Temperature Induced Stress of ZnSe Quantum Dots in Glass Matrix Thin Films Grown by Pulsed Laser Deposition

Ja-Chin Jan, Shou-Yi Kuo, Sun-Bin Yin and Wen-Feng Hsieh[¤]

Institute of Electro-Optical Engineering, National Chiao Tung University
Hsinchu, Taiwan 300, R.O.C.

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By analyzing the temperature dependent spectral shifts and broadenings of both photoluminescence (PL) and Raman modes from the ZnSe-doped glass thin films grown by pulsed laser deposition, we found that temperature induced stress causes excess shifts of the PL emission bands to higher energies when the samples were kept below 100K. The compressed stress may be a result of the different thermal expansion of the ZnSe nanocrystal and the glass matrix; it is further confirmed by the temperature dependent excess Raman shift in this quantum dot sample as compared with the crystal data in the high-pressure experiment. In addition, we found the activation energies of the nonradiative decay channels associated with the edge-emission and deep-level bands are close to 1TO and 1LO of ZnSe phonon energies.

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I. Introduction

In recent years, considerable studies have been conducted on the electronic and vibrational properties of wide band gap II-VI materials, such as ZnSe and ZnTe, for their applications in optoelectronic devices with response in the blue region, such as light-emitting diodes and lasers. The optical properties of size effects in II-VI semiconductor nanostructure due to the three dimensional confinement is another important area in solid-state physics. Various approaches have been developed to fabricate multilayer structures in which the excited carriers confined to the quantum states result in an enhanced lasing performance. In addition to quantum wells and quantum wires, semiconductor quantum dots are receiving much attention, due to their large optical nonlinearity and fast response [1-4].

The ability to perform optical experiments on semiconductors over a wide temperature range has many fundamental and applied ramifications. The temperature dependence of the energy shift and broadening of the band-gap emission can yield important information about electron-phonon interactions, behavior of defects and excitonic effects [5-10]. An increase in temperature leads to a redshift of the band gap and an increase in the linewidth. In the previous study [11], we have presented the Raman and photoluminescence (PL) results of ZnSe microcrystal-doped glass films deposited on a silicon substrate by pulsed laser deposition, and analyzed the influence of the heat treatment on ZnSe crystalline particulates with a spatial correlation model. We found that most of the particulates are smaller than 10 nm and the annealing only causes an aggregation of particulates without merging the grain boundaries and releasing the stress. In this paper we report

the temperature dependence of the as-deposited ZnSe quantum dots thin films in Raman and PL measurements between 14 K and 300 K. The temperature dependent spectral shifts and broadening of both photoluminescence (PL) and Raman modes indicates that the temperature induced stress causes excess shifts of the PL emission bands to higher energy when the samples were kept below 100 K.

II. Experimental

By using sol-gel method reported earlier [12] to fabricate target for pulsed laser deposition, we first dissolved tetramethyl orthosilicate [Si(CH$_3$O)$_4$, TMOS] in methanol, which was then mixed with water to obtain a molar ratio of TMOS:H$_2$O:CH$_3$OH=1:4:4.5. By stirring for 20 to 25 min under ammonia (NH$_4$OH) catalysis, the TMOS was partially hydrolyzed and then mixed with dimethylforamide [HCON(CH$_3$)$_2$, DMF], as we continued to stir for additional 5 min. In order to uniformly disperse the ZnSe powder in the colloidal sol, the pH value of the solution was set at 6.5 by adding a few drops of nitric acid before mixing with 1/4 mole of ZnSe powder of 99.999%. Thin films of SiO$_2$ doped with ZnSe microcrystallites were prepared by pulsed laser deposition. High-quality n-type silicon wafers were used as substrates. The growth of the thin films was carried out in a high vacuum system with a base pressure of about $5 \pounds 10^{i 5}$ Torr. The substrates were mounted onto a stage in the chamber. High-purity SiO$_2$ thin film doped with ZnSe microcrystallites was vaporized with a Nd-YAG laser operating at a wavelength of 1064 nm with pulse width of 90 ns. The average pulse energy was 10-20 mJ. In order to ensure that the laser beam vaporized the target uniformly and efficiently, the laser beam was focused to a spot of about 0.3 mm diameter on the target, which was mounted onto a small rotating motor. The Raman scattering measurements were performed with an Ar-ion laser as an excitation source emitting at wavelength of 488 nm, and in the photoluminescence measurements a 325 nm He-Cd laser was used to excite the sample at different temperatures range from 14 K to 300 K. These measurements were taken in the 45$^\pm$ reflection geometry with the samples placed on a micrometer stage in front of a triple grating spectrograph (SPEX 1877C) which is equipped with a liquid-nitrogen cooled charge coupled device (CCD) detector array (Phometrics CC200). We identified the composition of ZnSe in the semiconductor-doped glass (SDG) thin film to be Zn:Se=0.46:0.54 using electron probe microanalyzer (EPMA).

