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Raman study of ZnSe/SiO_x multilayers

M. J. ŠĆEPANOVIĆ[a*], M. GRUJIĆ-BROJČIN[a], I. BINEVA[b], D. NESHEVA[b], Z. ANEVA[b], Z. LEVI[b], Z. V. POPOVIĆ[a]
[a]*Center for Solid State Physics and New Materials, Institute of Physics, Pregrevica 118, 11080 Belgrade, Serbia*
[b]*Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria*

Multilayers of ZnSe/SiO_x having different ZnSe layer thicknesses (2.0, 3.5, 4.0, 5.0, 7.0 and 10 nm) have been prepared by thermal evaporation in vacuum. Raman scattering measurements have been performed at room temperature using the 442 nm line of a He-Cd laser. Two bands, which appear at about 250 and 500 cm^{-1}, have been attributed to the 1LO and 2LO modes from "pure" ZnSe in multilayers. Both modes show a large homogeneous broadening. The 1LO Raman mode displays an asymmetric shape and redshift, which can be related to the phonon confinement effect, due to the nanometric size of the ZnSe layers. The size effect on the band shape has been simulated by using a one-dimensional phonon confinement model for ZnSe nanolayers. The comparison of experimental and calculated data also implies the existence of surface phonon modes. Moreover, a change in the intensity of Raman scattering with ZnSe layer thickness points to the resonant enhancement of the Raman bands when the photon energy of the exciting light (2.8 eV) approaches the energy band gap of some samples.

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1. Introduction

Zinc-selenide (ZnSe) based nanostructures have great potential for various optical device applications, due to their nonlinear optical properties. The size-dependent effects on the properties of ZnSe nanostructures play a very important role in these applications. Raman spectroscopy has been recognized as an important technique for the study of the vibrational and structural properties of low-dimensional materials. The properties of the first order longitudinal (1LO) Raman mode in ZnSe nanostructures have been studied earlier [1-4], but the size effects on this mode are still tentative. Some authors did not notice any frequency shift [1,3], while others observed either a red- [2], or a blue-shift [4]. The asymmetric broadening was explained either by the phonon confinement model [1] or by the presence of surface phonon modes [2,3].

In this work, we study reduced space dimension effects on the Raman spectra of ZnSe/SiO_x multilayers. The influence of the ZnSe layer thickness on the frequency shift and asymmetrical broadening of the 1LO Raman mode is analyzed by applying an one-dimensional (1D) phonon confinement model. The shoulder between the TO and LO modes is attributed to Raman scattering from surface phonon modes.

2. Experimental details

Multilayers (MLs) of ZnSe/SiO_x (x~1.7, [5]) were prepared by consecutive thermal evaporation of ZnSe (Merck, Suprapure) and glassy SiO from two independent tantalum crucibles at a vacuum of 10^{-5} Torr. Corning 7059 glass substrates maintained at room temperature were used. The film thickness and deposition rate (0.2 nm/s for SiO and 1.5 nm/s for ZnSe) were controlled by two quartz crystal monitors (type MIKI-FFV), calibrated in advance. The thickness of the ZnSe layers was varied between 2.0 and 10 nm, while that of the SiO_x layers was between 2.5 and 6.0 nm A step-by-step procedure was applied in the deposition of each layer in the multilayers (ML). This procedure allowed the fabrication of nanocrystalline/amorphous MLs with smooth interfaces and good periodicity [6].

Raman measurements were performed in the backscattering geometry using the 442 nm line of a He-Cd laser, a Jobin-Yvon U1000 monochromator and a photomultiplier as the detector. The measurements were performed in air at room temperature.

3. Experimental results

The Raman spectra of ZnSe/SiO_x MLs of various thickness are shown in Fig. 1. The spectrum of a 100 nm ZnSe film is also shown. Two bands at ~250 and ~500 cm^{-1} are seen, attributed to first order (1LO) and second order (2LO) longitudinal optical scattering from "pure" ZnSe in MLs. The changes in the intensity of the LO modes with the ZnSe layer thickness (Fig. 1) imply the presence of resonant Raman enhancement.

