Multiphonon Raman scattering resonant with two kinds of excitons in a $(CdTe)_2(ZnTe)_4/ZnTe$ short-period-superlattice multiple quantum well

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A study of the multiphonon resonant Raman scattering in a $(CdTe)_2(ZnTe)_4/ZnTe$ short-period-supperlattice multiple quantum well (SSQW) has been performed. Overtones up to the 13th order for the ZnTe longitudinal-optical (LO) phonons were observed and identified as due to Raman scattering. The Raman scattering was involved in the ZnTe LO phonons confined in the barriers of SSQW and in short-period superlattices resonant with two kinds of excitons in the barriers and wells of the SSQW, respectively. This may account for up to 13th orders of multiphonon scattering being observed.

In the past decade, Raman scattering has been widely used to study the phonons in low-dimensional semiconductor systems, and significant experimental and theoretical results have been achieved.[1,2] Unlike first-order Raman scattering, multiphonon (MP) Raman scattering in semiconductor superlattices (SL's) and quantum wells (QW's) has received less attention. It is only recently that MP scattering in short-period GaAs/AlAs SL's has been studied in detail.[3,4] For II-IV semiconductor SL's, multiphonon scattering has also been investigated in ZnTe/ZnSe, CdTe/HgTe, ZnSe/SnSeS, and $CdTe/Cd_xMn_{1-x}Te$.[5-8] Nakashima *et al.*[5] observed 6th-order overtones of ZnTe longitudinal-optical (LO) phonons in ZnTe/ZnSe SL's; however no detailed analysis has been given.

The wide band-gap CdTe/ZnTe system is of current interest because of its potential applications in short-wavelength optoelectronic devices, but the large lattice mismatch (6.4%) makes it very difficult to grow CdTe/ZnTe SL's of high quality. Li *et al.*[9] have designed $(CdTe)_m(ZnTe)_n/ZnTe$ (where m and n are the molecular layer numbers) short-period-superlattice multiple quantum wells (SSQW's) in which the well region is a short-period $(CdTe)_n(ZnTe)_m$ superlattice, in order to make the barrier and the well layers less mismatched. Here we present an investigation of MP Raman spectra from a SSQW.

The sample studied, referred to as $Z1$, was grown by atomic layer epitaxy; the details of growing are described elsewhere.[9] A ZnTe buffer layer 1–2 μm thick was first deposited on a GaAs(001) substrate before six periods of QW's were grown. The barriers and wells of the SSQW's were 80 monolayers of ZnTe and seven periods of $(CdTe)_2(ZnTe)_4$ short-period superlattices, respectively. The Raman experiment was performed in near-backscattering geometry at nitrogen temperature (80 K). An Ar^+ laser was used to excite the sample. The scattered light was dispersed by a SPEX-1403 double monochromator coupled to a third monochromator and detected by a cooled photomultiplier tube and photon counting electronics. In the spectral measurements, we chose the coordinates X, Y, and Z parallel to the crystal axes (100), (010), and (001), respectively.

The electronic band structure of $Z1$ was characterized by a photoluminescence (PL) spectrum.[10] The PL spectrum displayed two main emission peaks at energy positions of 2.36 and 2.19 eV, respectively, and a defect band at a lower energy of 1.80 eV. The subband calculation in terms of the Kronig-Penney model has been performed and showed that there are two exciton transitions of the light-hole excitons in the barrier (referred to as E_{BL}) at 2.32 eV and heavy-hole excitons in the well (referred to as E_{WH}) at 2.11 eV for sample $Z1$.[10] In comparison with the above theoretical expectation we attribute emissions at 2.36 and 2.19 eV to E_{BL} and E_{WH}, respectively, as shown in Fig. 1.

Figure 2 shows the first-order polarized Raman spectra of sample $Z1$. In Fig. 2 there are four peaks at 181.5, 209.5, 218.5, and 240.0 cm^{-1} and a weak peak at about 207 cm^{-1}. Because of the thick buffer layer and the thinner CdTe layer, the sample is seen to be pseu-

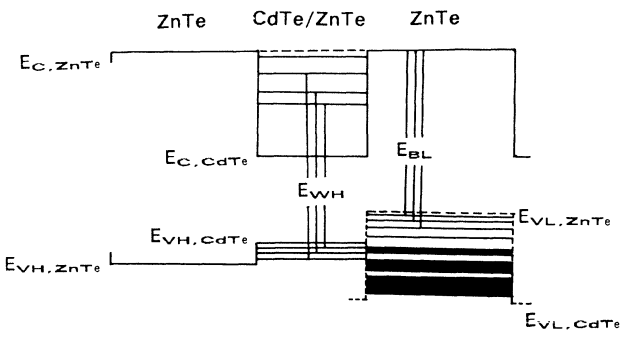

FIG. 1. The band diagram and possible transitions E_{WH} and E_{BL} for sample $Z1$. E_C, E_{VH}, and E_{VL} are the energy positions of the conduction electron, heavy hole, and light hole, respectively.

