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Outgoing multiphonon resonant Raman scattering and luminescence near the $E_0+\Delta_0$ gap in epitaxial CdTe films

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We have measured resonant Raman scattering and photoluminescence from thin (001) CdTe films grown by pulsed laser evaporation and epitaxy on (001) GaAs. CdTe LO phonon overtones up to sixth order are observed under outgoing resonance conditions near the $E_0+\Delta_0$ (conduction Γ_6 and spin-orbit split-off valence Γ_7 bands) gap. We discuss mechanisms for LO phonon overtones. Photoluminescence from the $E_0+\Delta_0$ gap is seen at 80 K, for the first time without the help of carrier confinement from a superlattice, and is analyzed in detail.

Multiphonon resonant Raman scattering in semiconductors has been an interesting topic in the past two decades.[1,2] Overtones of the longitudinal-optical (LO) phonon, excited by photons resonant with the fundamental valence-to-conduction band (Γ_6-Γ_8) gap E_0, are characteristic of wurtzite and zinc-blende II-VI compounds.[2] Overtones up to order $m=4$–9 have been reported[3–9] for CdS, CdSe, ZnSe, and ZnTe. This contrasts with elemental semiconductors and with most III-V crystals. Only a few of the latter, like GaP (Ref. 10), show even third-order overtones. Most authors consider phonon overtones to originate from multiple phonon Raman scattering, although some propose hot exciton luminescence to explain these sharp lines at intervals of the LO phonon energy.[5,11]

To date, Raman spectra from bulk and film CdTe have shown only first- and second-order phonons.[12–18] CdTe phonon peaks up to $m=4$ have been reported by Olego and co-workers[19,20] only for HgTe-CdTe superlattices, and then only near resonance with the CdTe spin-orbit split-off $E_0+\Delta_0$ (Γ_6-Γ_7) gap. They also observed photoluminescence (PL) recombination across the $E_0+\Delta_0$ gap, normally 10^{-4}–10^{-5} times weaker than that across the E_0 gap.[20–22] They explained its appearance in the superlattices by quantization of the Γ_7 valence states in the high quality CdTe layers.[20] Although the $E_0+\Delta_0$ emission has been observed in some bulk materials, such as GaAs,[21–24] it has not yet been seen in bulk or film CdTe.

Resonance Raman work in CdTe and closely related compounds has been limited. Two groups[25,26] have studied one- and two-phonon resonant Raman scattering in $Hg_{1-x}Cd_xTe$ ($x=0.5$–1.0) near the $E_0+\Delta_0$ gap. Although both groups used sample orientations and polarizations different from ours, these results give some basis for comparison. We have also previously reported resonant enhancement near the $E_0+\Delta_0$ transition in CdTe for the $Cd_{1-x}Mn_xTe$-CdTe superlattice, where the CdTe LO mode and its second and third harmonics appeared.[27]

Here we report both high-order Raman phonon overtones (up to $m=6$) and PL across the $E_0+\Delta_0$ gap in thin CdTe films grown on GaAs by pulsed laser evaporation and epitaxy (PLEE). The overtones come from outgoing resonant Raman scattering, which occurs as the energy of the scattered photon approaches $E_0+\Delta_0$. This differs from work in other II-VI compounds,[3–9] where the incoming photons resonate with the fundamental band gap.

The (001) CdTe films were grown on (001) semi-insulating GaAs substrates by the PLEE method at the National Research Council of Canada. PLEE growth, recently reviewed by Dubowski,[28] uses a high-power pulsed Nd:YAG (where YAG denotes yttrium aluminum garnet) laser beam incident on a solid target (in this case, polycrystalline CdTe obtained from Cominco) to generate vapor for epitaxial growth. Only a small part of the target is at high temperature during growth, eliminating sources of contamination which must be considered in other growth methods. By counting pulses, the film thickness can be controlled down to the submonolayer level.

The PLEE technique has successfully grown CdTe epilayers on GaAs substrates,[28,29] including four (001) CdTe/(001) GaAs samples prepared for this study, at an optimum substrate temperature of $\sim 300\,^{\circ}C$, with film thicknesses of 1.55, 1.62, 2.4, and 6.2 μm.

