

行政院國家科學委員會專題研究計畫成果報告

凝態非線性光學材料之結構與其光學特性之相關研究(III)-
子計畫二：非線性光學材料複晶粉末和單晶之製備和雷射光譜
研究

Fabrication and laser spectroscopy of powder and single crystals of nonlinear optical materials

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一、中文摘要

我們已成功地用溶膠凝膠自製的靶材以雷射濺鍍成長摻 ZnSe 的微晶玻璃薄膜，並證實空間相干模型可用在此樣品的 LO 拉曼模。相干長與 SEM 結果不同可能是一個晶粒中可能含有較小的晶域由晶界隔開所致。

關鍵詞：硒化鋅，微晶，薄膜，雷射濺鍍，量子尺度效應，拉曼光譜，空間相干模型。

Abstract

We have successfully fabricated ZnSe semiconductor doped glass (SDG) thin films by PLD from ZnSe embedded in sol-gel glass targets and showed that the spatial correlation model is applicable for the LO Raman mode of ZnSe SDG thin films. The correlation lengths differ from the real sizes of the particulates by SEM may be due to the particulate is consisted of polycrystalline separated by grain boundaries. The correlation length just provides a measure of separated averaged grain dimension. The PL indicates that the carriers may tunnel through the grain walls in the polycrystalline particulates.

Keywords: ZnSe, microcrystal, thin films, pulsed laser deposition, quantum size effect,

Raman scattering, spatial correlation model

二、緣由與目的

The optical property of size effect in SDG due to 3D confinement is one of the important areas in solid state physics. The semiconductor quantum dots are receiving much attention for their large optical nonlinearity and fast response.¹⁻⁴⁾ Although the properties of semiconductor microcrystals, such as CdS, CdSe, CuCl and GaAs embedded in insulators have been investigated extensively, research on ZnSe microcrystals is limited. Brus and Chestoy et al⁵⁾ have reported results on the optical extinction spectra of ZnSe microcrystals in liquid. Li and Nogami⁶⁾ prepared successfully borosilicate glass films containing up to 40 wt% ZnSe crystallines on silica glass substrates by the sol-gel process. With the conventional melting and quenching method, ZnSe microcrystals have also successfully been embedded into Pyrex glass⁷⁾ and silica glass⁸⁾ matrix.

A model including the size effect was proposed by Richter et al.⁹⁾ in the study of the Raman scattering in the microcrystalline silicon and was proved to be effective for some III-V or II-VI compound semiconductors.¹⁰⁾ They investigated the

relationship between the spectral linewidth and the size of microcrystal. We will present the result of the fabrication and characterization of ZnSe SDG films deposited on silicon substrate by PLD. The quantum-size effect is realized by softening of the 1LO Raman mode and the PL measurement. With the spatial correlation model, we have also analyzed the influence of heat treatment on ZnSe crystalline.

三、研究報告應含的內容

We first used the sol-gel fabrication method mentioned previously¹¹⁾ to prepare SDG target. Then the thin films of SiO₂ doped with ZnSe microcrystallites were prepared by PLD. High quality n-type silicon wafers were used as substrates. The thin film was grown in a high vacuum system with a base pressure of 5×10^{-5} Torr. The substrate temperature was kept at 150°C. High-purity SiO₂ thin film doped with ZnSe microcrystallites was deposited with a Nd-YAG laser at wavelength of 1064 nm with pulse width 90 ns and pulse energy 10-20 mJ. In order to ensure that the laser beam vaporized the target uniformly and efficiently, the laser beam was focused to 0.3 mm in diameter on the target that was mounted on a small rotating motor. The as-deposited thin films were then post-annealed at various temperatures ranging from 50 to 200°C for 1 to 24 h in air.

