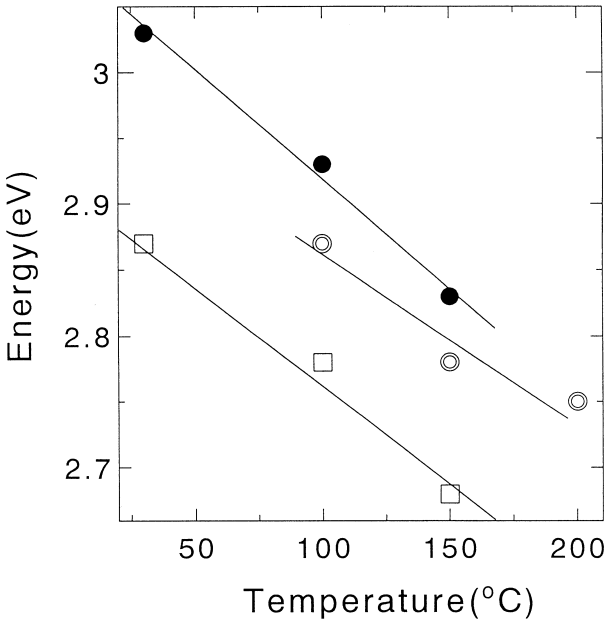

Fig. 11. Peak energy of the fluorescence spectra for the gels containing: ●, 1.5 wt.%; ◎, 3.0 wt.% and □, 6.0 wt.% ZnO reacted with H_2S gas for 1 h at various temperatures.

4. Conclusion

The sol–gel process was applied to prepare ZnS doped silica gels. Gels prepared through the hydrolysis and condensation of a solution of tetraethoxysilane and zinc acetate were reacted with H_2S gas to disperse ZnS crystals in silica gel matrix. From XRD and TEM observation, crystal size was determined to be 1–4 nm in diameter. The optical absorption edge exhibited a blue shift comparedto that of the bulk ZnS and its energy decreased reciprocally with the square of the crystal size. These blue shifts are also seen in the peak enregy of the fluorescence spectra. It was revealed that ZnS microcrystals in the silica gels are capable of exhibiting a quantum size effect.

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