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# Multiphonon Raman scattering in ZnSe/$Zn_{0.80}Cd_{0.20}Se$ superlattices

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## Abstract

A study of the multiphonon (MP) Raman scattering in ZnSe/$Zn_{0.80}Cd_{0.20}Se$ superlattices has been performed for the first time. Two kinds of longitudinal optical phonon modes were observed under the excitation of the 457.9 nm (2.71 eV) and 488.0 nm (2.54 eV) lines of an $Ar^+$ ion laser at room temperature. A systematic discussion to distinguish the MP Raman scattering from hot luminescence is presented.

*Keywords:* Raman scattering; Superlattices; Luminescence; Chemical vapour deposition

## 1. Introduction

Semiconductor superlattices have recently attracted much attention because of their unique optical and electrical properties. In particular, the wide-gap II–VI semiconductor superlattices are potentially useful for blue-light-emitting diodes, injection laser, and optical bistability devices. Recently, Raman scattering has widely been used to study the phonon modes in semiconductor quantum wells and superlattices. Significant experimental and theoretical results have been obtained from the study of first-order Raman scattering. Huang et al. [1] presented a systematic microscopic theory for optical–phonon Raman scattering in multi-quantum wells (MQWs). Lozykowski and Shastri [2] studied the Raman properties of ZnSe/$Zn_{1-x}Cd_xSe$ single quantum wells. Hou et al. [3] studied resonant Raman scattering in $(CdSe)_1(ZnSe)_3$/ZnSe short-period superlattice MQWs and observed two kinds of ZnSe-like longitudinal optical (LO) phonon in barrier layers and well layers, respectively. Unlike first-order Raman scattering, multiphonon (MP) Raman scattering in semiconductor superlattices has received less attention. For II–VI semiconductor quantum wells and superlattices, MP Raman scattering has also been investigated in ZnTe/ZnSe, CdTe/$Cd_xMn_{1-x}Te$, CdTe/HgTe, ZnSe/ZnSeS, CdTe/ZnTe, and $(CdTe)_2(ZnTe)_4$/ZnTe [4–9]. In this paper we report the results of MP Raman scattering in ZnSe/$Zn_{0.80}Cd_{0.20}Se$ superlattices.

## 2. Experiments

The sample used in this experiment was grown at 320 °C by metal–organic chemical vapour deposition (MOCVD). A ZnSe buffer layer with a thickness of 1 μm was first deposited on a (001) GaAs substrate before the superlattices were grown. The superlattices were composed of one hundred $Zn_{0.80}Cd_{0.20}Se$ wells of thicknesses $L_w = 4.0$ nm, separated by the ZnSe barrier layers with $L_b = 6.0$ nm.

The Raman spectra were taken using backscattering geometry under the excitation of various lines of an $Ar^+$ ion laser. The coordinates $X$, $Y$ and $Z$ were chosen to be parallel to the crystal axes (100), (010) and (001), respectively. The scattered light was analyzed with a SPEX-1403 double monochromator and detected by a RCA-C31034 cooled photomultiple tube.

## 3. Results and discussion

Fig. 1(a) and 1(b) shows room temperature (RT) Raman spectra excited by the 457.9 nm (2.71 eV) and 488.0 nm (2.54 eV) lines, respectively. In the backscattering geometry, the transverse optical (TO) phonon mode is forbidden and LO mode is allowed according to the selection rules. So, phonon modes observed in Fig. 1 can be attributed to the LO phonon-like mode. Two different phonon modes, $LO_1$ and $LO_2$, were observed, respectively. Under excitation of the

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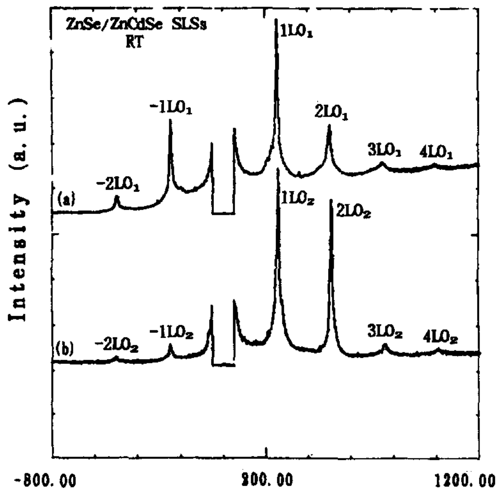

Fig. 1. Raman spectra of ZnSe/$Zn_{0.80}Cd_{0.20}Se$ excited by the (a) 457.9 nm and (b) 488.0 nm lines of an $Ar^+$ ion laser, taken at RT.