Raman and resonant Raman measurements were performed in the near-backscattering geometry at Emory University. The samples, mounted on a cooled copper block, were held at 80 K and were excited by an Ar^+ laser with a focused beam of diameter <0.3 mm. The scattered light was dispersed by a triple spectrometer and accumulated by an optical multichannel analyzer (OMA), which gave high sensitivity with resolutions of 2–3 cm^{-1}.

Figure 1 shows eight Raman spectra from the 1.62-μm-thick sample, excited by laser lines with energies of 2.4090–2.7067 eV (514.54–457.94 nm). The spectra show a variety of sharp lines at multiples of the LO phonon frequency, and broad bands. Table I lists details, including an integrated intensity for each phonon overtone which helps trace the development of resonance.

The sharp Raman lines can be explained by considering three cases: no resonance (NR), incoming resonance (IR), and outgoing resonance (OR), defined relative to

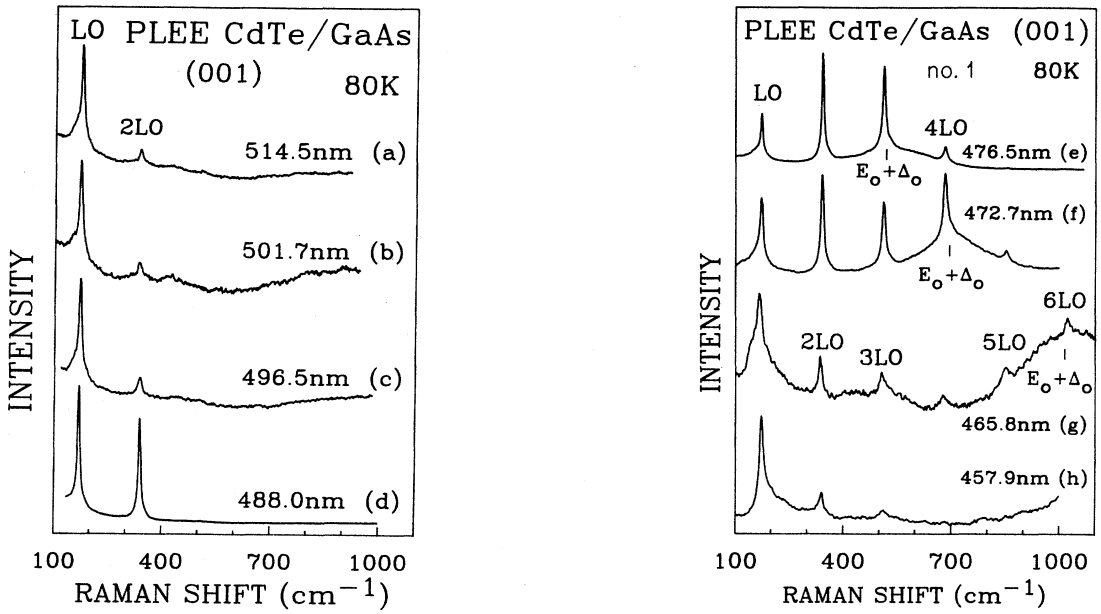

FIG. 1. Raman and resonant Raman spectra of PLEE-grown (001) CdTe film (1.62 μm thick) on (001) GaAs at 80 K, excited with eight Ar^+ laser lines. Details are given in text and Table I.

the $E_0+\Delta_0$ gap by Eqs. (1)-(3), respectively:

$$E_{in} < E_0+\Delta_0 \quad (NR), \tag{1}$$

$$E_{in} \sim E_0+\Delta_0 \quad (IR), \tag{2}$$

$$E_{out} = E_{in} - m\hbar\omega_{LO} \sim E_0+\Delta_0 \quad (OR). \tag{3}$$

Incoming resonance is well known. Outgoing resonance has been analyzed by Menendez and co-workers, for instance.[25,30] They show that the Raman scattering efficiency has a maximum when the energy E_{out} of the scattered photon matches some energy gap E_g in the band structure. If an incoming photon of energy E_{in} is scattered m times by LO phonons, the final outgoing photon is emitted with energy $E_{out}=E_{in}-m\hbar\omega_{LO}$, giving Eq. (3) as the condition for outgoing resonance with $E_g=E_0+\Delta_0$.

