## Defect-like nature of the interface in AB/CD-type superlattices

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Based on the calculation of lattice dynamic properties and observation of first-order Raman spectra for the Zn-Se localized microscopic interface mode of the  $(CdSe)_4/(ZnTe)_4$  superlattice, multiphonon (MP) Raman scattering of up to five orders has been observed. The linewidth variation with MP order and temperature as well as the frequency and intensity behavior with MP order can be interpreted by the anharmonic decay of the localized mode into extended band modes. These results show the defectlike nature of interfaces in AB/CD-type superlattices.

In AB/CD-type superlattices [(SL's), e.g., the CdSe/ZnTe SL], whose two constituents do not share a common atom (or ion), contrast with the case of AC/BCtype SL's (e.g., GaAs/AlAs SL), there exist "wrong bonds" at interfaces (e.g., Zn-Se and Cd-Te bonds in CdSe/ZnTe SL), which are different from the bonds in constituent layers (e.g., Cd-Se and Zn-Te bonds). These wrong bonds can be considered as a kind of localized distortion, i.e., a certain "defectlike" impurity, with respect to the host superlattice structure.<sup>1</sup> We refer to the vibrational modes due to these wrong bonds as microscopic interface (MIF) modes, in order to distinguish them from SL interface modes arising from different macroscopic dielectric constants for the two constituent layers.<sup>2</sup> A similar MIF mode also exists in A/B-type SL's (e.g., the Si-Ge MIF mode in the Si/Ge SL although that is not Raman active). Since 1986, some theoretical papers on MIF modes have been published,<sup>3</sup> but, to the best of our knowledge, no experimental work on these modes was published until we reported on the first-order Raman spectra of the MIF mode in CdSe/ZnTe SL's.<sup>4</sup> In this paper, we report mainly on the multiphonon (MP) Raman spectra of a MIF mode.

The sample studied here, is an 80-period  $(CdSe)_4/$  $(ZnTe)_4$  SL (where the subscript represents the number of monolayers), grown by atomic layer epitaxy on a (001)GaAs wafer with a 2- $\mu$ m ZnTe buffer to eliminate lattice mismatch between the SL layer and the GaAs substrate. The crystalline axes in the experiments were designated as X = [100], Y = [010], Z = [001]. The Raman scattering experiments were performed in near backscattering configuration from a (001) surface, so that the LO and MIF Raman phonons both with  $A_1$  symmetry can be observed. An Ar ion laser was used as the excitation light source. The scattered light is dispersed by a SPEX-1403 double monochromator and detected by the conventional photon counting electronics. The widths of incident slits are 200 and 400  $\mu$ m for the experiments at 80 K and in the 80-230-K regions, respectively; the response functions of the spectrometer have a triangular shape in our experiments. The observed peak curve should be the convolution of the Lorentzian curve of actual phonons with the response function of the spectrometer. However, as a simplified procedure, we fitted the observed spectra with the Lorentzian profile and assume that this fitting linewidth is the width expected by the convolution procedure. Based on this consideration, the actual linewidth [full width at half maximum (FWHM)] of phonons was obtained after the instrumental broadening correction.

The lattice dynamic properties of the sample  $(CdSe)_4/(ZnTe)_4$  SL has been calculated along the [001] growth direction in terms of a linear-chain model assuming only nearest-neighbor interaction. The nearestneighbor force constants, reduced masses, and frequencies of LO bulk modes of ion bands in the CdSe/ZnTe SL used in the calculation were the same as those used in Ref. 4. The calculated dispersion curves and ionic displacement patterns are shown in Fig. 1(a) and 1(b), respectively. From Fig. 1(a), besides LO and folded longitudinal acoustic (FLA) phonon bands usually existing in AC/BC-type SL's, we see three modes located outside these two phonon bands, where usually no phonon mode occurs for AC/BC-type SL's. One of them at 223  $cm^{-1}$ , labeled MIF<sub>0</sub>, lies above all the phonon bands, and the other two, labeled  $MIF_1$  at 176 cm<sup>-1</sup> and  $MIF_2$  at  $134 \text{ cm}^{-1}$ , lie in the gap between the LO and FLA bands. Figure 1(b) shows that the maxima of ionic displacement of  $MIF_0$  and  $MIF_1$  modes appear at the ZnSe interface, and for MIF<sub>2</sub> lies at the Cd-Te interface. Furthermore, the ionic displacement for the  $MIF_0$  mode demonstrates its fast evanescent character into the two constituent layers both less than 1 ML; the  $MIF_1$  and  $MIF_2$  modes have no such characteristic. Therefore, we refer to the  $MIF_0$ and MIF<sub>1</sub> modes as the Zn-Se localized and extended MIF modes, respectively, and the  $MIF_2$  mode as the Cd-Te extended MIF mode. The localized MIF (LMIF) mode obviously originates from the Zn-Se interface in the CdSe/ZnTe SL ( i.e., a two-dimensional defect in SL's).