III. Results and discussions

Fig. 1 shows the PL spectra of the as-deposited ZnSe quantum dots in glass thin film at various temperatures between 14 K and 300 K as indicated in the figure. At 300 K, only two bands are realized, the high-energy band near 2.9 eV is the edge-emission band and the low-energy band around 2.53 eV is tentatively assigned as Y-band [13]. The band gap at room temperature being shifted from 2.72 eV for the bulk ZnSe crystal to 2.9 eV is attributed to the quantum size effect. As the temperature decreases, the line centers of these bands shift with raising intensity toward high energy and the two other bands progressively appear. At temperature below 200 K four bands are observed, the lower two bands being assigned as Zn-vacancies [14] and Z-band [13] together with Y-band are attributed to the structure defects of the ZnSe crystal.
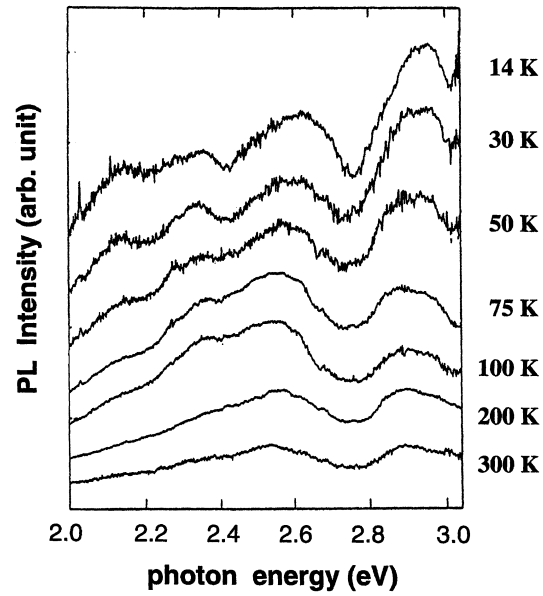
FIG. 1. The PL spectra of ZnSe quantum dots at various temperatures between 14 K and 300 K.
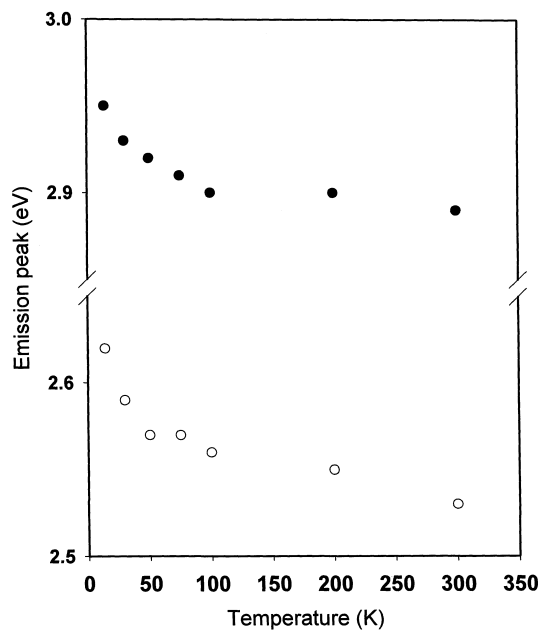

FIG. 2. The temperature dependence of the line centres in the PL spectra. The dark circles are the
edge-emission band and the open circles are assigned as Y-band emission.

