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Raman Scattering of $Zn_{1-x}Cd_xSe/ZnSe$ Strained Superlattices Under Hydrostatic Pressure

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The Raman scattering in $Zn_{0.74}Cd_{0.26}Se/ZnSe$ superlattices under hydrostatic pressures up to 4.53 GPa at room temperature has been studied. The pressure-dependences of the ZnSe-like LO-phonon (LO_b) and the $Zn_{0.74}Gd_{0.26}Se$-like LO-phonon (LO_w) have been obtained. At 2.7 GPa, the pressure-coefficients of both LO_b and LO_w phonon energies increase abruptly. The $2LO_w$-phonon resonance has been observed at 1.82 GPa with 488.0 nm excitation for the $Zn_{0.75}Cd_{0.25}Se/ZnSe$ superlattices.

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Wide-gap II–VI superlattices (SLs) and quantum wells derived from ZnSe have attracted much attention for several years because of their unique optical and electrical properties.[1,2] In particular, the $Zn_{1-x}Cd_xSe/ZnSe$ heterostructures have shown both strong exciton transition and low-threshold optically pumped lasing at room temperature.[3] Recently, Raman scattering has widely been used to study the phonon modes in semiconductor quantum wells and SLs. Significant experimental and theoretical results have been obtained from the study of first-order Raman scattering. Huang *et al.*[4] presented a systematic microscopic theory for optical-phonon Raman scattering in multi-quantum wells (MQWs). Lozykowski *et al.*[5] studied preliminarily the Raman spectra of $Zn_{1-x}Cd_xSe/ZnSe$ single quantum wells. Hou *et al.*[6] studied resonant Raman scattering in $(CdSe)_1(ZnSe)_3/ZnSe$ short-period superlattice MQWs. Chi *et al.*[7] observed and identified ZnSe-like LO-phonon (LO_b) mode from the barrier layers and $Zn_{0.76}Cd_{0.24}Se$-like LO-phonon (LO_w) from the well layers in $Zn_{0.76}Cd_{0.24}Se/ZnSe$ SLs. However, as far as we know, there have been no previous studies about the pressure dependence of Raman scattering of $Zn_{1-x}Cd_xSe/ZnSe$ quantum wells and superlattices. In the present work we have studied the effects of hydrostatic pressure on the LO_w-phonon in strained well layer and the LO_b-phonon in strained barrier layer of the $Zn_{0.74}Cd_{0.26}Se/ZnSe$ SLs. In addition, we have also investigated the pressure-induced resonant Raman scattering in the $Zn_{0.75}Cd_{0.25}Se/ZnSe$ SLs.

The samples of $Zn_{1-x}Cd_xSe/ZnSe$ strained-layer SLs were grown by metal-organic chemical vapour deposition method. The substrates were (001)-oriented GaAs. A ZnSe buffer layer with thick of 1.2 μm was first deposited on the substrates, followed by 150 periods of SLs. The SLs consist of 4.0 nm thick of $Zn_{1-x}Cd_xSe$ well layers, separated by 6.0 nm thick of ZnSe barrier layers. Finally, a ZnSe Cap layer with the thick of 0.3 μm was grown on the surface.

In order to perform studies under pressure, the GaAs substrate was thinned to about 50 μm, and the cleaved rectangular sample-pieces of about 100 μm in linear dimension were mounted in a sample chamber of miniature diamond-anvil pressure cell. A methanol-ethanol mixture with a ratio of 4 : 1 was used as a pressure-transmitting medium, which ensures a truly hydrostatic pressure up to about 10 GPa. The pressure was calibrated by the ruby fluorescence technique.[8] The back scattering Raman spectra at different pressures were measured by a Spex-1403 Raman spectrometer with excitation of 457.9 and 488.0 nm lines from an Ar^+ laser. All Raman spectral measurements were carried out at room temperature.