The resonant Raman effect appears if the energy of the exciting light is close to that of a stationary electronic transition in the sample. The strongest enhancement is observed when the exciting light approaches the optical band gap of the material [7]. A band gap of ~2.67 eV was obtained for the 100 nm ZnSe thin film, from its PL spectrum shown in Fig. 2. Due to a rather strong PL emission from the Corning glass substrate, we were not

able to determine correctly the position of the PL from the ZnSe layers in the ZnSe/SiO$_x$ MLs. Values of 2.7 eV, 3.0 eV, and 3.3 eV have been reported [8] (obtained from the second derivative of the optical absorption spectra) for the band gap of ZnSe films having thicknesses of 8, 4.6 and 3.2 nm, respectively. Based on these

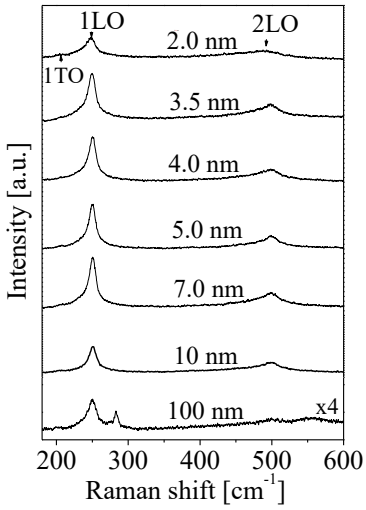

Fig. 1. Experimental Raman spectra of ZnSe/SiO$_x$ multilayers and a ZnSe film.

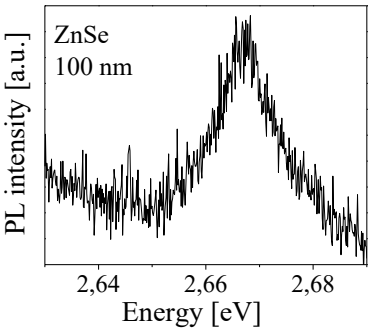

Fig. 2. PL spectra of a 100 nm ZnSe thin film.

data, one can estimate that the gap of a ZnSe film of thickness 7 nm is ~ 2.8 eV. This value is very close to the photon energy (2.805eV) of the exciting light, and we assume that because of this the intensity of the 1LO Raman mode is greatest, in the ZnSe/SiO$_x$ ML in which the ZnSe layer thickness is 7 nm (Fig. 1). The observation of resonance Raman scattering indicates that a blue shift of the optical band gap of the nanocrystalline ZnSe layers in MLs takes place with decreasing layer thickness.

The asymmetric shape, blueshift and broadening and shape of the first order Raman LO mode at ~251 cm^{-1} will be analyzed in the following text.

4. Model

According to the phenomenological phonon confinement model of Richter et al. [9] and Campbell et al. [10] using a Gaussian confinement function, the resulting Raman intensity $I(\omega)$ is usually presented as a superposition of weighted Lorentzian contributions over the whole Brillouin zone:

$$I(\omega) \propto \int_0^{\infty} \rho(L)\, dL \int_{BZ} \frac{\exp\left(\frac{-q^2L^2}{8\beta}\right) d^3q}{[\omega - \omega(q)]^2 + \left(\frac{\Gamma_0}{2}\right)^2} \qquad (1)$$

For the one-dimensional confinement model which can be applied to ultra thin films or quantum wells $d^3q \propto dq$, where q is the wave vector (expressed in terms of π and the unit cell parameter). L is the layer thickness, while $\rho(L)$ is the layer thickness distribution, β denotes the strength of confinement, and Γ_0 is the intrinsic line width. The dispersion relation $\omega(q)$ of an optical phonon is fitted to match experimental phonon dispersion curves for bulk ZnSe from Ref [11], by the cosine function:

$$\omega(q) = A - B(1 - \cos(\pi \cdot q)) \qquad (2)$$

where the parameter A=251 cm^{-1} is the phonon frequency at the centre of the Brillouin zone, while B=21 cm^{-1} determines the phonon behaviour outside the zone centre.