Figures 2(a), (b), (c), (d), and (e) show the MP  $Z(XX)\overline{Z}$  polarized spectra excited by 514.5-, 496.5-,



FIG. 1. (a) Calculated longitudinal-phonon dispersion of a (001) grown  $(CdSe)_4/(ZnTe)_4$  superlattice. (b) The ionic displacement patterns corresponding to the dispersion curves of (a).

488.0-, 476.5-, and 457.9-nm laser lines at 80 K, respectively, for the sample. Since the spectra of low-wavenumber part in Fig. 2 consist of two overlapping spectral peaks, the method of least-square fitting with Lorentzian profile was used to resolve the MP spectra into two spectra A and B. The corresponding fitting spectra of the first- and second-order scattering are shown in Fig. 2 (Insert 1), along with the experimental spectra (solid line). We assigned the peak  $B_1$  at 223.5 cm<sup>-1</sup> (dashed line) in Fig. 2 (Insert 1) to the first order Raman spectrum of the Zn-Se LMIF mode, since its frequency is in good agreement with the calculated frequency  $223 \text{ cm}^{-1}$ of the LMIF mode shown in Fig. 1. The peak  $A_1$  (dotted line) at 211.5  $\rm cm^{-1}$  was tentatively assigned to the firstorder Raman scattering of the bulklike ZnTe LO mode, as its frequency corresponds closely to the frequency of the ZnTe bulk LO mode.<sup>4</sup> Regarding the frequency up-shift of the ZnTe bulklike mode from its bulk mode, we think it may be due to compressive strain in the SL layer induced by incomplete elimination of the lattice mismatch between the SL layer and the substrate. The frequency  $\omega_k$ , linewidth (FWHM)  $\Delta \omega_k$ , and peak intensity  $I_k$  of the k-order MP peaks  $A_k$  and  $B_k$ , for the MP spectrum excited by 488.0-nm laser line, are listed in Table I.

The MP spectra could be attributed to either Raman scattering or hot luminescence (HL). The main distinguishing feature between these two processes is the polarization memory.<sup>5</sup> We recorded carefully the first-order and second-order  $Z(XX)\overline{Z}$  and  $Z(XY)\overline{Z}$  polarized spectra excited by 488.0-nm laser line [see Fig. 2 (Insert 2)]. We see, from Fig. 2 (Insert 2), that the second-order spectra  $A_2$  and  $B_2$  are, respectively, similar to the firstorder spectra  $A_1$  and  $B_1$  in polarization property, that is,



FIG. 2. Multiphonon Raman spectra excited by (a) 514.5nm, (b) 496.5-nm, (c) 488.0-nm, (d) 476.5-nm, and (e) 457.9nm laser lines at 80 K for the  $(CdSe)_4/(ZnTe)_4$  SL sample.

the polarization memory is maintained, and this is true for all the higher-order spectra we recorded. This clearly indicates that the MP spectra shown in Fig. 2 can be attributed to the Raman process. Therefore, the above results indicate that the LMIF mode is undoubtedly observed in Raman spectra.

