Biaxial splitting of optical phonon modes in ZnSe-ZnS strained-layer superlattices

Aishi Yamamoto, Yoichi Yamada, and Yasuaki Masumoto
Institute of Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

(Received 26 November 1990; accepted for publication 16 February 1991)

Raman scattering studies were performed on ZnSe-ZnS strained-layer superlattices with the incident light parallel as well as perpendicular to the interface plane. We found for the first time that the optical phonon modes split into two types, that is a singlet and a doublet, by the built-in biaxial stress. A new method to characterize the directional stress is demonstrated.

Recently, much attention has been paid to the various kinds of semiconductor heterojunctions. This is because they have novel electrical and optical properties applicable to many kinds of devices. However, most of them have inherent stress at the heterojunction interface due to the lattice mismatch. For example, the lattice mismatch in ZnSe-ZnS superlattices is about 4.5%. They become strained-layer superlattices (SLSs) within the critical thicknesses.[1] There exists a stress lying in the plane parallel to the interface. In this sense they have quasi-two-dimensional structures.

These strains induce a change in the band structure, and then affect the optical properties.[2] Therefore, it is essentially important to measure the strains in SLSs. Many researchers have estimated the strains in the SLSs by means of Raman scattering.[3–8] All of the previous Raman studies of the strains measured the peak shifts of longitudinal optical (LO) phonons from bulk energies in a backscattering configuration with the incident light perpendicular to the interface plane. In this configuration, however, we cannot observe the directional stress directly. The biaxial stress may induce the biaxial splitting of optical phonons. In order to find the biaxial splitting of the phonon modes, we newly measured Raman scattering with the incident light parallel as well as perpendicular to the interface plane. As a result, we were able to observe two types of phonon modes, that is a singlet and a doublet, for the first time.

The unstrained lattice constants of bulk ZnSe and ZnS are 5.6687 Å (a_{ZnSe}) and 5.4093 Å (a_{ZnS}), respectively. Thus ZnSe layers are under biaxial compressive stress, while ZnS layers are under biaxial tensile stress. The lattice constant of the strained layers in the plane parallel to the interface ($a_\parallel$) is given by the following equation:[9]

$$a_\parallel = a_{\mathrm{ZnSe}}\left(1 - \frac{f G_{\mathrm{ZnSe}} L_{\mathrm{ZnSe}}}{G_{\mathrm{ZnS}} L_{\mathrm{ZnS}} + G_{\mathrm{ZnSe}} L_{\mathrm{ZnSe}}}\right), \quad (1)$$

where L_{ZnSe} and L_{ZnS} are the thicknesses of ZnSe and ZnS, f is the lattice mismatch of the unstrained ZnSe and ZnS layers defined by the equation, $f = (a_{\mathrm{ZnSe}} - a_{\mathrm{ZnS}})/a_{\mathrm{ZnS}}$, G_{ZnSe} and G_{ZnS} are shear moduli of ZnSe and ZnS, respectively.

The components of strain-tensor parallel to the interface plane are given by

$$\epsilon_{xx} = \epsilon_{yy} = (a_\parallel - a)/a = (S_{11} + S_{12})/X, \quad (2)$$

where S_{11} and S_{12} are elastic compliance constants and X is the strength of the stress. Following Cerdeira *et al.*,[10] we can obtain two types of the energy deviations from the energy of bulk modes (ω_0) under biaxial stress in the (001) plane:

$$\Delta\Omega_s = [pS_{12} + q(S_{11} + S_{12})]X/\omega_0, \quad (3a)$$

$$\Delta\Omega_d = [p(S_{11} + S_{12}) + q(S_{11} + 3S_{12})]X/2\omega_0, \quad (3b)$$

where p and q are parameters proportional to the changes of the spring constant induced by the strain. In Eq. (3), $\Delta\Omega_s$ indicates the shift of the singlet-type mode vibrating parallel to the ⟨001⟩ axis, while $\Delta\Omega_d$ indicates the shift of doublet-type modes vibrating perpendicular to the ⟨001⟩ axis. This splitting occurs because the biaxial stress makes the sample quasi-two-dimensional. Using the parameters listed in Table I and Eq. (3), we can derive the relation $|\Delta\Omega_s| > |\Delta\Omega_d|$, for both ZnSe and ZnS.