In CdTe at 80 K, $E_0=1.58$ eV, $E_0+\Delta_0=2.535$ eV (Ref. 20), and $\hbar\omega_{LO}=21.2$ meV (Ref. 31). Cases (a)-(c) of Fig. 1 and Table I show the nonresonant case $E_{in}<E_0+\Delta_0$. Here the first-order LO Raman line is much stronger than the second-order 2LO line, and the 3LO line is hardly visible.

However, the intensity ratio I_{2LO}/I_{LO} increases from 0.12 to 0.20 as E_{in} approaches the $E_0+\Delta_0$ gap at 2.53 eV. This represents the onset of incoming resonance. When E_{in} finally exceeds $E_0+\Delta_0$, but still lies very close to it, incoming resonance occurs [Fig. 1(d)] and the 2LO line becomes comparable to the LO line ($I_{2LO}/I_{LO}=0.92$). The 3LO line is much weaker and no higher-order overtones appear. Similar incoming resonance spectra have been seen[25] from $Hg_{0.034}Cd_{0.966}Te$.

As E_{in} increases further, other strong, sharp peaks appear at multiples of $\hbar\omega_{LO}$ with dramatic variations in their intensities [cases (e)-(h) of Fig. 1 and Table I]. These can be explained by the outgoing resonance relation, Eq. (3). In Fig. 1(e), for example, with $E_{in}=2.6013$ eV, Eq. (3) is nearly exactly satisfied for $m=3$. Therefore, the 3LO line resonates with the $E_0+\Delta_0$ gap and is extremely strong. Its intensity is nearly three times that of the LO line and only slightly less than that of the 2LO line. The 4LO and the 5LO lines also appear.

TABLE I. Energy and resonance information for spectra shown in Fig. 1. λ_{ex}, exciting laser wavelength; E_{in}, incoming photon energy. For outgoing resonances, the integers in parentheses are the values of m (phonon order) satisfying Eq. (3).

Spectrum	λ_{ex} (nm)	E_{in} (eV)	Resonance condition	Relative multiphonon intensity 1LO	2LO	3LO	4LO	5LO	6LO
(a)	514.54	2.4090	NR	1	0.12	0.03			
(b)	501.72	2.4705	NR	1	0.14				
(c)	496.51	2.4964	NR	1	0.20				
(d)	487.99	2.5400	IR	1	0.92	0.01			
(e)	476.49	2.6013	OR(3)	1	2.94	2.91	0.83	0.10	0.06
(f)	472.69	2.6222	OR(4)	1	1.23	0.82	1.05	0.17	0.02
(g)	465.79	2.6611	OR(6)	1	0.18	0.16	0.12	0.18	0.08
(h)	457.94	2.7067	OR(8)[a]	1	0.19	0.11	0.03		

[a]Not observable in present experiment.

In Fig. 1(f), with $E_{in}=2.6222$ eV, Eq. (3) is satisfied by $m=4$. Now the 4LO line is in resonance with $E_0+\Delta_0$ and is enhanced relative to the LO, 2LO, and 3LO lines. Also, the 5LO line becomes stronger than in Fig. 1(e). With an excitation energy of 2.6611 eV, the 6LO overtone is in resonance, and indeed appears [Fig. 1(g)] atop a broadband. Here the 2LO, 3LO, and 4LO lines lie far from the $E_0+\Delta_0$ band, so they appear weaker than in Figs. 1(e) and 1(f). This is the first time, we believe, that such high overtones ($m=5,6$) have been reported for CdTe. Finally, in Fig. 1(h), the high excitation energy of 2.7067 eV would give resonance for $m=8$. The 8LO line is outside our experimental range and those lower overtones which we observe lie too far from resonance to undergo enhancement. In fact, Fig. 1(h) resembles Fig. 1(a).

