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Longitudinal phonon modes in a $ZnSe/ZnS_xSe_{1-x}$ lattice-mismatched superlattice

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Longitudinal acoustic and optical phonon modes of a $ZnSe/ZnS_xSe_{1-x}$ ($x \simeq 0.20$) lattice-mismatched superlattice, prepared with atmospheric metal organic chemical vapor deposition method, have been investigated by light scattering measurements. Despite a lattice mismatch as large as 1% between the alternating layers, the measured longitudinal elastic constants are in agreement with the calculated values of an unstrained effective medium model. Furthermore, a correlative study was made by fitting the spectra to a spatial correlation model, which reproduces line shapes of the observed confined longitudinal-optical modes without incorporating the strain effects. The results demonstrate that a combination of Brillouin and Raman spectroscopy provides a good method to determine accurately the elastic constants and strain information of the lattice-mismatched superlattices and heterostructures.

I. INTRODUCTION

$ZnSe/ZnS_xSe_{1-x}$ superlattices are wide-bandgap II-VI semiconducting strained-layer materials, and recently attract much interest because of their importance as tunable blue-light emitting diodes and lasers.[1] The incorporation of the strains into the superlattices gives an additional degree of freedom for tailoring the band structures to achieve the desired physical properties for device applications. It has been shown that when the well-width is in the range of a few nanometers to several tens of nanometers, the lattice mismatch is accommodated by lattice deformation which may exhibit strong modulation effects on the electronic and vibrational properties of the materials. Numerous studies have been devoted to the strain effects on the phonon modes in the superlattices, both theoretically and experimentally.[2] In the region of very low frequencies, acoustic phonons can propagate across the interfaces of the superlattice and exhibit zone folding. The frequencies of the doublets can be accurately calculated by the product of phonon wavevector and the phase velocity. However, the phonon propagation in a strained superlattice may suffer an influence of lattice deformation.[3]

One can extract strain information from a lattice-mismatched superlattice by observing Brillouin scattering (BS) of the acoustic phonons. The strain sensitivity of the Brillouin method is actually comparable to that of Raman scattering, since it is easy to observe a frequency shift less than 0.05 cm^{-1}. However, the BS only samples the averaged strain over the entire layers of the superlattice since the wavelengths of the acoustic phonon are much greater than the thickness of the alternating layers. Thus, the BS spectra of a superlattice with compressive and tensile strains may appear identical to those of an unstrained lattice-matched structure.

Optical phonons can be confined in the layers and quantized into discrete modes for thin ZnSe layers. It has been demonstrated that the confinement effect in $ZnSe/ZnS_xSe_{1-x}$ superlattices can shift the optical phonon towards lower frequencies.[4] In addition to the confinement effect, the strain-induced lattice deformation could also cause a shift in phonon frequency. The lattice mismatch between ZnSe and ZnS_xSe_{1-x} layers causes compressive strains in the ZnSe layers and tensile ones in the ZnS_xSe_{1-x} layers. Although the compressive strain will induce a blue shift in the longitudinal-optical (LO) modes of ZnSe that may balance the red shift due to confinement, the tensile strain-induced effect and the confinement-induced effect will shift the LO modes of ZnS_xSe_{1-x} in the same direction. Since Raman scattering can yield important information about the nature of the material on the scale of the order of 10 Å, it allows us to distinguish confinement induced effects from strain-related effects.

In this paper, we present a correlative study of longitudinal phonon modes on a lattice-mismatched $ZnSe/ZnS_xSe_{1-x}$ ($x \simeq 0.20$) superlattice by Brillouin and Raman light scattering. For a superlattice of two constituents with cubic symmetry, the longitudinal elastic constants ($c_{11} \simeq c_{33}$) are very sensitive to the change of the built-in strains. The accurate determination of c_{11} for lattice-

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mismatched superlattices is an important step towards the understanding of the energy band structure. We observed the scattering of the longitudinal acoustic mode for different scattering angles, where a very weak anisotropy was found. The measured longitudinal elastic constants are consistent with the predicted values obtained from an unstrained effective medium model,[5] in which the superlattice is regarded as a homogeneous film with its effective properties as an average of the two constituents. To verify the interrelationship of the measured elastic constants and the lattice mismatch, a Raman spectroscopy measurement was conducted. A detailed line-shape of the confined optical phonons was fitted to a modified spatial correlation model[6] which excluded the strain effects. Using this model, the normalized experimental Raman spectra can be fitted well by the two subpeaks of the confined modes in both ZnSe and ZnS_xSe_{1-x} layers.