Raman scattering was measured with an Ar-ion excitation laser @488.2 nm and PL measurement used a 325 nm He-Cd laser with the 45°-reflection geometry. The samples measured at room temperature was placed on the micrometer stage prior to a triple grating spectrograph (SPX 1877C) equipped with a liquid-nitrogen cooled CCD (Phometrics CC200). Finally, we identify the composition of ZnSe in the SDG thin film to be Zn : Se =

0.46:0.54 by EPMA.

四、結果與討論

Fig.1 shows the Raman spectra of the as-deposited ZnSe SDG thin films and annealed at 100°C and 200°C for 4 h, respectively (labeled as a, b and c). The first peak around 250 cm⁻¹ is 1LO phonon peak, and 520 cm⁻¹ peak corresponds to n-type silicon substrate. We find that the 1LO-phonon peak becomes stronger and more symmetrical as the annealing temperature increases.

The effects of post-annealing may cause the growth of ZnSe clusters and make the crystalline better, so the intensity of 1LO phonon of annealed film in spectra (c) is stronger than that of spectra (a) and (b). In addition, the 1LO-phonon peak gradually shifts from lower frequency as 250 cm⁻¹ to 253 cm⁻¹. The softening of the LO mode with respect to that of the bulk ZnSe at 253 cm⁻¹ is due to the size-effect¹²⁻¹³⁾ Further evidence of quantum size effect may be observed from PL spectra.

The PL spectra of the as-deposited ZnSe SDG thin film and annealed at 100°C and 200°C for 4 h (labeled as a, b and c) measured at room temperature is shown in Fig.2. There are two peaks around 2.9 eV and 2.63 eV in Fig.2(a), 2.89eV and 2.61eV in Fig.2(b), and 2.87eV and 2.58eV in Fig.(c), in which the high energy peak is corresponding to the band edge emission and the low energy peak is the luminescence of Zn vacancies. The annealing causes the aggregate of the ZnSe particulates, so the evidence for the quantum size effect of the annealed sample will be weaker and the emission peak of the PL spectra shift to the lower energy as increasing annealing temperature. Though it is difficult to quantitatively represent the observed shift, as compared with the edge

emission of the bulk ZnSe (2.72 eV) crystals,¹⁴⁾ we can evaluate the radius of the microcrystal approximately. Under weak confinement condition,¹⁵⁾ the radius of the ZnSe microcrystalline in the as-deposited thin film is 39 Å (or 78 Å in diameter) which agrees well with SEM, where most of the particulates are smaller than 100 Å dispersed uniformly in the as-deposited thin film.

In microcrystal, the finite size of the phonon amplitude result in the breakdown of the q-selection rule, which gives rise to the relaxation of q=0 selection rule. A Gaussian spatial correlation function $\exp(-2r^2/L^2)$ has been used to account for q-vector relaxation, where L is the correlation length which was considered as the average diameter of the regions of perfect crystalline. Then the Raman intensity at frequency ω , $I(\omega)$, can be written as:⁹⁾

$$I(\omega) \propto \int \exp(-q^2 L^2 / 4) / \{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2\} d^3q,$$

where q is expressed in units of $2\pi/a$ with a being the lattice constant and Γ_0 the intrinsic FWHM of the LO phonon line shape known as 4.8 cm^{-1} for ZnSe. The dispersion relation of the LO phonon derived from 1D linear-chain model:

$\omega^2(q) = A + [A^2 - B(1 - \cos q)]^{1/2}$, where the two constants A and B are chosen according to Ref. 10 as $A = 3.2 \times 10^4 \text{ cm}^{-2}$, $B = 4.5 \times 10^8 \text{ cm}^{-4}$. For simplicity we assume a spherical Brillouin zone, then the theoretical line shape $I(\omega)$ could be calculated with different L. Fig.3 is expanded version of the 1LO peaks from the spectra (a), (b) and (c) of Fig.1 after the correction of instrumental resolution and background subtraction. The theoretical line shapes shown as the solid lines fit fairly well with experimental results shown as the hollow circles in the lower frequency region. In order to make the line shapes comparable

to the experimental results, we have artificially moved the theoretical spectra to locate with the experimental peaks. It shows the spatial correlation model is effective for the ZnSe SDG. The mismatch of the theoretical and experimental results in the higher frequency region indicate the shifts in the higher frequency region may be caused by the stress in the samples which was not considered in this model. We obtained the correlation length L is 23 Å, 27 Å and 29 Å for spectra (a), (b) and (c), respectively.