When incident and backscattered light are parallel to the ⟨001⟩ axis (case-I), the LO mode corresponds to the displacement of the atoms along the ⟨001⟩ direction. Therefore, it will shift as the singlet type. On the other hand, the TO modes correspond to the displacement in the plane parallel to the interface. Therefore, it will shift as the doublet type. Thus in this experimental configuration, Eq. (3) indicates the energy deviations of the LO and TO modes as

$$\Delta\Omega_s^{\mathrm{LO}} = [pS_{12} + q(S_{11} + S_{12})]X/\omega_0^{\mathrm{LO}}, \quad (4a)$$

$$\Delta\Omega_d^{\mathrm{TO}} = [p(S_{11} + S_{12}) + q(S_{11} + 3S_{12})]X/2\omega_0^{\mathrm{TO}}. \quad (4b)$$

We consider next the case where the incident and backscattered light are parallel to the ⟨110⟩ axis (case-II). In this configuration, we can expect the LO mode will shift as the doublet type and the TO modes will split into the singlet and doublet types. From Eq. (3) we can obtain

$$\Delta\Omega_d^{\mathrm{LO}} = [p(S_{11} + S_{12}) + q(S_{11} + 3S_{12})]X/2\omega_0^{\mathrm{LO}}, \quad (5a)$$

$$\Delta\Omega_s^{\mathrm{TO}} = [pS_{12} + q(S_{11} + S_{12})]X/\omega_0^{\mathrm{TO}}, \quad (5b)$$

$$\Delta\Omega_d^{\mathrm{TO}} = [p(S_{11} + S_{12}) + q(S_{11} + 3S_{12})]X/2\omega_0^{\mathrm{TO}}. \quad (5c)$$

To summarize the above mentioned expectation,[11] (i) we will observe two types of shifts, a singlet and a

TABLE I. Parameters for ZnSe and ZnS used in the calculation.

	ZnSe	ZnS
LO mode (cm^{-1})	252[a]	349[a]
TO mode (cm^{-1})	205[a]	271[d]
S_{11} (10^{-12} dyn^{-1} cm^2)	2.11[b]	1.89[e]
S_{12} (10^{-12} dyn^{-1} cm^2)	−0.78[b]	−0.72[e]
p (10^{28})	−0.41[c]	−0.39[e]
q (10^{28})	−0.59[c]	−0.99[e]

[a]Present work.
[b]In Landolt–Börnstein—Numerical Data and Functional Relationships in Science and Technology, Vol. 17b (Semiconductors—Physics of II-IV and I-VII Compounds, Semimagnetic Semiconductors), edited by O. Madelung, M. Schulz, and H. Weiss (Springer, Berlin, 1982), p. 145.
[c]Reference 10.
[d]W. G. Nilsen, Phys. Rev. **182**, 838 (1969).
[e]Reference 7.

doublet, of each of the LO and TO modes, corresponding to the two cases of the scattering configuration, and (ii) we will observe the singlet-type mode shifts larger than the doublet-type mode.

In the present work we used three samples grown by low-pressure metalorganic chemical vapor deposition (MOCVD)[12] on (001)GaAs substrates. All the samples have the same thickness of ZnS layers (40 Å) and consist of 150 periods of the superlattice, but the thickness of ZnSe layers are different [(a) 15 Å, (b) 20 Å, (c) 25 Å]. We used a (110) cleavage plane for the case-II configuration measurements.

For the case-I experiments, a quasi-backscattering configuration was used. Raman scattering measurements were performed at room temperature with the 4880 Å line of an Ar ion laser. The scattered light was analyzed by a double monochromator (Spex; 1403). For the case-II configuration, we used a Raman microprobe measurement system (Japan Spectroscopic Co., Ltd.; R-MPS-11) with a 25 cm filter double monochromator and a 1 m monochromator. Measurements were done at room temperature with the 5145 Å line of an Ar ion laser.

Figure 1 shows Raman spectra of samples (a), (b), and (c) in the case-I configuration. Strong peaks of TO and LO modes of a GaAs substrate are observed at about 268 and 291 cm^{-1}. The dashed lines indicate the positions of the unstrained bulk ZnSe and ZnS LO modes. Very weak ZnSe TO modes are observed at about 210 cm^{-1}, although they are forbidden in this experimental configuration. As seen in the figure, ZnSe LO modes shift toward the higher energies, while ZnS LO modes shift toward the lower energies. This is because the ZnSe layers are under compressive stress and the ZnS layers are under tensile

TABLE II. Observed energy deviation of the LO and TO modes from the energy of the bulk mode for the sample (c).