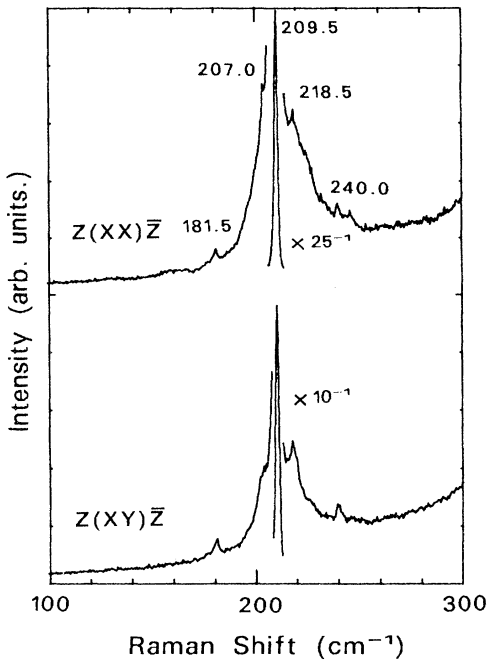

FIG. 2. First-order polarized Raman spectra excited by the 514.5-nm laser line for sample $Z1$.

domorphic, i.e., the strain exits only in the CdTe layer and cannot cause an energy shift of ZnTe LO phonons. On the other hand, the layer thicknesses of ZnTe in wells and barriers are 12.2 and 243.6 Å, respectively, thus the influence of confinement on ZnTe LO phonons should be considered for the phonons in the wells although it can be neglected for the phonons in the barriers. Since the frequency of bulk ZnTe LO phonons is 209 cm^{-1} (Ref. 11) and the calculated frequency of the confined ZnTe LO_1 phonon in wells of sample $Z1$ is 206.8 cm^{-1} in terms of the linear chain model, we attribute the Raman features at 209.5 and 207 cm^{-1} to the ZnTe LO modes confined in barriers of the SSQW's (referred to as LO_B) and in short-period superlattices (referred to as LO_W), respectively. According to the above, we identified the peaks at 181.5 and 240.0 cm^{-1} as being due to the ZnTe transverse-optical (TO) and ZnTe transverse-acoustic (TA)+LO modes, respectively. We found that the peak at 218.5 cm^{-1} has the same energy at room and nitrogen temperatures, and it is thus thought that it cannot be identified as being due to the lattice vibrational mode. The Raman selection rules of LO_W, confined as ZnTe LO_1 in the wells observed in Fig. 2, are different from the theoretical prediction[12] from which the LO_n phonon modes with n odd and even are expected to be observed in (XY) and (XX) geometry, respectively. We have tentatively ascribed this breakdown of selection rules to effect the barrier penetration of carriers in ultrathin superlattices. A more detailed discussion will be presented elsewhere.[13]

Figure 3 displays the MP Raman spectra in the $Z(XX)Z$ configuration with excitation by laser lines of 514.5 nm (a), 496.5 nm (b), 488.0 nm (c), 476.5 nm (d), and 457.9 nm (e), of which the incident photon energies, E_{in}, were 2.41, 2.50, 2.54, 2.60, and 2.71 eV, respectively, for sample $Z1$. Except for the spectrum (e), which may be due to far from resonance, the first-order spectra and their overtones up to 8th, 9th, 13th, and 10th order have been observed in the spectra (a), (b), (c), and (d). Their frequencies, ω, are listed in Table I.

