Above-band-gap photoluminescence from *n*-type CdTe:I grown by molecular-beam epitaxy

Jaesun Lee and N. C. Giles
Department of Physics, West Virginia University, Morgantown, West Virginia 26506-6315

C. J. Summers
Georgia Tech Research Institute, Atlanta, Georgia 30332-0800

(Received 6 December 1993)

We report the observation of above-band-gap radiative recombination from highly doped *n*-type CdTe:I epilayers grown by molecular-beam epitaxy. Radiative emission involving phonon absorption processes was observed at sample temperatures up to 30 K with excitation power densities as low as 300 mW/cm^2 using conventional phase-sensitive signal detection. The momentum-conserving phonon absorption photoluminescence (PL) process in the epilayers involves excitons with an average kinetic energy of 5 meV. Even though phonon emission bands of donor-related recombination have not been observed in CdTe, we see a clear indication of phonon absorption PL due to coupling with donor states. The dependence of PL intensity on incident excitation power density for near-band-edge and above-band-gap emissions reveals that phonon absorption processes increase at a slightly faster rate, indicative of the strong electron-phonon coupling in CdTe.

Photoluminescence (PL) spectroscopy has proved to be an effective, noncontact, and nondestructive characterization technique which allows sensitive identification of point defects, including substitutional impurities (donors, acceptors) and native (or intrinsic) centers, in semiconducting materials. Generally, PL emission energies are close to, but below, the band-gap energy E_g of the semiconductor. PL emission due to conduction-band electron-valence-band hole recombination (e,h) at $k=0$ in direct-gap II-VI materials is not commonly observed at low temperatures. Excitonic (free and bound) recombinations at energies less than E_g dominate the radiative emission spectrum in high quality II-VI semiconductors.

We report the observation of PL emission at energies in CdTe above the $k=0$ band gap, but well below the $E_0+\Delta_0$ energy. Our results are consistent with exciton-phonon absorption recombination. Observation of such an exciton-phonon quasiparticle at above-band-gap energies has been reported in InP.[1] A model for this new emission in InP has been recently proposed, and extended to other zinc-blende simiconductors, specifically GaAs and CdTe.[2] However, the authors in Ref. 2 concluded that observation of the exciton-phonon above-band-gap PL would *not* be observed in CdTe because of a smaller electron-phonon coupling constant in this II-VI material. In the present paper, we describe the phonon absorption (anti-Stokes) excitonic radiative recombination from high-quality CdTe:I epilayers at low temperatures, and we reexamine the electron-phonon coupling in these materials.

First, the direct observation of PL arising from phonon-absorption processes using a conventional low-temperature PL apparatus is surprising since the number of phonons available for absorption rapidly decreases as the sample temperature is lowered. The probability for phonon absorption is lower than the probability for phonon emission by a factor of exp $(\hbar\omega_{\rm ph}/k_B T)$,[3] where $\hbar\omega_{\rm ph}$ is the phonon energy, k_B is the Boltzmann constant, and T is temperature in degrees kelvin. The factor exp $(\hbar\omega_{\rm ph}/k_B t)$ is approximately 10^{23} at the liquid-helium temperature for CdTe (longitudinal-optical-phonon energy of 21.3 meV). Thus, in direct band-gap semiconductors, phonon-assisted processes usually produce luminescence involving phonon emission. In addition, phonon emission gives rise to photons of energy *less than* the band-gap energy and are thus less subject to self-absorption. Phonon-absorption luminescence related to near-band-edge recombination gives rise to photon energies *above* E_g, and the probability for observing such transitions is further reduced.

With the arguments presented above, it would not be likely to observe the anti-Stokes, or phonon absorption, process in low-temperature PL spectra. However, during the excitation of PL, phonons resulting from the Stokes process (phonon emission) can subsequently participate in the anti-Stokes process. Key issues related to the direct observation of anti-Stokes PL are then (1) the strength of the electron-optical phonon coupling in the semiconducting material of interest, and (2) the threshold of excitation powers required to create the high density of optical phonons such that absorption can take place.

At the liquid-helium temperatures which are required for high-resolution emission spectroscopy, PL bands involving phonon emission processes are fairly common in high-quality II-VI materials. In high-purity bulk CdTe, which displays narrow bound exciton emission lines at liquid-helium temperatures, we typically observe several orders of phonon replicas of free exciton (X) and acceptor-bound exciton (A^0,X) emission lines. The electron-phonon coupling[4] can be described by the coupling constant

$$A(q)=-\frac{i\hbar\omega}{q}\left[\frac{\hbar}{2m^*\omega}\right]^{1/4}\left[\frac{4\pi\alpha}{V}\right]^{1/2}, \qquad (1)$$