		ZnSe (cm^{-1})	ZnS (cm^{-1})
LO	singlet	+7.5	−14.0
	doublet	+2.5	−21.4
TO	singlet	+14.5	−35.8
	doublet	+6.7	···

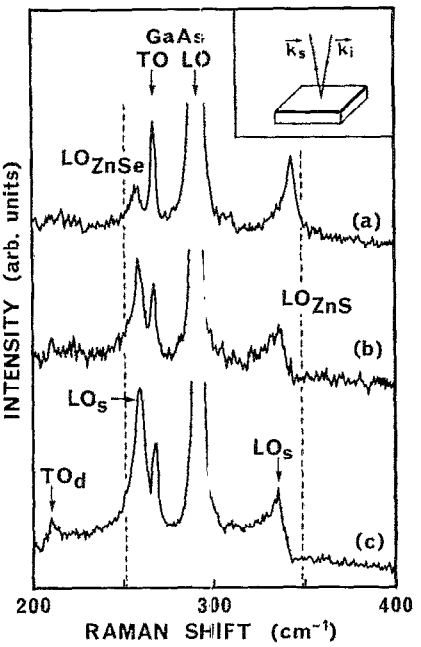

FIG. 1. Raman spectra of ZnSe-ZnS SLSs with a fixed ZnS layer thickness (40 Å) and various ZnSe ones: (a) 15 Å, (b) 20 Å, (c) 25 Å. The dashed lines show the unstrained bulk frequencies. The inset shows schematically the experimental configuration: the incident light is parallel to the ⟨001⟩ axis (case-I). The subscripts of s and d denote a singlet and a doublet, respectively.

stress. Although the shift of the ZnSe LO mode in three samples does not differ from each other, the shift of the ZnS LO mode decreases with increasing ZnSe thickness. These observations are consistent with the previous works.[3–8] As mentioned above, in the case-I configuration, we can regard the shift of LO modes as the singlet type and that of TO modes as the doublet type.

Raman spectra in the case-II configuration are shown in Figs. 2 and 3. The incident light was polarized perpendicular or parallel to the ⟨001⟩ axis. The doublet TO mode is allowed for both polarizations, while the singlet TO mode is allowed only for the perpendicular polarization. Taking into account this selection rule, we identified the peaks of 210 and 240 cm^{-1} as doublet TO(ZnSe) and singlet TO(ZnS), respectively. Very weak peaks of about 255 cm^{-1} are identified as the forbidden ZnSe LO(doublet) mode. We can see small peaks at about 220 cm^{-1} in Fig. 3. We identified them as the forbidden singlet TO(ZnSe) mode. It is allowed for the perpendicular polarization. However, it is not observed in Fig. 2. This is because the singlet TO(ZnSe) mode is superposed on the singlet TO(ZnS) mode. This identification is justified by the following reasons. First of all, the intensity of the 220 cm^{-1} mode increases with the increase in thickness of the ZnSe layer. Thus the mode is of ZnSe. Second, because of the selection rule, the intensity of the mode is weaker than that of the doublet TO(ZnSe) mode.

Based on the above-mentioned identification, we can summarize the energy deviation of all the modes in Table II. Table II shows the energy deviation from the energy of the bulk mode for sample (c). As for ZnSe modes, we can

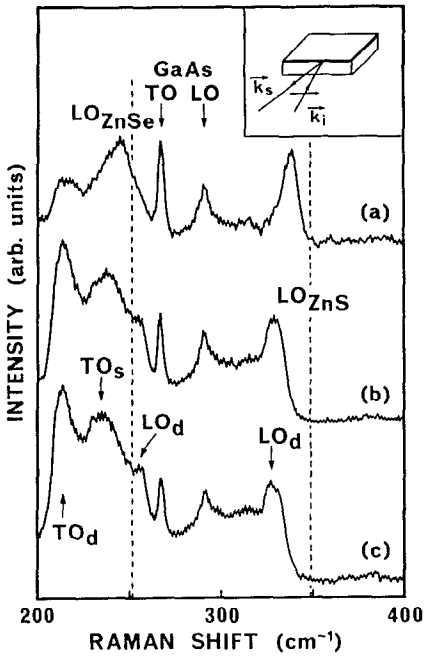

FIG. 2. Raman spectra of ZnSe-ZnS SLSs with a fixed ZnS layer thickness (40 Å) and various ZnSe ones: (a) 15 Å, (b) 20 Å, (c) 25 Å. The dashed lines show the unstrained bulk frequencies. The inset shows schematically the experimental configuration: the incident light is perpendicular to the ⟨001⟩ axis (case-II) and is polarized perpendicular to the ⟨001⟩ axis. The subscripts of *s* and *d* denote a singlet and a doublet, respectively.