Since hot luminescence (HL) and resonance Raman scattering (RRS) display similar spectral features, it is of considerable importance to distinguish them. According to the definition of Takagahara,[14] RRS 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. In order to identify whether the observed overtones originate from RRS 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 and are listed in Table I. From Table I, we found that the polarization memory is, on the whole, not lost and the highest-order overtones still remain polarized. Concerning the linewidths, we measured the linewidths of the overtones resonant with only E_{BL} as shown in Fig. 3(d). The linewidths are all about 1.6 meV

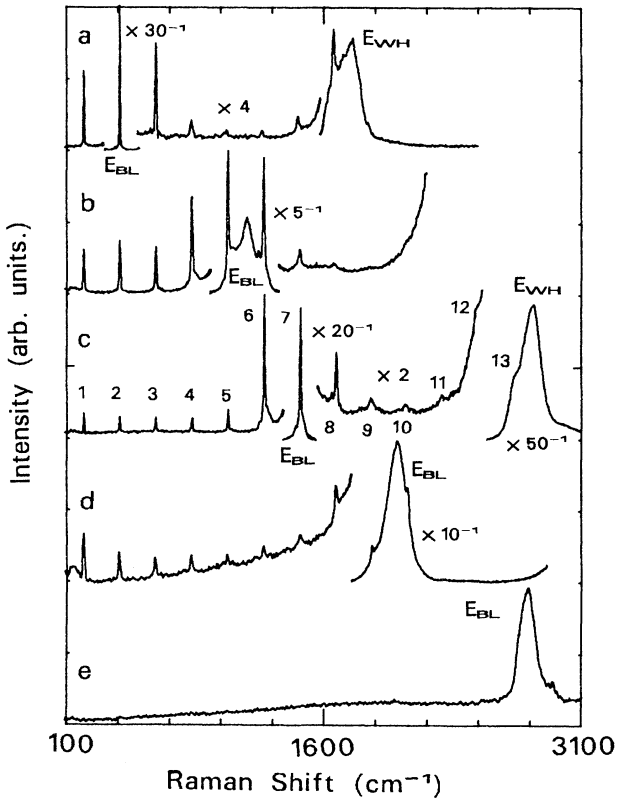

FIG. 3. Multiphonon Raman spectra in a $Z(XX)Z$ configuration with excitation laser lines of 514.5 nm (a), 496.5 nm (b), 488.0 nm (c), 476.5 nm (d), and 457.9 nm (e), of which the incident photon energies, E_{in}, are 2.41, 2.50, 2.54, 2.60, and 2.71 eV, respectively, for sample $Z1$.

TABLE I. The frequencies ω (in cm^{-1}) and depolarization ratios of the ZnTe longitudinal-optical (LO) multiphonon Raman lines in Fig. 3. The frequencies in parentheses are not precisely determined as the peaks and are too weak.

E_{in} (eV)		1 LO	2 LO	3 LO	4 LO	5 LO	6 LO	7 LO	8 LO	9 LO	10 LO	11 LO	12 LO	13 LO
	ω	209.5	420	630	836	(1040)	1244	1454	1658					
2.41														
	I_{dp}	2.5	1.7	1.6	2	1.6	2	2	1.5					
2.50	ω	209.5	419	628	838	1048	1256	1466	1658	(1868)				
2.54	ω	209.5	418	628	838	1048	1258	1466	1678	1876	2076	2288	(2424)	(2708)
2.60	ω	209.5	418	626	834	1046	1256	1467	1674	1884	(2090)			

from the 1st- to 8th-order overtones, and a similar situation also exists in the other spectra. For the overtone energies, we have found that the overtone frequencies are a strict integer multiple of 1st-order frequency for all spectra (for detail, see the following discussion of Fig. 4). What has just been mentioned differs significantly from hot-luminescence overtones in the ZnTe/MnTe QW's as reported by Pelekanos *et al.*[15] Therefore, the spectra in Fig. 3 can only be viewed as resulting from coherent scattering of the Raman process, and gets rid of the possible generation of the overtones from the hot-luminescence process.

In the spectra of Fig. 3, as the incident photon energies are all above the exciton energies E_{BL} and E_{WH}, the observed resonant scattering is the outgoing resonant scattering. Moreover, up to 8th-, 9th-, 13th-, and 10th-order Raman lines of ZnTe LO MP are clearly seen in the spectra (a)–(d) of Fig. 3. As far as we know, they are all higher than any previous observation of ZnTe LO MP Raman scattering in bulks, QW's, and SL's. In addition,