II. EXPERIMENT

The $ZnSe/ZnS_xSe_{1-x}$ ($x \simeq 0.20$) superlattices (SLS) were grown on (001)-oriented GaAs substrates by a metal organic chemical vapor deposition (MOCVD) technique at atmospheric pressure using dimethylzinc (DMZ), H_2Se, and H_2S as the sources for Zn, Se, and S, respectively.[7] The substrate temperature during growth was kept in the range of 290–420 °C. The flow rates of DMZ, H_2Se, and H_2S are chosen as 9.91, 17.8, and 12.3 μmol/min, respectively. To minimize effects due to the mismatch with the substrate, the multilayers were grown on a 0.5-μm-thick $ZnS_{0.05}Se_{0.95}$ buffer layer. With this buffer layer the elastic strain from the mismatch with the substrate is completely relaxed. The sample studied has well-width $d_{ZnSe}=100$ Å and barrier-width $d_{ZnS_xSe_{1-x}}=70$ Å, and the associated modulation period is $d=170$ Å. The thickness of the sample is 1.7 μm. The refractive indices of the superlattice can be estimated from ZnSe and ZnS bulk materials[8] by linear interpolation. The estimated refractive indices for the two sublayers and the superlattice at $\lambda=5145$ Å are 2.40, 2.72, and 2.69, respectively.

Brillouin and Raman light scattering were performed in a backscattering geometry, with 50–100 mW of p-polarized 5145 Å radiation from Ar^+ laser at room temperatures. In the case of Raman scattering, the spectrum was taken with an Instruments-SA 1-m THR1000 triple monochromator and with an Olympus microscope and a charge-coupled device (CCD) detecting system. The light scattered by acoustic phonons was measured by a tandem Fabry–Pérot interferometer, with a finesse of about 100 and a contrast ratio greater than 5×10^{10}. The in-plane wavevector of acoustic phonons is given by $q_\parallel=4\pi/\lambda \sin\theta$, and the normal wave vector is $q_\perp=4\pi/\lambda\cos\alpha$, where $\alpha=\sin^{-1}(n^{-1}\cos\theta)$ with the [001] normal to the superlattice film. In our experiments the data collection time for each spectrum was typically 0.5 h.

III. RESULTS AND DISCUSSION

A. Acoustic phonons and the related elastic constants

Since the $ZnSe/ZnS_xSe_{1-x}$ SLs are transparent materials, they allow an observation of the inelastic scattering from bulk acoustic phonons. At least one mode was clearly observed in our measurements. Typical spectra are shown in Fig. 1 for different θ and $q_\parallel$ in the [100]-axis. The peak at $\tilde{\nu}_B=(42.3\pm0.5)$ GHz is identified as scattering from the longitudinal acoustic bulk mode (labeled "LA"), where the measured phase velocity of $v_l\simeq4050$ m/s is comparable to that of pure ZnSe material.[8] The weak peaks ranging from 12 to 25 GHz probably arise from a combined contribution of the scattering from transverse acoustic modes and the longitudinal guided acoustic mode.[9] They are too weak in intensity to be discerned definitively, even after we have changed the $q_\parallel$ to be 15° off the [100]-axis. Therefore we only pay our attention to the LA mode in the present work. Due to the transparency of the superlattice, a broad peak at ~ 73 GHz from the longitudinal acoustic phonons of the GaAs substrate is observed. We note that the elastic scattering from the superlattice is so strong that the Rayleigh surface phonon signals are not discernible in the spectrum.