0163-1829/94/49(16)/11459(4)/$06.00

where α, the dimensionless coupling constant (Fröhlich) is given by

$$\alpha=\frac{e^2}{\hbar}(\varepsilon_\infty^{-1}-\varepsilon_0^{-1})\left[\frac{m^*}{2\hbar\omega}\right]^{1/2}. \quad (2)$$

Using the dielectric constants, effective masses, and optical-phonon energies given in Ref. 2 for InP, GaAs, and CdTe, we find that α (CdTe) $>\alpha$(InP)$>\alpha$ (GaAs) with the following ratios 5:2.5:1. The strength of the coupling constant A [given by Eq. (1)] is only slightly greater in InP than for CdTe. We find A (InP) $>A$ (CdTe) $>A$ (GaAs), according to 1.5:1.4:1. Thus, it is not clear on the basis of the electron-coupling constant that above-band-gap PL would not be observed in CdTe. This is in contrast to the conclusion reached in Ref. 2. We do, however, agree that the coupling in GaAs is smaller than the coupling predicted for the materials in which phonon-absorption PL is observed.

The n-type doped CdTe:I epilayers investigated in this study were grown at the Georgia Tech Research Institute by molecular-beam epitaxy using ethyliodide as the gas source for the dopant precursor. The doped epilayers were grown on bulk 2° off (001) CdTe substrates at substrate temperatures from 170 to 250 °C and exhibit room-temperature excess electron concentrations between 8.2×10^{16} and 3.1×10^{18} cm^{-3}.[5] Low-temperature and room-temperature below-band-gap PL studies from these n-type doped epilayers have been reported previously.[6,7] The CdTe:I epilayers exhibited extremely bright PL emission, being much brighter at room temperature than the bulk CdTe sample which we have used as a standard in our work.

The samples were excited using the 514.5-nm (2.41-eV) single-line output from a Laser Ionics Model 552A argon-ion laser, which provides photon energies significantly higher in energy than the liquid-helium E_g of CdTe at 1.606 eV. PL data were taken with incident power densities from 0.8 mW/cm^2 to 25 W/cm^2. The PL signals were detected with an Instruments SA, Inc. HR-640 spectrometer and photomultiplier tube with GaAs cathode and analyzed with a lock-in amplifier. The emission lines from a Hg(Ar) lamp were used to calibrate the wavelength response of the spectrometer to within ±0.4 Å (±0.1 meV for emission near E_g of CdTe). Sample temperature was controlled by flowing helium vapor across the sample surface in a Janis Super Varitemp Dewar.

A typical low-temperature (4.9 K) near-band-edge PL emission spectrum from the CdTe:I epilayers is shown in Fig. 1(a). The PL spectrum was excited with an incident power density of 810 mW/cm^2 and shows emission bands at 1.5927 eV and 1.5892 eV. The brighter emission band at 1.5927 eV was identified as the superposition of (D^0,h) and (D^0,X) recombinations[6] related to the I_{Te} shallow donor, and exhibits a full width at-half maximum of 1.5 meV. The 1.5892-eV emission band is the superposition of several (A^0,X) emission lines.[6] The free-exciton emission line which is typically seen at 1.5954 eV in bulk CdTe was not resolved separately from the (D^0,h) and (D^0,X) emission band due to the high-doping level. The high-energy tail of the donor emission band, however, is seen to extend well above the free-exciton energy.

Figure 1(b) shows representative above-band-gap, phonon absorption PL from an n-type CdTe:I epilayer at 4.9 K. The PL spectrum was also excited with an incident power density of 810 mW/cm^2. The emission peak occurs at 1.619 eV, with a small shoulder at 1.615 eV on the low-energy side, and a high-energy tail extending to above 1.63 eV. The PL emission energy is clearly greater than E_g at 1.606 eV, and is approximately 4000 times smaller in signal intensity than the donor band at 1.5927 eV under equivalent excitation conditions. The above-band-gap PL could be clearly resolved at incident excitation power densities as low as 300 mW/cm^2 with our detector system under excitation with 514.5 nm laser light. We also observed the phonon absorption PL using the shorter wavelength 488-nm Ar laser output, which is even further off resonance with the band-gap energy. The emission peak of the above band-gap PL emission band is independent of the excitation wavelength.