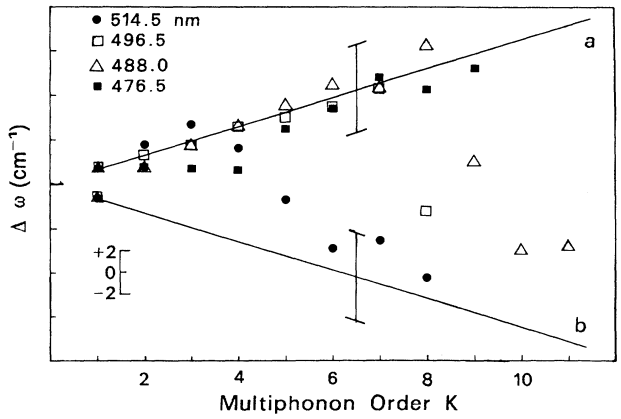

FIG. 4. Deviation $\Delta\omega$ of the observed overtone frequencies of ZnTe LO phonons LO_B and LO_W from the calculated multiphonon frequencies by $K\omega_{LO}$. K is the multiphonon order and ω_{LO} equals the observed frequencies of first-order LO_B (represented by the solid line a) or LO_W (represented by the solid line b). The positions of the solid lines a and b at integer K values ($K>1$) represent the calculated MP frequency positions for ZnTe phonons LO_B and LO_W, and were drawn so that the intervals at the same K value between solid lines a and b are equal to the calculated MP frequency difference of LO_B and LO_W. The vertical bars represent experimental error.

the combinations of ZnTe $(K-1)$LO+TO phonons up to $K=6$ was also observed, where K is the order index of ZnTe LO MP. In the following, we tentatively explain why such high-order Raman scattering lines of ZnTe LO MP can be observed.

First, we think that the high-order MP scattering observed in SSQW is associated with the two-dimensional structure, because a lowering of dimension enhances the exciton-phonon interaction and favors MP scattering, as has been reported in GaAs/AlAs SL's.[3] However, what attracted more attention is that the multiphonon lines, with scattered photon energy much lower than E_{BL} exciton energy, can also be observed. For example, in the case of the excitation of the 514.5-nm laser lines shown in Fig. 3(a), 2nd-order MP at in resonance with E_{BL} excitons up to 8th-order multiphonon lines far from the E_{BL} energy have been observed. The overtones are especially enhanced to be stronger and stronger from the 5th to the 8th order as the scattered photon energy approaches the energy of the E_{WH} excitons. This differs from previous observations where the MP line is resonant with only one kind of exciton and rapidly disappears when the scattered photon energy is below the exciton energy.

The MP outgoing resonant process can be described by the following equation:

$$E_{in}-K\hbar\omega_{LO}=E\ ,$$

where E_{in} and E are the incident photon energy and exciton energy, respectively. $\hbar\omega_{LO}$ is the phonon energy and K 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. The deviation of observed overtone frequencies from the calculated MP frequencies are plotted in Fig. 4. In Fig. 4 the positions of solid lines a and b at integer K values ($K>1$) represent the calculated MP frequency positions for ZnTe phonons LO_B and LO_W, and were drawn so that the intervals at the same K value between solid lines a and b are equal to the calculated MP frequency difference of LO_B and LO_W. The calculated MP frequencies are based on the observed frequencies of first-order LO_B and LO_W, which are equal to 209.5 and 207 cm^{-1}, respectively. From Fig. 4, we found that in the spectra excited by the 514.5-nm laser line the MP frequencies for before the 4th and after the 6th fall into the calculated frequency region for different kinds of ZnTe LO modes, where LO_B and LO_W are permitted by experimental error, whereas the frequency of the 5th-order MP lies be-

tween the two solid lines a and b and can be considered a "transition state" MP resonant with E_{BL} and E_{WH} excitons. With the decrease of E_{in} and the shift of the PL peak position towards a higher wave number, the transition state MP's shift up to higher wave numbers and the number of MP's in resonant with E_{BL} increases. Finally, in the spectrum excited by the 476.5-nm laser line shown in Fig. 3(d), we see the MP's resonant with E_{BL} and their frequencies only matching the calculated MP frequencies of LO_B. Therefore, the MP Raman scattering of sample $Z1$ results practically from different ZnTe LO-phonons, LO_B and LO_W, resonant with two kinds of excitons, E_{BL} and E_{WH}. This explains why the MP line does not disappear when the scattered photon energy is below the E_{BL} exciton energy, and so many order MP Raman lines are observed.

In summary, we have observed overtones up to the 13th order for ZnTe LO phonons in a $(CdTe)_2(ZnTe)_4/ZnTe$ SSQW and a detailed analysis shows that the overtones arise from resonant Raman scattering (RRS) and not from hot-exciton luminescence (HL). As far as we know, this is the highest-order multiphonon scattering observed up to now in semiconductor SL's and QW's. Moreover, the resonant multiphonon process involves two kinds of excitons, those in the SSQW wells and those on the SSQW barriers, and also two kinds of LO phonons. These have not been seen experimentally before and practically explain why so many orders of multiphonon Raman scattering were observed.

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