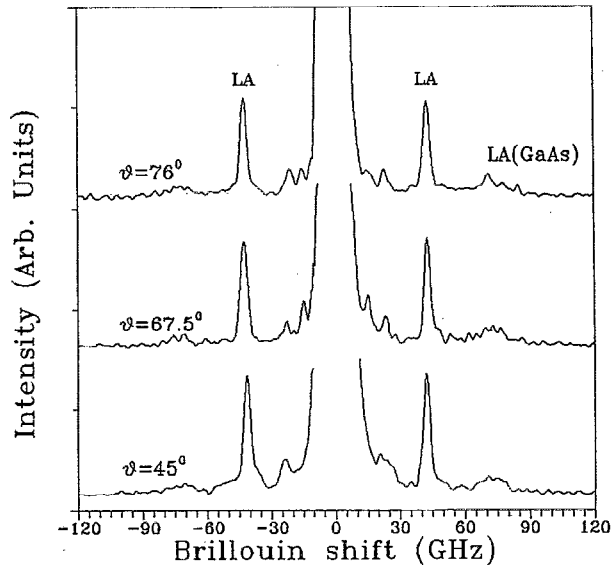

FIG. 1. Brillouin spectra from a $ZnSe/ZnS_xSe_{1-x}$ lattice-mismatched superlattice, with different θ angles, the weak scattering in between 12 and 25 GHz may be associated with the transverse acoustic modes or with the guided longitudinal acoustic modes.

The spectra from longitudinal modes for different scattering angles allow us to determine the effective longitudinal elastic constants of $ZnSe/ZnS_xSe_{1-x}$ SLs. Although the index of refraction is expected to be anisotropic due to the layered structure of the superlattice, it is only weakly angular dependent due to the similar chemical composition of the constituent layers in our sample. For simplicity, the difference of the refractive indices between the in-plane and out-of-plane ones is neglected. This is reasonable when the experimental uncertainty of frequency shifts of phonons (~1%) is greater than the anisotropy of the refractive indices. Thus, the effective longitudinal elastic constants are approximately given by

$$c_l=\rho_{SL}\tilde{\nu}_B^2\lambda^2/4n^2, \tag{1}$$

where ρ_{SL} is the mass density (5.17 g/cm^3) of the superlattice, a value obtained by an average of the two constituents

TABLE I. Elastic constants and mass densities for ZnSe, ZnS, ZnS_xSe_{1-x}, and $ZnSe/ZnS_xSe_{1-x}$ superlattice. The calculated and measured data are indicated by SL^{cal} and SL^{expt}, respectively.

	c_{11}	c_{33}	c_{12}	c_{13}	c_{44}	ρ
ZnSe	85.7	85.7	54.7	54.7	40.5	5.26
ZnS	100.0	100.0	65.0	65.0	34.0	4.09
$ZnS_{0.2}Se_{0.8}$	88.4	88.2	56.6	56.8	39.0	5.03
SL^{cal}	86.8	86.7	55.4	55.4	39.9	5.17
SL^{expt}	84.6±1.7	84.6±1.7	...	...	...	...

based on their ratio of the thicknesses. The longitudinal elastic constants are (84.6±1.7) GPa for c_{11} or c_{33} from Eq. (1).

The effective elastic constants of a periodic or quasiperiodic modulated superlattices can be calculated by the effective medium model.[5,10] In this model, one treats the superlattice/substrate system as a supported homogeneous film with a total thickness h, because the relevant phonon wavelengths are larger than the modulation period of the sample. Assuming the validity of Vegard's law, the elastic tensor and mass density (see Table I) of the ZnS_xSe_{1-x} layers were interpolated between the known ones for ZnS and ZnSe.[8] With the x_3 axis along the normal of the sample and with the continuities of the stresses and strains at the interfaces, the wave equations can be solved and the effective elastic constants (SL^{cal}) can be described by an arithmetic average value of the two constituent layers,[5] as shown in Table I. We found that the difference between the measured and calculated longitudinal constants is less than 3%, which is close to the experimental uncertainty. Although the unstrained effective medium model gives a good description for the measured elastic constants, it is difficult to know whether the structure is strained or not from the measurements of Brillouin scattering alone.