To investigate further the spectral features of the Zn-Se LMIF mode and the defectlike nature of the Zn-Te interface, it is necessary to understand the variation of the MP spectral characteristic parameters, i.e., the reduced frequency  $\omega'_k (= \omega_k/k)$ , reduced linewidth  $\Delta \omega'_k$  $(= \Delta \omega_k / \Delta \omega_1, \text{ where } \Delta \omega_1 \text{ is the first-order linewidth}),$ and reduced intensity  $I'_k (= I_k/I_1$ , where  $I_1$  is the firstorder intensity), with MP order k. These parameter values for the spectrum excited by the 488.0-nm laser line are listed in Table I. Figures 3(a), 3(b), and 3(c) show the variation of  $\omega'_k$ ,  $\Delta \omega'_k$ , and  $I'_k$  vs k for the spectra from the ZnTe LO bulklike and the Zn-Se LMIF modes for excitations by 488.0- and 496.5-nm laser lines. In Fig. 3(c), the intensity scale is a log scale, which makes corrections for absorption and laser power unnecessary. From the data of set A (i.e., the ZnTe LO bulklike Raman mode) in Table I, we found surprisingly, that the greatest difference between the high-order  $\omega'_k$  and the first-order frequency  $\omega_1$  is only 0.2 cm<sup>-1</sup> (< 0.1% of  $\omega_1$ ). This is consistent with that in the bulklike and bulk modes, in **BRIEF REPORTS** 

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	k		1	2	3	4	5	6
ω	$\omega_k$	A	211.5	423.0	633.9	845.0	1056.8	1268.5
		B	223	444.2	662.1	880	1096	
	$\omega'_k$	A	211.5	211.5	211.3	211.3	211.4	211.4
		B	223	222.1	220.7	220.0	219.2	
Δω	$\Delta \omega_k$	A	8.3	6.7	6.2	7.8	8.8	7.2
		B	7.8	14.6	23.2	34.8	42.9	
	$\Delta \omega'$	A	1.0	0.81	0.75	0.94	1.06	0.87
	$\Delta w_k$	B	1.0	1.88	2.97	4.46	5.50	
	$I_k$	A	60	55	45	42	54	207
Ι		B	190	117	62	15	7	
		A	1.0	0.92	0.75	0.70	0.90	3.5
	1 k	B	1.0	0.61	0.33	0.079	0.037	

TABLE I. The results of  $\omega_k(\omega'_k)$ ,  $\Delta \omega_k(\Delta \omega'_k)$ , and  $I_k(I'_k)$  of the k-order MP peaks  $A_k$  and  $B_k$ , in the MP spectrum excited by 488.0-nm laser line for the  $(CdSe)_4/(ZnTe)_4$  SL sample.

which the Raman frequency of MP modes are multiples of the single phonon frequency within 1%.<sup>6-8</sup> The variations of  $\Delta \omega_k$  and  $I'_k$  with MP order k exhibit features also similar to the bulklike and bulk MP Raman modes reported in Refs. 6-8. These characteristics also further confirm that the spectrum of set A is due to the MP Raman scattering of the ZnTe LO bulklike mode. For the data of set B (i.e., the LMIF mode) in Table I, we see features completely different from those of the ZnTe LO bulklike mode:

(1) First, from Table I, we see that the MP reduced frequency of the LMIF mode,  $\omega'_k$ , decreases with increasing k and the greatest difference between the high-order  $\omega'_k$ and the first-order frequency  $\omega_1$  is about 4 cm<sup>-1</sup> (about 2% of  $\omega_1$ ), which is about 20 times that for the ZnTe MP bulklike modes. Such a large difference was not observed either in the bulk nor in the SL bulklike Raman MP spectra. Similar features could also be seen in the spectrum for excitation by the 496.5-nm laser line shown in Fig. 3(a).

(2) Second, we found that the observed  $\Delta \omega_k$  of the LMIF mode increases linearly with k, as seen in Table I and Fig. 3(b). This feature is completely different from the unchanged case of  $\Delta \omega$  in bulk and bulklike modes,<sup>6-8</sup> and also from the case in set A of Table I and Fig. 3(b) for the ZnTe bulklike LO mode.

(3) Third, with the increase of k, the  $I_k$  of the LMIF

mode drops monotonously from its maximum (the nearest laser frequency position) while the peak intensities of the ZnTe bulklike LO MP mode exhibit a typical outgoing resonance feature; that is, the intensities decrease on leaving the laser frequency position, and then increase to their maxima on approaching the position of the exciton peak and finally drop rapidly once the energy of the MP peak is lower than the energy of the exciton peak.