Figures 1(a) and 1(b) show the first and second order Raman scattering spectra of the $Zn_{0.74}Cd_{0.26}Se/ZnSe$ SLs at ambient and elevated pressures. The phonon modes in Fig. 1 can be attributed to LO phonon mode. In Fig. 1 (a), the observed frequency, $254\,cm^{-1}$, approximately equals the LO phonon frequency of pure ZnSe. Thus it is reasonably assigned to the LO-phonon of barrier layer ZnSe and abbreviated to LO_b. The observed $250\,cm^{-1}$ band in Fig. 1(b) is assigned to the LO-phonon mode of well layer $Zn_{0.74}Cd_{0.26}Se$ and abbreviated to LO_w. The frequency $254\,cm^{-1}$ of LO_b at ambient pressure is $4\,cm^{-1}$ higher than that of LO_w in Fig. 1(b) at the same pressure. At room temperature the incident photon energy of 457.9 nm, 2.708 eV, is quite near to the band gap of ZnSe, 2.69 eV. The Raman scattering by the ZnSe barrier layers is in nearly resonant condition. The LO_w cannot be observed under excitation of 457.9 nm laser beam because it is too weak comparing to the strong resonant LO_b mode. Thus 488.0 nm laser beam was used to observe the Raman scattering of the $Zn_{0.74}Cd_{0.26}Se$ well layers. Under excitation of 488.0 nm, the ZnSe barrier layers are transparent because the incident photon energy is lower than the energy gap of ZnSe. However, the $\mathrm{Zn_{0.74}Cd_{0.26}Se}$ well layers are not transparent.

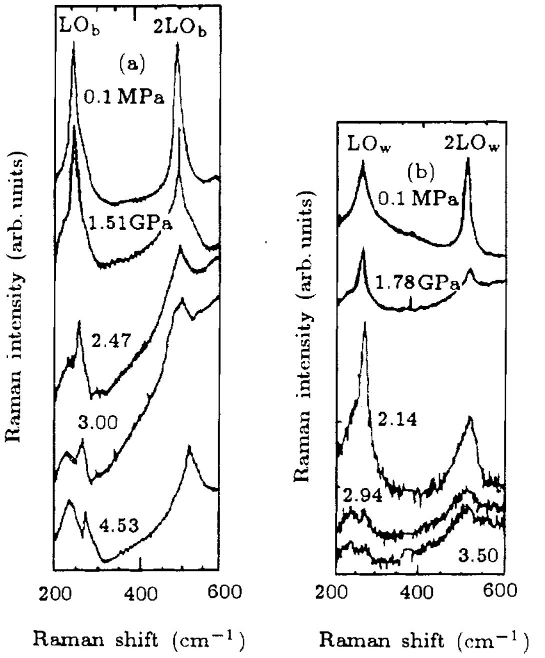

Fig. 1. Raman spectra of the $\mathrm{Zn_{0.74}Cd_{0.26}Se/ZnSe}$ SLs at different pressures. (a) $\mathrm{LO_b}$ and $\mathrm{2LO_b}$ peaks excited by 457.9 nm line of argon-ion laser; (b) $\mathrm{LO_w}$ and $\mathrm{2LO_w}$ peaks excited by 488.0 nm line.

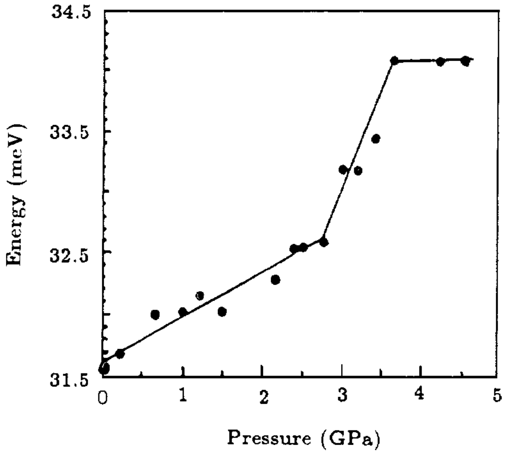

Fig. 2. Pressure dependence of the $\mathrm{LO_b}$-phonon energy for the $\mathrm{Zn_{0.74}Cd_{0.26}Se/ZnSe}$ SLs.