B. Optical phonons and strain information

Although acoustic phonons can propagate across the well and barrier of the superlattice, optical phonons in wells will not propagate through barriers and those in barriers do not through wells if their dispersions do not overlap. The optical phonons in the well are confined, quantized into discrete modes, and their properties are independent of those of the barrier. It has been demonstrated that the confinement effect shifts the optical phonon energies as compared to the bulk phonon energy at long wavelength limit. On the other hand, the lattice-mismatch-induced elastic strains would also cause a shift in phonon energy. For $ZnSe/ZnS_xSe_{1-x}$ superlattices, the compressive strain will induce a blue shift for longitudinal-optical (LO) frequency of ZnSe that balances the red shift due to confinement. However, the confinement and strain effects will shift the LO mode of the ZnS_xSe_{1-x} layers in the same direction.[4,11] Therefore, this behavior will allow us to separate the effects of confinement from those of strain by a Raman observation and an analysis of the line shape.

In the following we present the observed phonon spectrum of the confined LO modes in the range of 240–260 cm^{-1}. This spectrum is analyzed and fitted by using a spatial

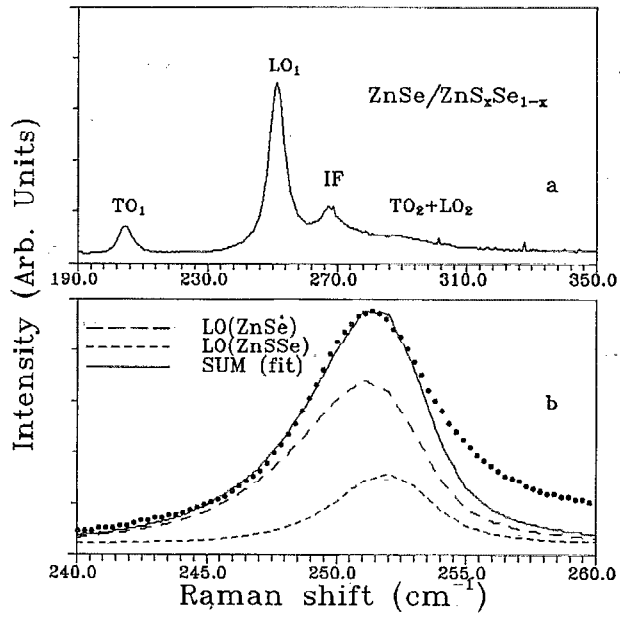

FIG. 2. Raman spectrum of the $ZnSe/ZnS_xSe_{1-x}$ superlattice, where TO_i and LO_i are confined transverse and longitudinal optical modes. (b) The decomposed profiles correspond to the LO_1 modes localized at the alternating layers, calculated using the spatial correlation model with a Gaussian-type confinement function.

correlation model. This approach, first presented by Parayanthal and Pollak,[6] was used to quantitatively interpret the broadening and asymmetry of the first-order longitudinal-optic phonon Raman spectrum in semiconductors, and lately has been applied to ZnS_xSe_{1-x} films by Hayasm *et al.*[12] For a crystalline superlattice, this model can be modified in the following ways. One can assume the confinement of the LO modes in the individual layers to be Gaussian-type, with the phonon correlation length equal to the thicknesses of the alternating layers, i.e., $\exp(-2r^2/d_i)$ (i=ZnSe and ZnS_xSe_{1-x}). The scattering intensity of the LO modes without strain-induced effects can be written as

$$I(\omega)\simeq\sum_{i=1}^{2}\frac{d_i}{d}\int_0^1\frac{\exp(-q^2d_i^2/4)d^3q}{[\omega-\omega(q)]^2+(\Gamma/2)^2}, \tag{2}$$