A localized mode associated with defects will decay into typical extended band modes due to anharmonic interaction.<sup>9</sup> For the localized mode, much of its energy is concentrated near the defect, where the amplitude of the ionic displacement is very large as shown in Fig. 1(b): We would expect strong anharmonic interaction and decay. The observation of MP scattering of up to five orders for the LMIF mode implies that this is the case. Thus, the above features may be accounted for in terms of anharmonic decay of localized modes.

First, the theoretical calculation of MP scattering due to anharmonic decay of the localized mode by Martin<sup>10</sup> verified that the k- and the first-order Raman linewidths of the localized mode satisfy the relation  $\Delta \omega_k = k \Delta \omega_1$ , and moreover, predicted that the linewidth is independent of temperature below a critical temperature and increases linearly with temperature above the critical temperature. The order dependence of the observed MP scattering linewidth of the Zn-Se LMIF mode, as shown



FIG. 3. Variation of (a)  $\omega'_k$ , (b)  $\Delta \omega'_k$ , (c)  $I'_k$  as a function of k for MP spectra due to the Zn-Se LMIF, and the ZnTe LO bulklike modes in the (CdSe)<sub>4</sub>/(ZnTe)<sub>4</sub> superlattice sample, with excitation of 488.0- and 496.5-nm laser lines. (The  $\Delta \omega'_k$  values for 496.5-nm line is up-shifted by 0.5.)

in Fig. 3(b), is in good agreement with that derived by Martin.<sup>10</sup> In order to test the variation of  $\Delta \omega_k$  with temperature T, we measured the MP spectra excited by the 476.5-nm laser line in the region 80–293 K and plotted the results as shown in Fig. 4. The inset of Fig. 4 shows the variation of  $\Delta \omega_1$  with T and indicates that with temperature variation the  $\Delta \omega_1$  remains essentially unchanged up to room temperature; this is different from the prediction by the localized mode theory based on the assumption of the homogeneous broadening of linewidths.<sup>10</sup> In the localized mode theory, at low temperatures the linewidth of the localized mode should be independent of temperature: at high temperatures a linear dependent is expected, and the critical temperature turns out to be the order of 70 K for the present case. Thus, the above observed dependence of  $\Delta \omega_k$  with temperature T indicates that there may exist a significant component of inhomogeneous broadening for the first-order Raman spectrum of the Zn-Se LMIF mode. Further evidence for this is also indicated by the large observed  $\Delta \omega_k$  of about 8 cm<sup>-1</sup> as compared to the Raman linewidth, about  $6 \text{ cm}^{-1}$ , of bulk ZeSe.11

Second, the observed downshift of  $\omega_k$  with k for the localized mode can also seen in the MP Raman spectra of additively colored CsI (Ref. 10) and MnO<sub>4</sub><sup>2-</sup>-doped CsI.<sup>12</sup> However, the authors did not pay attention to this phenomena. The decay of the localized mode into extended modes is due to the anharmonic component of the interatomic forces, which means that the higher the order, the lower the phonon frequency. This would result in a frequency downshift with an increase in MP order.

Third, the fact that the  $I_k$  behavior with k of the Zn-Se LMIF mode is different from that of the ZnTe LO mode could possibly arise from their different scattering mechanisms. According to the lattice-relaxation model of the MP Raman processes for bulk modes,<sup>13</sup> the excited phonons exist only in the excited electronic states and the MP Raman scattering of bulk modes is associated with the number change of excited phonons in excited electron states. Consequently, the MP Raman scattering occurs mainly in the outgoing resonance process. Contrary to this, the MP Raman scattering due to anharmonic decay of the localized mode involves only the excited phonons can exist in either of the ground- and excited electron states.<sup>12</sup> Thus, we think that the  $I_k$  behavior

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FIG. 4. Multiphonon Raman spectra excited by 476.5-nm laser line at different temperatures T for the  $(CdSe)_4/(ZnTe)_4$  SL sample. The inset is the plot of the variation of  $\Delta\omega_1$  with T.

is different from that of outgoing resonance, that is, a monotonic variation in the  $I_k$  with k for the Zn-Se LMIF mode could be expected.

The above-mentioned confirms that the interface of AB/CD-type SL's could be considered as a defect, which represents a basic unique feature and is very significant in distinguishing this type of superlattice from other superlattice types. That also demonstrates that the multiphonon Raman scattering is a particularly revealing experimental method for the study of such defectlike interface.

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