Fig. 2 shows the temperature dependence of the line centers of the edge-emission band and the Y-band of the ZnSe quantum dots presented in Fig. 1. We find the line centers of both the edge-emission and Y-band shift to higher energy with decreasing temperature and the lower the temperature is, the more energy shifts. Since the energy shift of the edge-emission band of semiconductors with variations of temperature and pressure can be represented as: [15]

$$\Delta E = \frac{\partial E}{\partial T}\Delta T + \frac{\partial E}{\partial P}\Delta P \tag{1}$$

which means that the line center of the edge-emission band shifts linearly with decreasing temperature if P keeps constant or $\Delta P = 0$. However, the stress may exist in the samples so ΔP is no longer a constant since the compressibility and thermal expansion coefficients of ZnSe and glass are quite different [16]. Being a function of pressure and temperature, the volume of these materials may change differently. The temperature change may modify the volume in turn the induced stress may change the electro-optical properties of the ZnSe quantum dots. In Fig. 2, we can find the edge-emission band shifts to higher energy quite linearly with $\partial E/\partial T \approx -5.0 \times 10^{-5}$ eV K^{-1}, while -1.5×10^{-4} eV K^{-1} for Y-band shift, being less than that of bulk ZnSe crystal [15] (being -7.2×10^{-4} eV K^{-1}) when the temperature decreases from the room temperature. The low temperature coefficient had also been reported [14]. As the temperature decreasing further and being below 100 K, the edge-emission band further increases with $\partial E/\partial T \approx -5.4 \times 10^{-4}$ eV K^{-1} and -6.17×10^{-4} eV K^{-1} for Y-band shift. This indicates the stress is releasing or even stretching at the interface due to shrinkage of quantum dots in glass matrix with decreasing temperature from the room temperature and the stress may exist between quantum dots and glass matrix when the sample was cooled down below 100 K. The thermal expansion coefficients of ZnSe and glass are quite different, shown as in Fig. 3. Because ZnSe shows large negative thermal expansion coefficient by contrast with small positive one for glass matrix, when the temperature decrease below 100 K. The compress stress causes bandgap energy blue shift.

Fig. 4 is the temperature dependent PL intensities of the edge-emission and the Y-band of the ZnSe quantum dots presented in Fig. 1. The intensities of these bands raise as the temperature decreases, and the variation of intensity versus temperature can be expressed as the exponential gap law [14]:

$$I(T) = \frac{A}{[B + C\exp(-\Delta E/k_B T)]} \tag{2}$$

where A and B are constants, C is the probability of de-excitation by some nonradiative traps via thermal activation at high temperature and ΔE is the activation energy of the process. Eq. (2) has been used to fit these experimental data shown in Fig. 4 to obtain the activation energies for the edge-emission band and deep-level band about 237 cm^{-1} and 266 cm^{-1}, respectively. These energies are close to the optical phonon energies of 1TO at 210 cm^{-1} and 1LO at 254 cm^{-1} for ZnSe crystal at room temperature.
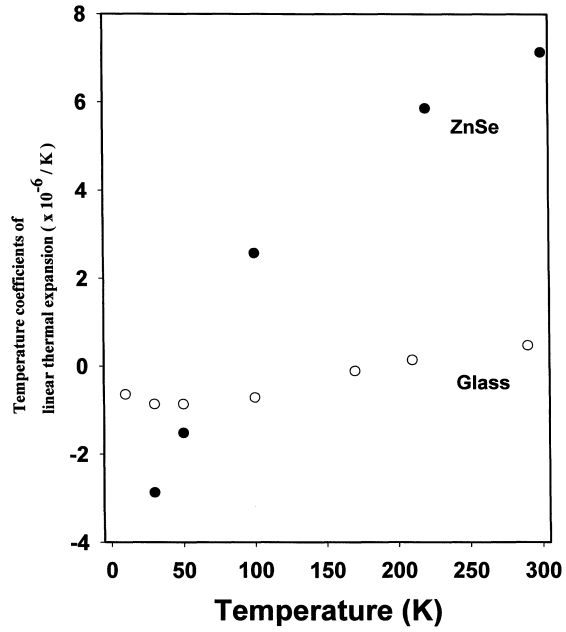
FIG. 3. The thermal expansion coefficients of ZnSe (dark circles) and quartz glasses (open circles) between 14 K and 300 K.
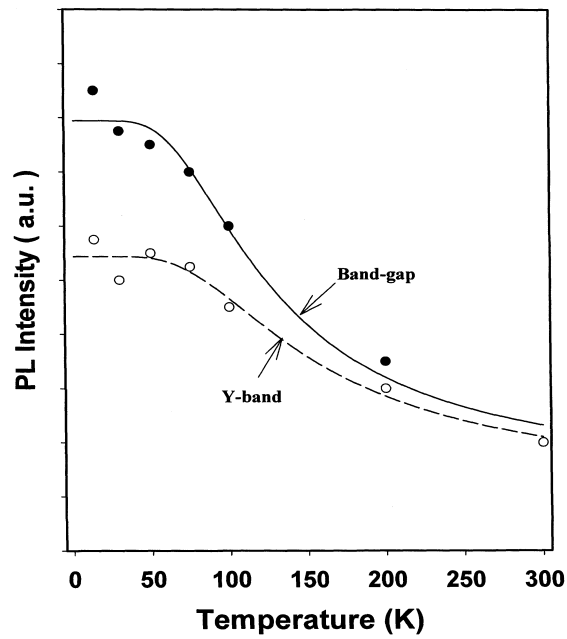