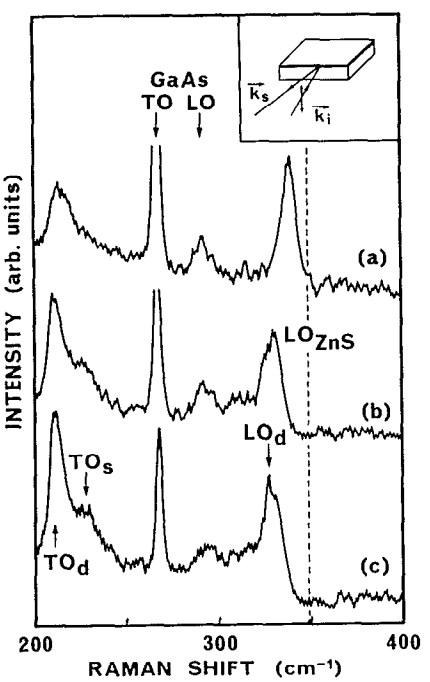

FIG. 3. Raman spectra of ZnSe-ZnS SLSs with a fixed ZnS layer thickness (40 Å) and various ZnSe ones: (a) 15 Å, (b) 20 Å, (c) 25 Å. The dashed line shows the unstrained ZnS energy. The inset shows schematically the experimental configuration: the incident light is perpendicular to the ⟨001⟩ axis (case-II) and is polarized parallel to the ⟨001⟩ axis. The subscripts of *s* and *d* denote a singlet and a doublet, respectively.

observe the singlet-type and doublet-type shifts for both LO and TO modes induced by the biaxial stress. The singlet-type mode shifts larger than the doublet-type one as was expected. On the other hand, for ZnS modes, we can also observe the singlet-type and doublet-type LO modes. However, the shift of the singlet type is not larger than that of the doublet type. This strange behavior may be explained by the following model. The dielectric continuum model[13] shows that the optical phonon mode, which propagates in the layer plane, can appear at new energy level. The energy deviation varies with change in the relative thickness of the two different dielectric layers. These effects enhance the energy deviation of the doublet-type LO(ZnS) mode. For this reason, the doublet-type LO(ZnS) mode can shift larger than the singlet-type one.

In conclusion, we studied Raman scattering of ZnSe-ZnS strained-layer superlattices with the incident light perpendicular and parallel to the interface plane. We observed for the first time two types of the optical phonon shift, a singlet and a doublet, induced by the biaxial stress. We obtained reasonable relations between the stress and the direction of the shift and between the layer thickness and the shift. The singlet-type mode shifts larger than the doublet-type mode for the ZnSe optical phonon modes. Not only strained-layer superlattices, but there are many systems having directional stress in semiconductor devices. The method of this work will become a new characterization tool for measuring the directional stress in these systems.

This work was supported in part by Scientific Research Grant-in-Aid No. 02205016 for Scientific Research on Priority Areas, New Functionality Materials—Design, Preparation and Control—by the Ministry of Education, Science and Culture of Japan. This work was done at the Cryogenic Center, University of Tsukuba.

[1] G. C. Osbourn, IEEE J. Quantum Electron. **QE-22**, 1677 (1986).
[2] T. Taguchi and Y. Yamada, Mater. Res. Soc. Symp. Proc. **161**, 199 (1990).
[3] M. Nakayama, K. Kubota, H. Kato, and N. Sato, Solid State Commun. **51**, 343 (1984).
[4] F. Cerdeira, A. Pinczuk, J. C. Bean, B. Batlogg, and B. A. Wilson, Appl. Phys. Lett. **45**, 1138 (1984).
[5] B. Jusserand, P. Voisin, M. Voos, L. L. Chang, E. E. Mendez, and L. Esaki, Appl. Phys. Lett. **46**, 678 (1985).
[6] S. Nakashima, Y. Nakakura, H. Fujiyasu, and K. Mochizuki, Appl. Phys. Lett. **48**, 236 (1986).
[7] L. H. Shon, K. Inoue, K. Murase, H. Fujiyasu, and Y. Yamazaki, Solid State Commun. **62**, 621 (1987).
[8] L. H. Shon, K. Inoue, O. Matsuda, K. Murase, T. Yokogawa, and M. Ogura, Solid State Commun. **67**, 779 (1988).
[9] J. W. Matthews and A. E. Blakeslee, J. Cryst. Growth **32**, 265 (1976).
[10] F. Cerdeira, C. J. Buchenauer, F. H. Pollak, and M. Cardona, Phys. Rev. B **5**, 580 (1972).
[11] In Eq. (3), ω_0 may be the bare optical phonon energy due to spring constants only. But in Refs. 3 and 5–8, ω_0 has been treated conventionally as ω_{LO} or ω_{TO} in the calculation of each energy shift. We followed the conventional treatment in Eqs. (4) and (5). Anyhow, our conclusion is not influenced at all, whichever values are used.
[12] Y. Yamada and T. Taguchi, Tech. Rep. Osaka Univ. **39**, 211 (1989).
[13] C. Colvard, T. A. Gant, M. V. Klein, R. Merlin, R. Fischer, H. Morkoc, and A. C. Gossard, Phys. Rev. B **31**, 2080 (1985).