The correlation length does slightly increase as increasing annealing temperature, however, it is inconsistent with the result deduced from PL spectrum and SEM photographs that the diameters of the ZnSe particulates are in the range of 80 to 100 Å. The discrepancy maybe results from the polycrystalline nature of the ZnSe particulates. Each of the particulates may be a combination of grains with different orientations separated by grain boundary. A twinned glass-sequestered ZnSe nanocrystal with size of 120 Å was also found by the HRTEM shown in Fig.4 of Ref.8. Furthermore, phonon is a collective vibration mode of a perfect crystal with specific orientation localized in a grain of the particulate and the correlation length of LO phonon mode represents a measure of averaged size of crystallites having the same orientation. The averaged size evaluated from LO Raman spectrum is smaller than that of the particulates in SEM photograph and thus no detectable X-ray peaks are found. On the other hand, the electrons and holes created by pumping photons may tunnel through the grain boundaries or defects and the whole particulate acts as a 100-Å quantum dot. Therefore, the size of microcrystal evaluated from the PL spectrum agrees with that of SEM photographs.

Furthermore, low temperature annealing (100°C and 200°C far below the melting point 1520°C of ZnSe) may merge ZnSe particulates to form larger ones but leave the grain boundaries unaffected. The stress did not release as shown in Fig. 3 with a slightly change in the correlation length of LO phonon and Raman shift in high frequency region.

五、結論

We have successfully fabricated ZnSe SDG thin films by pulsed laser deposition from ZnSe powder embedded in sol-gel glass targets. We have also showed that the spatial correlation model is applicable for the LO Raman mode of ZnSe SDG thin films. The reason why the correlation lengths differ from the real size of the particulates observed by SEM may be due to the particulates is consisted of polycrystalline with different orientations separated by grain walls. The correlation length of LO phonon provides a measure of separated averaged grain dimension. However, the diameter of quantum dot evaluated from the PL spectrum indicates that the carriers may tunnel through the grain walls in the polycrystalline particulates. Low temperature annealing only cause aggregate of particulates without merging the grain boundaries and releasing the stress.

六、自我評估

本年度中我們完成拉曼光譜研究摻 ZnSe 量子點玻璃薄膜，以所謂空間相關模型，由求得相關長度推斷微晶顆粒之大小。由變溫螢光和拉曼光譜證實此 SDG 薄膜具有量子侷限效應。由於 ZnSe 和玻璃具有不同之熱膨脹係數，在變溫光譜中我們也發現由於應力造成額外的能隙和震動頻率的位移。此結果已投稿 JJAP。最近我們從事非線性折射率量測初步的成果發現此樣品具有相當高的非線性折射係數，比已

報導的 SDG 塊材的非線性折射係數大了三至四個數量級，這個結果正進行進一步確認。如確認無誤，則我們可期待低功率全光交換的夢成為可行。

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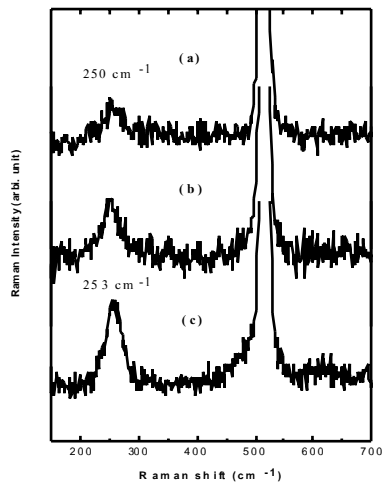