Menendez, Cardona, and Vodopyanov[25] noted that the exact spacing between the first- and second-order LO peaks is significant and can help decide among models for Raman scattering. They measure a spacing of $1.04\hbar\omega_{LO}$ for CdTe. Our data for the sample in Fig. 1 and Table I, and other samples, excited at laser energies from 2.4 eV to 2.7 eV, give a spacing of $(1\pm0.01)\hbar\omega_{LO}$.

In addition to the striking multiple peaks, Figs. 1(e)–1(g) show broadbands on which the 3LO, 4LO, and 6LO lines, respectively, are superimposed. These bands move with respect to the Raman lines as E_{in} varies, but in absolute terms all are centered at 2.535 eV, the energy of the $E_0+\Delta_0$ gap. We therefore ascribe them to PL produced by recombination across this gap.

All our samples exhibit spectra like those in Fig. 1, except that the $E_0+\Delta_0$ band is very strong in some cases. Figure 2 shows Raman spectra for the 2.4-μm-thick sample. As in Figs. 1(e)–1(g), the outgoing 3LO, 4LO, and 6LO lines each resonate in turn with the $E_0+\Delta_0$ band and are enhanced, but now the $E_0+\Delta_0$ PL band is much stronger than any of the phonon lines, rather than weaker as in Figs. 1(a) and 1(f).

The sample-to-sample variation in intensity of the $E_0+\Delta_0$ band, along with a slight shift in its position, may come from different carrier concentrations or impurity levels, as occurs in GaAs (Ref. 21). To explore this, we examined high-purity CdTe crystals from several sources. They exhibited the same outgoing Raman resonances as our CdTe films, but lacked the $E_0+\Delta_0$ luminescence.[32] In analogy to behavior in bulk GaAs (Ref. 21), this may be because the carrier density is too low to give significant recombination across Γ_6-Γ_7.

The CdTe Γ_6-Γ_7 band has been seen only in HgTe-CdTe superlattices,[19,20] where carrier confinement increased the concentration of Γ_7 holes in the CdTe layers so the Γ_6-Γ_7 transition was strengthened. Our results show that carrier confinement is not necessary. The Γ_6-Γ_7 transition appears even at nitrogen temperature in samples of sufficient quality with adequate carrier density.

Figure 3 shows, for the same sample as in Fig. 2, the Raman spectrum, the $E_0+\Delta_0$ PL band, and (see inset) a PL band at 1.58 eV, near the fundamental E_0 (Γ_6-Γ_8) gap energy. To prevent uncontrolled changes in the spectral intensities, these features were recorded by changing only the wavelength response of the OMA system at fixed laser power and without moving the laser beam on the sample. After correcting for the OMA response, we find that the $E_0+\Delta_0$ band is 10^{-4}–10^{-5} times weaker than the E_0 band. This is similar to results in bulk GaAs (Ref. 22) and the HgTe-CdTe superlattice.[20]

The 1.58-eV band in Fig. 3 is asymmetrically stronger on its high-energy side. This probably reflects a main contribution from the free exciton at 1.584 eV, with a high-energy shoulder from the band-to-band transition across the E_0 gap, which lies $\sim$2 meV above the free-exciton transition.

On the other hand, the $E_0+\Delta_0$ band in Fig. 3 is symmetric. We believe that it consists of only the bare Γ_6-Γ_7 band-to-band transition with no excitonic contribution.

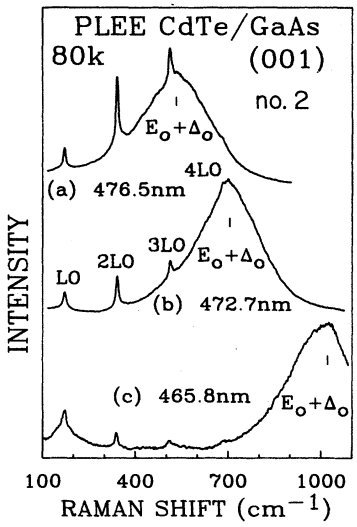

FIG. 2. Outgoing multiphonon resonant Raman spectra of PLEE-grown (001) CdTe film (2.4 μm thick) on (001) GaAs measured at 80 K, excited by three Ar^+ laser lines. The CdTe LO phonon overtones are superimposed on a strong $E_0+\Delta_0$ PL band.