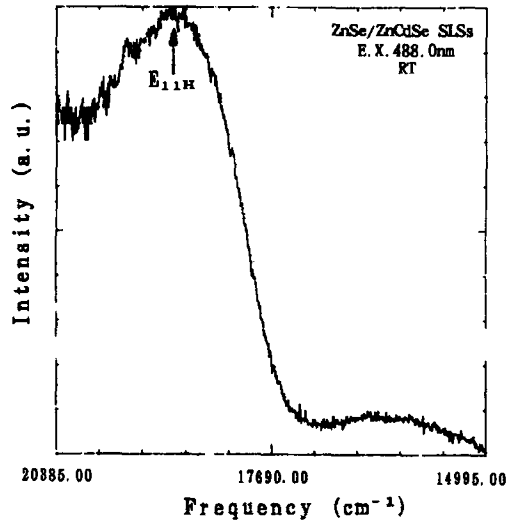

Fig. 2. Photoluminescence spectrum of ZnSe/$Zn_{0.80}Cd_{0.20}Se$ excited by the 488.0 nm line of an $Ar^+$ ion laser, taken at RT.

488.0 nm (2.54 eV) line of an $Ar^+$ ion laser, the ZnSe barrier layers were transparent for the incident light of the 488.0 nm (2.54 eV) line, which is in near-resonant conditions with the photoluminescence of the $Zn_{0.80}Cd_{0.20}Se$ well layers. The frequency of $LO_1$ was 249 $cm^{-1}$. Recent investigations of the Raman spectra of $Zn_{1-x}Cd_xSe$ bulk mixed crystal have shown that LO phonon spectrum versus crystal composition is the one-mode type [10]. The LO phonon mode shifted monotonically to the lower energy side from $\omega_{LO} = 252$ $cm^{-1}$ for pure ZnSe ($x=0$) to $\omega_{LO}=245$ $cm^{-1}$ for $x=0.25$ ($Zn_{0.75}Cd_{0.25}Se$). Assuming that the LO phonon frequency in the well layer with $x=0.20$ is the same as in bulk mixed crystal, according to Valakh' result, we can give the $Zn_{0.80}Cd_{0.20}Se$-like frequency $\omega_{LO}=249$ $cm^{-1}$. Thus, it is reasonable to attribute $LO_1$ in Fig. 1(a) to $Zn_{0.80}Cd_{0.20}Se$-like LO phonon modes from the $Zn_{0.80}Cd_{0.20}Se$ well layers. The frequency of $LO_2$ is 252 $cm^{-1}$, 3 $cm^{-1}$ greater than that of $LO_1$. At RT, the incident photon energy of the 457.9 nm (2.71 eV) line of an $Ar^+$ ion laser was quite near to the bandgap of ZnSe barrier layers, leading to resonant Raman scattering through band-edge transitions of electrons. Thus, $LO_2$ modes are reasonably assigned to those of the ZnSe barrier layers.

Fig. 2 shows the photoluminescence (PL) spectrum of ZnSe/$Zn_{0.80}Cd_{0.20}Se$ superlattices excited by the 488.0 nm line of an $Ar^+$ ion laser at RT. The PL spectrum exhibits one peak $E_{11H}$. ZnSe barrier layers are transparent for the incident light of the 488.0 nm (254 eV) line, so the incident light directly excites the $Zn_{0.80}Cd_{0.20}Se$ quantum wells. In II–VI wide-gap superlattices, the enhancement of the exciton binding energy and the large oscillator strength make it possible to observe photoluminescence of the $n=1$ heavy-hole (HH) exciton recombination of $Zn_{0.80}Cd_{0.20}Se$ well layers at RT, so the emission peak $E_{11H}$ in Fig. 2 can be attributed to the free exciton transition between the $n=1$ electron subband ($E_{1E}$) and the $n=1$ heavy-hole subband ($E_{HH}$) of the $Zn_{0.80}Cd_{0.20}Se$ wells [11].

Fig. 3 shows polarized and depolarized multiphonon Raman scattering spectra of the $LO_w$ line under excitation of the 488.0 nm line of $Ar^+$ ion laser at RT. The $Zn_{0.80}Cd_{0.20}Se$-like LO phonon located at 249 $cm^{-1}$ and its overtones were observed. There is no difference in the polarized Raman spectrum and depolarized Raman spectrum except for the intensity.