Fig. 1 Raman spectra of the as-deposited ZnSe SDG thin films, and those annealed at 100 °C and 200°C for 4 h (labeled as a, b and c, respectively)

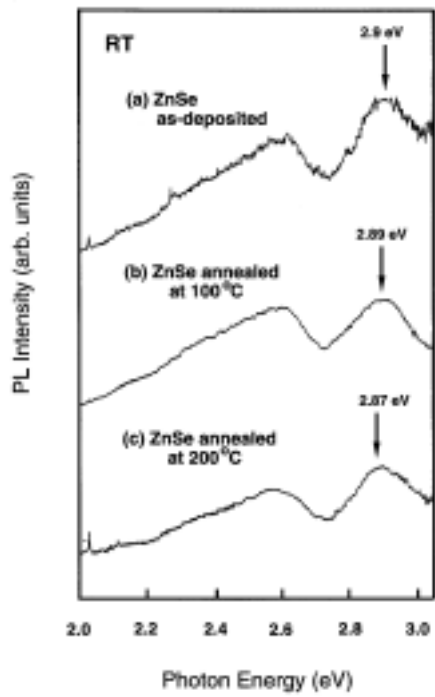


Fig. 2 Photoluminescence spectra of the as-deposited ZnSe SDG thin films, and those annealed at 100 °C and 200 °C (labeled as (a), (b) and (c), respectively). The experiments were performed at room temperature.

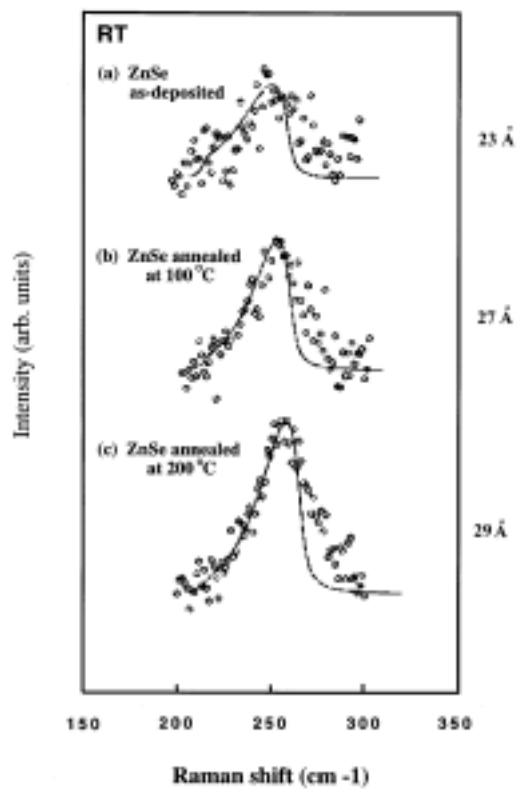


Fig. 5 The expanded ILO spectral peaks of spectra (a), (b) and (c) in Fig. 5-1. The theoretical results are shown by the solid lines and the open circles indicate the experimental results

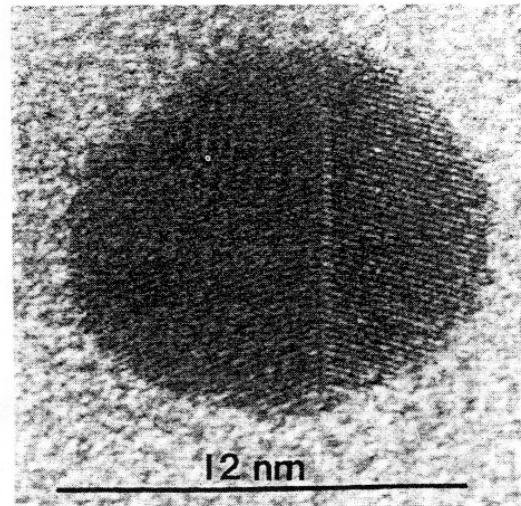


Fig.4 The HRTEM image of a twinned glass-sequestered ZnSe nanocrystal