At high pressure a new band appears on low-energy sides of both $\mathrm{LO_b}$ and $\mathrm{LO_w}$ bands. This band is not yet clearly understood at present and conjectured to be caused by the SLs distortion. From Fig. 1(b) we also find that at ambient pressure the intensity of $\mathrm{2LO_w}$ is stronger than that of $\mathrm{LO_w}$. This phenomenon could be explained by a double resonance.[7]

At various pressures the $\mathrm{LO_b}$- and $\mathrm{LO_w}$-phonon energies of the $\mathrm{Zn_{0.74}Cd_{0.26}Se/ZnSe}$ SLs are presented in Figs. 2 and 3, respectively. From Figs. 2 and 3 it was found that the pressure-coefficients of both the $\mathrm{LO_b}$- and $\mathrm{LO_w}$-phonon energies all change abruptly at 2.7 GPa. Before and after 2.7 GPa, the pressure-coefficients of $\mathrm{LO_b}$-phonon energy are 0.37 and 1.63 meV/GPa, respectively, which approximately equal to those of $\mathrm{LO_w}$-phonon energy at corresponding pressure region. For $\mathrm{LO_b}$-phonon the slope of its energy curve changes again at abut 3.7 GPa. The intensities of both the $\mathrm{LO_b}$- and $\mathrm{LO_w}$-phonon peaks decrease with the increasing pressure, and when $p >$ 3.5 GPa, the scattering intensity of the $\mathrm{LO_w}$-phonon is too weak to be observed.

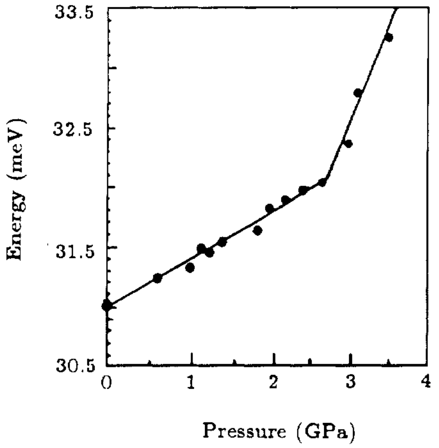

Fig. 3. Pressure dependence of the $\mathrm{LO_w}$-phonon energy for the $\mathrm{Zn_{0.74}Cd_{0.26}Se/ZnSe}$ SLs.

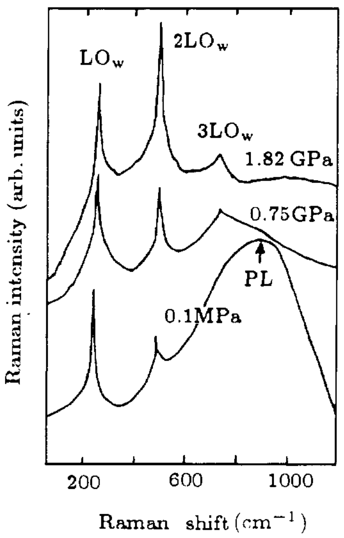

Fig. 4. Pressure tuned resonance Raman scattering in $\mathrm{Zn_{0.75}Cd_{0.25}Se/ZnSe}$ SLs. When p = 1.82 GPa, the $\mathrm{2LO_w}$ peak falls right on top of the PL peak and the resonance occurs.