FIG. 4. The temperature dependent PL intensities of edge-emission band (dark circles) and the Y-band (open circles).
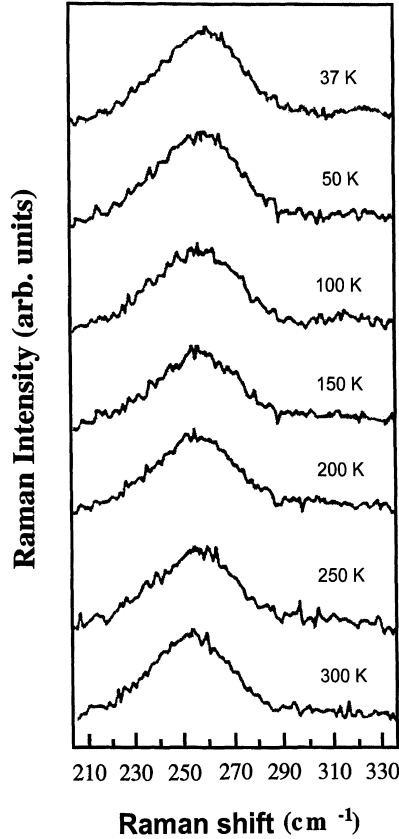
FIG. 5. The Raman spectra of ZnSe quantum dots at various temperatures between 14 K and 300 K.

The Raman spectra of ZnSe quantum dots at various temperatures between 37 K and 300 K are shown in Fig. 5. The line center of the 1LO Raman mode with different temperatures is plotted in Fig. 6 with dark circles. We can find the line center shifts to lower frequency as the line width becomes broadened with increasing temperature. The broadening of the line width results from the large thermal interaction at higher temperature, which decreases the phonon mean free path, and leads to the increased line width at higher temperature. The temperature-dependent shift can be attributed to anharmonicity in the vibrational potential. If we consider all possible decay channels, the temperature variation equation of the phonon line center can be written as [16]:

$$\omega(T) = \omega_0 + C \left(1 + \frac{1}{[\exp(\frac{h\omega}{k_B T}) - 1]} + \frac{1}{[\exp(\frac{h(\omega_0 - \omega)}{K_B T}) - 1]} \right) \tag{3}$$

where ω and $\omega_0 - \omega$ are the frequencies of the two final phonons, respectively. Eq. (3) has been used to fit these experimental data to obtain the constants ω_0, ω and C. The fitting result is plotted as a solid curve in Fig. 6 with fitting parameters as 258.9 cm^{-1}, 48.5 cm^{-1} and -0.172, respectively. The solid curve matches the experimental result quite well in temperature region
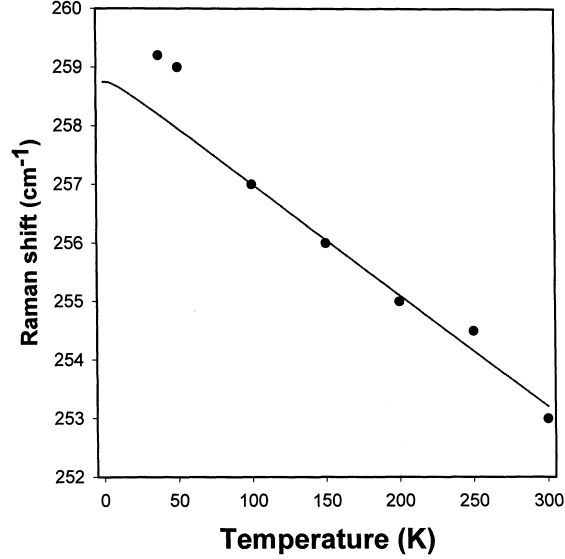
FIG. 6. The temperature dependence of the line centre of the 1LO Raman mode. The solid curve is the fitting result to the experimental data for the LA(48.5 cm^{-1})+TO(210.4 cm^{-1}) decay channel in <100> direction.