where $\omega(q)$ is the phonon dispersion and Γ (=3.0 cm^{-1}) is the natural linewidth, and i (=1 and 2) corresponds to the two alternating layers. In the absence of strain, the phonon dispersion $\omega(q)$ of the LO vibrations can be obtained by fitting the neutron scattering data,[13] namely,

$$\omega(q)=(A+\{A^2-B[1-\cos(\pi q)]\}^{1/2})^{1/2}, \tag{3}$$

where q is a normalized wavevector ranging from 0 to 1, $A=3.2\times10^4$ cm^{-2}, and $B=4.5\times10^8$ cm^{-4}.

Figure 2(a) shows the first-order Raman spectrum of this superlattice, where the TO_i and LO_i (i=1 and 2) correspond to the transverse and longitudinal optical modes, localized in the ZnSe and the ZnS_xSe_{1-x} layers, respectively.[4,12] A small peak at $\omega\simeq270$ cm^{-1} was observed. We cannot attribute this peak to the TO mode of the GaAs substrate because the stronger LO mode of the GaAs at $\omega\simeq291$ cm^{-1} was not observed. It may arise from the scattering of optical interface

(IF) modes.[4] The weak scattering ranging from 290 to 310 cm^{-1} is a combined contribution of the confined TO_2 and LO_2 modes. In Fig. 2(b), the LO_1 mode at the range of 240–260 cm^{-1} is fitted by a calculation using Eqs. (2) and (3). In the case of strain-free sample, the frequencies and line shapes of the LO modes in the superlattice depend only upon the confinement of the optical modes in the alternating layers. If we ignore the influence of the optical interface (IF) mode at the higher-frequency end, the spectral profile of the LO_1 modes at $\omega \simeq 252$ cm^{-1} is well reproduced. We found that the LO_1 mode actually consisted of two subpeaks, and its normalized intensity was accurately determined by the thickness ratio of the ZnSe and ZnS_xSe_{1-x} layers, without any other fitting parameters.

Even though the ZnSe is compressed and the blue shifts have been partially balanced by the confinement of the phonon modes, we cannot find any observable deviation from the frequency predicted by the confinement effect on the LO modes of the ZnS_xSe_{1-x} layers. We can conclude from this calculation that the superlattice should be an unstrained structure, and the agreement between the measured and predicted longitudinal elastic constants suggests the relaxation of built-in strains.

IV. CONCLUSIONS

In summary, we presented a correlative study of longitudinal acoustic and optical phonons on a unstrained ZnSe/ZnS_xSe_{1-x} superlattice with use of light scattering measurements. The lattice mismatch between ZnSe and ZnS_xSe_{1-x}, given by $f=2(a_{ZnSe}-a_{ZnS_xSe_{1-x}})/(a_{ZnSe}+a_{ZnS_xSe_{1-x}})$, is as large as 1% for $x \simeq 0.2$. We demonstrated that the structure associated with this mismatch does not show any evident changes for both acoustic and optical phonons. The strain information was extracted from the spectrum of confined optical phonons in terms of a modified spatial correlation model in which the correlation length is taken as the thickness of the alternating layers. The observed Raman spectrum is well reproduced by using this calculation which does not incorporate the strain-related effects. These results imply that the lattice mismatch between the layers may have been accommodated by the buffer layer. We have thereby demonstrated that a combination of the Brillouin and Raman spectrometers can provide a good method to accurately determine the elastic constants and strain information of lattice-mismatched superlattices and heterostructures.

In addition, we would like to point out that there are no noticeable discrepancies between the measured values and the predicted elastic constants from a number of different theories which have been proposed to explain the anomalous elastic effects in metallic superlattices.[14] Our experiments are also consistent with the results of the semiconductor superlattices of GaAs/AlAs,[15] a-Si:H/a-SiN_x:H,[16] NbN/AlN,[17] and of a-Si:H/a-$Si_{1-x}C_x$:H.[18]

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