Fig. 4 shows the MP Raman spectra with excitation by the lines of (a) 476.5 nm (2.60 eV), (b) 488.0 nm (2.54 eV), and (c) 514.5 nm (2.41 eV) of an $Ar^+$ ion laser. The frequencies of the LO overtones are listed in Table 1. The LO frequencies excited by 514.5 nm line are smaller than those excited by 476.5 nm and 488.0 nm lines. The reason for this is not yet clear. In Fig. 4(a) and 4(b), LO phonons appear superimposed on the PL band from $n=1$ HH exciton emission. Overtones up to the 4th order were observed. It can be

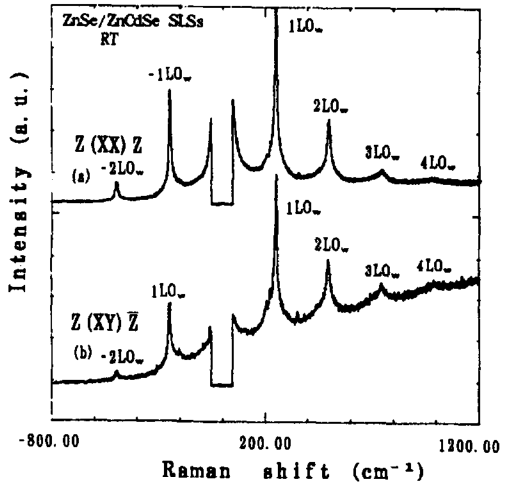

Fig. 3. Polarized and depolarized Raman spectra of ZnSe/$Zn_{0.80}Cd_{0.20}Se$ excited by the 488.0 nm line of an $Ar^+$ ion laser, taken at RT.

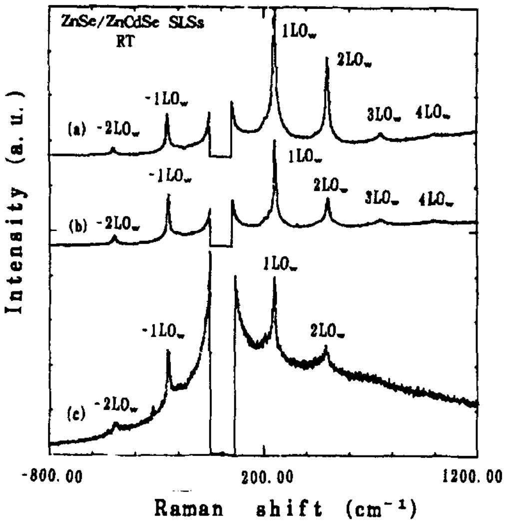

Fig. 4. Stokes and anti-stokes Raman spectra of ZnSe/$Zn_{0.80}Cd_{0.20}Se$ excited by the (a) 476.5 nm, (b) 488.0 nm and (c) 514.5 nm lines of an $Ar^+$ ion laser, taken at RT.

Table 1
The peak positions and FWHM of LO multiphonon Raman lines

| $E_{in}$ (eV) | | −2LO | −1LO | 1LO | 2LO | 3LO | 4LO |
|---|---|---|---|---|---|---|---|
| 2.71 | $\omega$ ($cm^{-1}$) | 502 | 252 | 252 | 504 | 753 | 1003 |
| | FWHM ($cm^{-1}$) | 19 | 20 | 16 | 15 | 23 | 25 |
| 2.60 | $\omega$ ($cm^{-1}$) | 499 | 249 | 249 | 497 | 745 | 997 |
| | FWHM ($cm^{-1}$) | 17 | 15 | 14 | 16 | 21 | 26 |
| 2.54 | $\omega$ ($cm^{-1}$) | 498 | 248 | 249 | 497 | 743 | 990 |
| | FWHM ($cm^{-1}$) | 17 | 14 | 17 | 21 | 20 | 24 |
| 2.41 | $\omega$ ($cm^{-1}$) | 492 | 246 | 246 | 492 | | |
| | FWHM ($cm^{-1}$) | 17 | 14 | 17 | 20 | | |

ascribed to the outgoing resonant process [9]. The process can be described by the equation:

$$E_{in} - K\hbar\omega_{LO} = E \qquad (1)$$

where $E_{in}$ and $E$ are the incident photon energy and exciton energy, respectively, $\hbar\omega_{LO}$ is the phonon energy and $K$ is the MP order. The equation means that when the energy of the scattered photon approaches the exciton energy $E$, the Raman line becomes strongly enhanced.