The above-mentioned abrupt changes of pressure-coefficient at 2.7 and 3.7 GPa are reminiscent of a phase change in the SLs. However the structural transition in the bulk ZnSe is above 10 GPa and the bulk $\mathrm{Zn_{0.74}Cd_{0.26}Se}$ shows no structrual phase transition at least up to 7 GPa.[9] We note that phase transitions in SL structure occur at pressures which are different from those of the component materials in their bulk state. Since the abrupt-change pressure, 2.7 GPa, is much lower than the phase transition pressures of the well and barrier bulk materials, the observed phenomenon at 2.7 GPa is unlikely to be caused by structural phase transition. It may be due to the SL distortion, which is associated with the shear stresses introduced between layers by the different compressibilities of the adjacent layers. On the basis of the similar reason, the abrupt change of the pressure-coefficient at 3.7 GPa for $\mathrm{LO_b}$ is also unlikely to be caused by structural phase transition.

From the pressure dependence of the $\mathrm{LO_b}$(or $\mathrm{LO_w}$) vibrational mode, the mode Grüneisen parameter defined by

$$\gamma_{\mathrm{o}} = \frac{B_0}{\omega_0}\frac{\mathrm{d}\,\omega}{\mathrm{d}\,p}\bigg|_{p=0}$$

can be obtained, where ω is the frequency of the mode and B the bulk modulus, the subscript '0' represents ambient pressure. The values of B_0 in ZnSe and $\mathrm{Zn_{0.74}Cd_{0.26}Se}$ are 61.0 and 58.9 GPa,[10] respectively. By use of our experimental data we get

$$\gamma_{\mathrm{o}} = 0.7$$

for modes $\mathrm{LO_b}$ and $\mathrm{LO_w}$.

In resonant Raman scattering experiments, usually the incident photon energy is varied, and the electronic energy gaps of the system remain constant. However, the energy gaps in $\mathrm{Zn_{1-x}Cd_xSe/ZnSe}$ SLs can be easily tuned by pressurization because of their large pressure-coefficient. Thus pressure offers an alternate route to study resonant Raman scattering.

The $\mathrm{LO_w}$-, $\mathrm{2LO_w}$-, and $\mathrm{3LO_w}$-phonon Raman scatterings are given in Fig. 4 along with the photoluminescence (PL) for the $\mathrm{Zn_{0.75}Cd_{0.25}Se/ZnSe}$ SLs at ambient and elevated pressures. The sample is excited with 488.0 nm (2.540 eV) laser line. At ambient pressure the energy of the PL peak is 2.43 eV, corresponding to the exciton transition from $n = 1$ electron subband to the $n = 1$ heavy-hole subband. The $\mathrm{2LO_w}$-phonon peak near the PL peak and falls on the high-energy side of the PL peak. With the increasing pressure, the PL peak shifts towards higher energy, the separation between the $\mathrm{2LO_w}$-phonon peak and the PL peak reduces, and finally the $\mathrm{2LO_w}$ peak falls right on top of the PL peak at 1.82 GPa (see Fig. 4). The out-going resonance occurs precisely, and the direct gap of the SLs is revealed, which equals the difference between the energies of the incident photon and the scatterd phonon $\mathrm{2LO_w}$.

In conclusions, the effect of hydrostatic pressure on the ZnSe-like $\mathrm{LO_b}$ phonons in ZnSe barrier layers and the $\mathrm{Zn_{0.74}Cd_{0.26}Se}$-like $\mathrm{LO_w}$-phonons in the well layers has been studied for the $\mathrm{Zn_{0.74}Cd_{0.26}Se/ZnSe}$ SLs. The pressure dependences of $\mathrm{LO_b}$- and $\mathrm{LO_w}$-phonon energies are obtained. At 2.7 GPa, the pressure coefficients of both $\mathrm{LO_b}$- and $\mathrm{LO_w}$-phonon energies increase abruptly from 0.37 to 1.63 meV/GPa. The mode Grüneisen parameters $\gamma(\mathrm{LO_b})$ and $\gamma(\mathrm{LO_w})$ are evaluated. The $\mathrm{2LO_w}$-phonon resonance is obtained at 1.82 GPa with 488.0 nm excitation for the $\mathrm{Zn_{0.75}Cd_{0.25}Se/ZnSe}$ SLs.

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