The shape of a Raman mode calculated from Eq. 1 strongly depends on the layer thickness. The phonon confinement calculations with 2.0, 3.5, 5.0, 7.0 and 10 nm layer thicknesses, shown in Fig. 1, were performed with the following parameters: intrinsic line width Γ_0 =12.5 cm^{-1}, factor $\beta \approx 12$, and a Gaussian layer thickness distribution with a

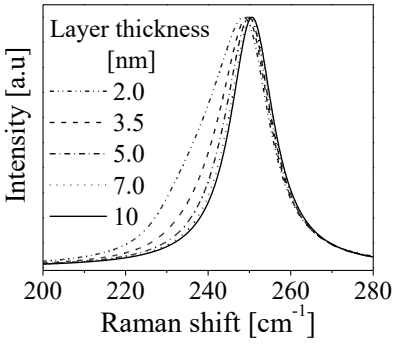

Fig. 3. Phonon confinement effect in ZnSe/SiO$_x$ multilayers calculated by using Eq. 1.

halfwidth of 0.10L_0. It is obvious that for layer thicknesses L_0>5.0 nm, the Raman mode position is near the bulk position, with an almost symmetric shape, while for L_0<5.0 nm the mode is blueshifted and broadened, with an asymmetric shape.

5. Discussion

The comparison of the experimental and calculated Raman spectra for several layer thicknesses is shown in Fig. 4. The calculated spectra were obtained as the sum of

contributions from two optical phonon modes, longitudinal (LO) and transverse (TO), as well as the so-called surface phonon mode (SP).

The intensity of the LO Raman mode was calculated according to the phonon confinement model described in the previous paragraph. Instead of the natural width for the bulk material of 6 cm^{-1}, the intrinsic line width Γ_0 used in these calculations was 12.5 cm^{-1}. Such large homogeneous broadening of the Raman spectra seems to be a common characteristic of II-VI nanocrystals and quantum dots [2]. The phonons confined in the nanocrystals frequently collide and relax at the interface, due to a reduction in the phonon mean free path as the dimensions of nanocrystal decrease. Lattice distortion and structure defects are common features of most nanostructured materials, which also result in a shortening of the phonon lifetime and contribute to the large homogeneous broadening [2].

In the literature, the factor β varies from 1 in the Richter confinement model to $2\pi^2$ in Campbell model, depending on the confinement boundary conditions in different nanomaterials [9, 10]. We obtained the best agreement between the experimental results and the 1D phonon confinement model by using a confinement strength of β=12.

In accordance with results obtained from atomic force microscope (AFM) measurements, a Gaussian layer thickness distribution with halfwidth $0.10L_0$ was used [5].

As can be seen from Fig. 4, the applied 1D phonon confinement model gives very good results in the estimation of the LO mode position and width. Some discrepancies from the experimental results at the higher frequency side of this mode might be also attributed to the lattice distortion and structural defects. Moreover, a compressive strain in ZnSe nanostructures can cause a blueshift of the LO Raman mode [4]. Therefore, for precise determination of the mode behaviour at the higher frequency side, strain data from XRD measurements are necessary.

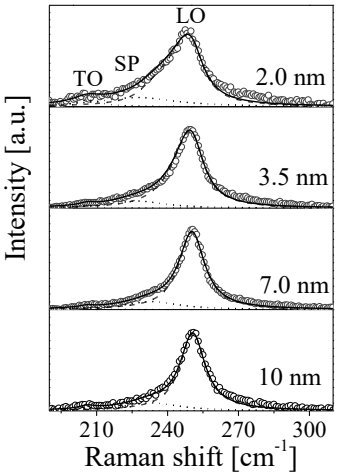

Fig. 4. Normalized experimental Raman spectra (o) *of ZnSe/SiO$_x$ MLs and calculated results* (*thick line*)*. Dotted lines denote TO and SP Lorentzian peaks. The dashed line represents the LO mode calculated from the 1D phonon confinement model.*

For fitting the TO mode, a Lorentz function with the peak at 206 cm^{-1} was used. The width and integrated intensity of this mode are listed in Table 1.