Since hot luminescence (HL) and MP Raman scattering show similar spectral features, it is important to distinguish them. HL arises from the emission of a photon after one or more quanta of vibrational energy have been lost through anharmonic decay. Resonant Raman scattering arises from the creation or destruction of a phonon in the ground electronic state following virtual excitation. Martin [12] offered a much simpler criterion for distinguishing between the two processes. For the hot luminescence processes, the spectral widths of the emitted radiation would be expected to decrease with order. Concerning the line widths, we measured the linewidths of the overtones in Fig. 3. The line widths are all about 17 $cm^{-1}$, and have a few $cm^{-1}$ broadened. Another criterion for distinguishing between the two processes is the definition of Takagahara [13], MP Raman scattering can be viewed as a one-step coherent process where the observed emission spectrum is precisely correlated with incident light in terms of the energy of excitation and polarization. Raman lines remain the polarization memory up to the highest-order overtones. In order to identify whether the observed overtones originate from MP Raman scattering or HL processes, we measured the depolarization ratios, $I_{dp}$, which are defined as the peak intensity ratio of the parallel polarization to the perpendicular polarization in Fig. 3. The $I_{dp}$ are all about 2. This indicates that the polarization memory is on the whole not lost and the highest order overtone still remain polarized. In addition, the observation of anti-stokes Raman scattering could provide efficient evidence for distinguishing the MP Raman scattering from HL [14]. The main differences for these two kinds of processes are in the relaxation feature of elementary excitations. MP Raman scattering is a relaxation process through a virtual immediate state accompanied by both MP absorption and an emission process, while a HL process is one through a real state accompanied by cascade emissions of LO phonons. In a Raman scattering process, we could observe both stokes an anti-stokes Raman scattering by LO phonons whenever the incident light energies are higher or lower than the $E_{11H}$ level. However, it is impossible to observe a HL process when incident photon energies are lower than $E_{11H}$ level. In Fig. 4(c) we observed both stokes and anti-stokes Raman scattering under the excitation of the 514.5 nm (2.41 eV) line, of which the incident photon energy is lower than the $E_{11H}$ level. According to the above criterions, we attribute the features in Fig. 1 and Fig. 3 and 4 to MP Raman scattering rather than HL.

## 4. Conclusions

In conclusion, the ZnSe-like $LO_b$ phonons in ZnSe barrier layers and $Zn_{0.80}Cd_{0.20}Se$-like $LO_w$ phonons in the well layers were observed under excitation of the 457.9 nm (2.71 eV) line and the 488.0 nm (2.54 eV) line of an $Ar^+$ ion laser at RT, respectively. Overtones up to the 4th order of $Zn_{0.80}Cd_{0.20}Se$-like $LO_w$ modes were presented by the 488.0 nm (2.54 eV) line and the 476.5 nm (2.60 eV) line of an $Ar^+$ ion laser excitation. We also provided some methods to distinguish the MP Raman scattering from HL.

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## References

[1] Kun Huang, Bang-fen Zhu and Hui Tang, *Phys. Rev., B41* (1990) 5825.

[2] H.J. Lozykowski and V.K. Shastri, *J. Appl. Phys., 69* (1991) 3235.

[3] Y.T. Hou, G.S. He, S.L. Zhang, Z.L. Peng, J. Li and S.X. Yuan, *Acta Phys. Sinica, 42* (1993) 1707.

[4] S. Nakashima, A. Wada, H. Fujiyasu, M. Aoki and H. Yang, *J. Appl. Phys., 62* (1987) 2009.

[5] E.-K. Suh, D.U. Bartholomew, A.K. Ramdas, S. Rodrigues, S. Venugopalan, L.A. Kolodzieiski and R.L. Gunshor, *Phys. Rev. B, 36* (1987) 4326.

[6] Z.C. Feng, S. Perkowitz and O.K. Wu, *Phys. Rev., B41* (1990) 6057.

[7] K. Shahzad, D.J. Olego, C.G. Van de Walle and D.A. Cammack, *J. Lumin., 46* (1990) 109.

[8] S.L. Zhang, Y.T. Hou, M.Y. Shen, X.J. Zhang, J. Li and S.X. Yuan, *Chin. J. Semicond., 13*(7) (1992).

[9] S.L. Zhang, Y.T. Hou, M.Y. Shen, J. Li and S.X. Yuan, *Phys. Rev. B47*, (1993) 12937.

[10] M.Ya. Valakh, M.P. Lisitsa, G.S. Pekar, G.N. Polysskii, V.I. Sidorenko and A.M. Yaremko, *Phys. Status Solidi (b), 113* (1982) 635.

[11] J.Y. Zhang, X.W. Fan, B.J. Yang, Z.P. Guan, Y.M. Lu and D.Z. Shen, *J. Cryst. Growth, 138* (1994) 838.

[12] T.P. Martin, *Phys. Rev. B, 13* (1976) 3618.

[13] T. Takagahara, in R. Kubo and E Hanamura (eds.), *Relaxation of Elementary Excitations*, Springer Series in Solid-State Sciences, Vol. 18, Springer-Verlag, New York, 1980, p. 45.

[14] Z.P. Wang, H.X. Han, Z.X. Liu, W.T. Qin, Z.L. Peng and S.X. Yuan, unpublished work.