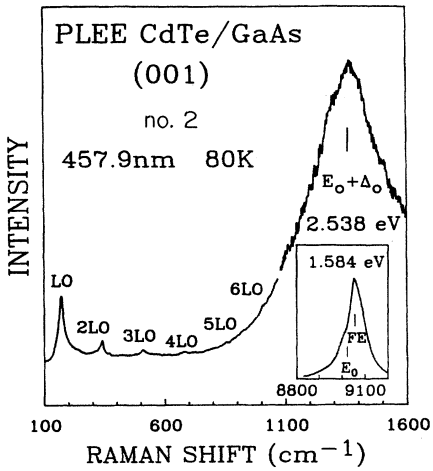

FIG. 3. Raman spectrum, $E_0+\Delta_0$ PL band, and E_0 PL band (inset) of PLEE-grown (001) CdTe film (2.4 μm thick) on (001) GaAs at 80 K.

From intensity considerations, it has been shown that τ_7, the lifetime of the Γ_7 hole, is much less than τ_8, that of the Γ_8 hole. [The ratio τ_7/τ_8 is about 10^{-4} for CdTe in HgTe-CdTe superlattices and for n-type GaAs (Refs. 20 and 22)]. Therefore, an exciton is far less likely to form between a Γ_7 hole and a Γ_6 electron than between a Γ_8 hole and a Γ_6 electron, reducing or eliminating excitonic features associated with the $E_0+\Delta_0$ transition.

The lack of excitons connected with the $E_0+\Delta_0$ band is evidence that resonant multiphonon scattering, not hot-exciton recombination, causes our observed Raman LO phonon overtones. This view is also consistent with our observation that the 2LO and 3LO lines in Fig. 1(d), and the 5LO and 6LO lines in Fig. 1(e) lie below $E_0+\Delta_0$. Hence they cannot arise from the hot-exciton recombination process described in Refs. 5 and 11.

Another feature of our spectra is noteworthy. In some cases (Fig. 1) resonant enhancement extends beyond the overtone satisfying Eq. (3) to an adjacent overtone. This may come from the relative breadth of the $E_0+\Delta_0$ band (Fig. 3). Its full width at half maximum (FWHM) of 50 meV is more than twice as large as $\hbar\omega_{\mathrm{LO}}$, whereas the FWHM of the free exciton or E_0 bands is only about 12 meV. Thus resonant behavior associated with the $E_0+\Delta_0$ band is sufficiently broad to affect a given overtone and an adjacent one, separated by the energy $\hbar\omega_{\mathrm{LO}}$.

Finally, we comment that while our sensitive OMA detection and resonant enhancement contribute to our unusual observations of high-order Raman lines and the weak $E_0+\Delta_0$ PL band at the high temperature of 80 K, such observations always require good crystalline quality. We consider them to be evidence of such quality in the PLEE-grown CdTe films. In a later, more complete study, we will compare these results to those in PLEE-grown (111) CdTe films and other bulk and film CdTe.

We have studied incoming and outgoing resonant multiphonon Raman scattering and luminescence near the $E_0+\Delta_0$ gap in epitaxial CdTe films grown by the PLEE technique. Incoming resonance gives only a strong 2LO phonon line and a weak 3LO line. The outgoing multiphonon resonance gives up to sixth-order LO phonon overtones seen at 80 K. We cite varied experimental evidence to show that the overtones originate from multiphonon resonant Raman scattering, not hot-exciton recombination. We observed the $E_0+\Delta_0$ luminescence for the first time from CdTe films without any enhancement from superlattice effects such as carrier confinement. These results make a good foundation for further theoretical work to describe higher order ($m \geq 3$) outgoing Raman resonance, to explain the intensity distribution of the LO phonon overtones, and to calculate the strength and shape of the $E_0+\Delta_0$ PL band. We hope that such analysis will appear in the near future.

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