The shoulder between the TO and LO peak is usually attributed to scattering from the Fröhlich mode and all the other surface modes [2, 3]. In the case of nanocrystals, surface modes have been observed [12], and their frequencies for ZnSe lie above the Frölich frequency for bulk material ω_F=223 cm^{-1} and below ω_{LO} (~251 cm^{-1}). Because of the weak intensity of these modes, we used one Lorentz function to describe their effects. The parameters of these Lorentzians for different film thickness are listed in Table 1.

Table 1. Lorentzian parameters for TO and surface phonon mode: ω - mode frequency, FWHM - full width at half maximum, I - integrated intensity.

Layer thickness	*TO phonon mode*			*Surface phonon mode* (SP)		
[nm]	ω [cm^{-1}]	FWHM [cm^{-1}]	*I* [a.u.]	ω [cm^{-1}]	FWHM [cm^{-1}]	*I* [a.u.]
2.0	206	14	2.0	227	40	8.0
3.5	206	8	0.4	227	28	4.0
7.0	206	8	0.3	233	28	4.5
10.0	206	8	0.5	233	28	4.5

6. Conclusions

ZnSe/SiO_x multilayers, prepared by thermal evaporation in vacuum, have been characterized by Raman spectroscopy. The spectra presented here were obtained at room temperature by using the 442 nm He-Cd laser line. The observed resonant behavior in the Raman spectra is related to size-induced change of the bandgap energy with layer thickness.

The homogeneous broadening of Raman spectra of the ZnSe/SiO_x multilayers can be related to lattice distortion and structure defects. The first order spectra are decomposed into TO, LO and SP modes. The size-dependent redshift of the LO mode frequency is analyzed by a 1D phonon confinement model, and good agreement between the calculated and experimental results is obtained. The asymmetric broadening at the lower frequency side of the LO mode is analyzed as a combined

contribution of phonon confinement and the influence of surface phonon modes.

This study has shown that a 1D confinement model is appropriate for analysis of the Raman spectra of ZnSe/SiO_x multilayers, and allows us to assume that ZnSe in these MLs can be treated as nanolayers rather than as isolated or weakly connected nanoparticles.

References

[1] D. Sarigiannis, J. D. Peck, T. J. Mountziaris, Appl. Phys. Lett. **80,** 4024 (2002).
[2] A. Hui-Zhi, Z. Qing, D. Wei-Min, Chin. Phys. **13**, 1753 (2004).
[3] X. Fu, H. An, W. Du, Mat. Lett. **59,** 1484 (2005).
[4] P. V. Teredesai, F. L. Deepak, A. Govindarai, A. K. Sood, C. N. Rao, J. Nanosci. Nanotechnol. **2**, 495 (2002).
[5] D. Nesheva, I. Bineva, Z. Levi, Z. Aneva, Ts. Merdzhanova, J. C. Pivin, Vacuum **68**, 1 (2003).
[6] D. Nesheva, in Handbook of Surfaces and Interfaces of Materials, ed. H.S. Nalwa, Academic Press, San Diego (2001), Vol. 3, p.239.
[7] D. Nesheva, J. Optoelectron. Adv. Mater. **7**, 185 (2005).
[8] J. Mazher, S. Badwe, R. Sengar, D. Gupta, R. K. Pandey, Phys, E **16**, 209 (2003).
[9] H. Richter, Z. P. Wang, L. Ley, Solid State Commun. **39**, 625 (1981).
[10] I. H. Campbell, P. M. Fauchet, Solid State Commun. **58**, 739 (1986).
[11] K. Kunc, M. Balkanski, M. A. Nusimovici, phys. status sol. b **72**, 229 (1975).
[12] M. I. Vasilevskiy, A.G. Rolo, M. J. M. Gomes, Solid State Commun. **104**, 381 (1999).

*Corresponding author: maja@phy.bg.ac.yu