100-300 K. Soften of 1LO with 250 cm^{-1} at the room temperature as compared with that of the ZnSe crystal [16] which is 254 cm^{-1} again is attributed to quantum size effect. The nonradiative decay is assigned as to the TO(210.4 cm^{-1})+LA(48.5 cm^{-1}) in the <100> direction. If we use this possible decay channel and consider the temperature and pressure effects independently, by subtracting experimental data (solid dots) by the solid curve to represent pressure dependent Raman shift, we can roughly evaluate the compress stress by using the relation in the Refs. [17] and [18]:

$$LO : \Delta\omega = 3.44P - 0.02P^2 \tag{4}$$

where $\Delta\omega$ is in cm^{-1} and P in MPa. Through temperature change the stress induced in the thin film is similar to the high-pressure effect [18], we estimate the stress in the samples is about 170 MPa.

IV. Conclusion

We have analyzed the temperature dependence of the spectral shifts and broadening of both Raman and PL emission of ZnSe quantum dots in glass thin film grown by PLD. By fitting the temperature dependent PL intensity curves, we obtained the activation energies of the edge-emission band and deep-level band close to 1TO and 1LO of ZnSe. We also found the temperature induced stress shifts the bandgap to higher energy when the temperature lowers below 100 K as a result of large negative thermal expansion of the ZnSe microcrystal and small positive glass matrix. From the excess Raman shift below 100 K, we further confirmed that the temperature-induced stress exists in the sample.

Acknowledgement

References

[1] S. C. Hsu and H. S. Kwok Appl. Phys. Lett. **50**, 1782 (1987).

[2] E. Hanamura, Phys. Rev. **B37**, 1273 (1988).

[3] J. Warnock and D. D. Awschalim, Appl. Phys. Lett. **48**, 425 (1986).

[4] M. C. Nuss, W. Zinth and W. Kaiser, Appl. Phys. Lett. **49**, 1717 (1986).

[5] P. Lautenschlager *et al*., Phys Rev. **B35**, 9174 (1987).

[6] P. Lautenschlager, M. Garriga, and M. Cardona, Phys. Rev. **B36**, 4813 (1987).

[7] P. Lautenschlager, P. B. Allen, and M. Cardona, Phys. Rev. **B33**, 5501 (1986).

[8] P. B. Allen and M. Cardona, Phys. Rev. **B23**, 1495 (1981).

[9] P. Lautenschlager, Phys. Rev. **B36**, 4821 (1987).

[10] S. Gopalan, P. Lautenschlager, and M. Cardona, Phys. Rev. **B35**, 5577 (1987).

[11] S. B. Yin, L. Chen and W. F. Hsieh, Jpn. J. Appl. Phys. **37**, 4154 (1998).

[12] S. B. Yin and W. F. Hsieh, Jpn. J. Appl. Phys. **36**, 5646 (1997).

[13] R. Triboulet *et al*., J. of Crys. Growth **159**, 156 (1996).

[14] S. Mochizuki and K. Umezawa, J. Phys: Condens. Matter **8**, 7509 (1996).

[15] N. Peyghambarian, S. T. Koch and A. Mysyrowicz: *Introduction to Semiconductor Optics* 1st ed. (Prentice-Hall, New Jersey) Chap. 5, p. 132.

[16] S. Anand *et al.*, physica **B226**, 331 (1996).

[17] S. Ves *et al*., Solid State Comm. **56**, 479 (1985).

[18] W. C. Chou *et al*., Chinese Journal of Physics **35**, 266 (1997).