To understand the origin of the above-band-gap emission, we note that the energy difference between 1.619 eV and (D^0,X) at 1.5927 eV, and between 1.615 eV and (A^0,X) at 1.5892 eV is ~26 meV. The PL photon energy associated with phonon absorption (E'_{PL}) is related to the

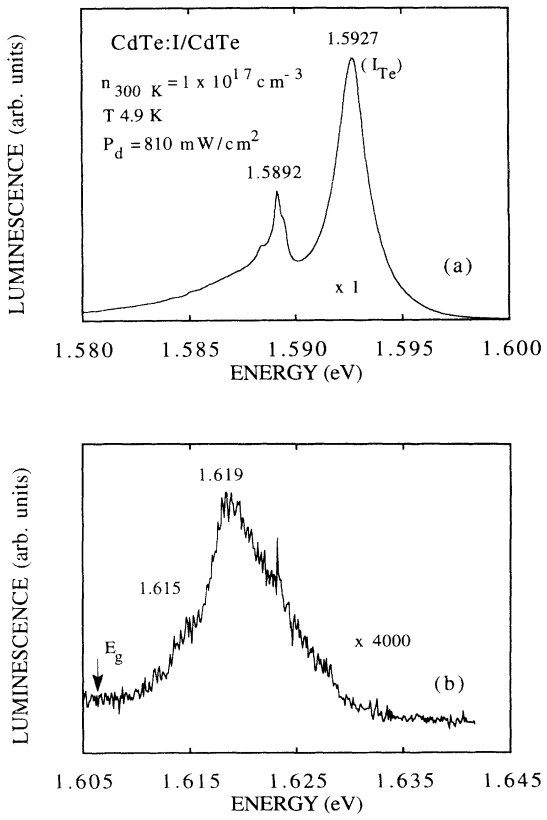

FIG. 1. Representative near-band-gap PL spectrum at 4.9 K from n-type CdTe:I epilayer ($n_{300K}=1\times10^{17}$ cm^{-3}) excited with power density of 810 mW/cm^2. Curve (a) shows the dominant edge emission at energies below E_g (1.606 eV). Curve (b) is the above-band-gap emission related to phonon absorption.

zero-phonon PL energy (E_{PL}) through the following expression:

$$E'_{PL}=E_{PL}+E_{LO}+E_K\ , \tag{3}$$

where $E_{LO}=21.3$ meV in CdTe, and E_k is the average kinetic energy of the exciton involved in the particular recombination process. From the data shown in Fig. 1, E_k is about 5 meV. We note that the range of exciton kinetic energies is limited to less than the energy difference between $1s\rightarrow 2s$ exciton states (energy difference of 7.5 meV) in the anti-Stokes PL process. Excitons with kinetic energy larger than the binding energy will disassociate and create free electrons and free holes.

It is surprising that the emission peak at 1.619 eV is the phonon-absorption PL of the I_{Te} donor-related emission at 1.5927 eV. This is significant since phonon emission bands of shallow donor-related recombination are not observed in CdTe,[8] owing to their much weaker ($\sim$700 times) Huang-Rhys factor than holes. We see, however, a clear indication of phonon-absorption PL due to coupling with donor states. The shoulder at 1.615 eV is related to (A^0,X) at 1.5892, where the exciton kinetic energy is also about 5 meV. The relative amplitudes in the phonon-absorption PL spectrum track the relative amplitudes in the zero-phonon spectrum.

To understand further the nature of above-band-gap PL emission, the power dependence of near-band-edge and above-band-gap emissions was studied. The dependence of PL emission intensity on excitation power density typically follows the relation

$$I_{PL}=CI_L^{\nu}\ , \tag{4}$$

where I_{PL} is the measured luminescence signal amplitude, C is a constant, I_L is the laser power density (or laser power is often used) on the sample surface, and ν is an exponent describing the rate at which the PL intensity for various recombination processes increases with excitation power density.[9-11] Figure 2 is the log-log plot of PL emission intensity on excitation power density from a CdTe:I epilayer. The (D^0,X) emission band at 1.5927 eV (black squares) increases at a rate described b $\nu=0.86$, and shows little deviation from a logarithmic relation even though the power density is varied by three orders of magnitude. The (A^0,X) emission line at 1.5892 eV (triangles) and above-band-gap emission band at 1.619 eV (black circles) exhibit $\nu=0.99$, and 1.01, respectively. Note that the phonon-absorption PL signal could be detected with incident power densities as low as 300 mW/cm^2. The value of $\nu\sim 1$ gives supporting evidence that the emission band at 1.619 eV is excitonic.[12] Even though these ν values observed from CdTe:I epilayers are smaller than those of bulk CdTe samples, which usually exhibit $1<\nu<2$ for near-band-edge excitonic emission bands, one can see that the phonon-absorption process actually increases at a slightly faster rate than the zero-phonon donor emission. This result agrees with our recent observations in bulk CdTe (Ref. 7) that multiphonon emission processes of X recombination (X-1LO and X-2LO) increase in signal intensity at a faster rate than the zero-phonon recombination band. Therefore, both types of phonon-assisted (emission and absorption) radiative recombination in CdTe indicate strong exciton-phonon coupling.

The above-band-gap PL was observed from CdTe:I at sample temperatures up to 30 K. The line shape and peak energy of this emission band depend on sample conductivity, as is shown in Fig. 3. Both spectra were excit-

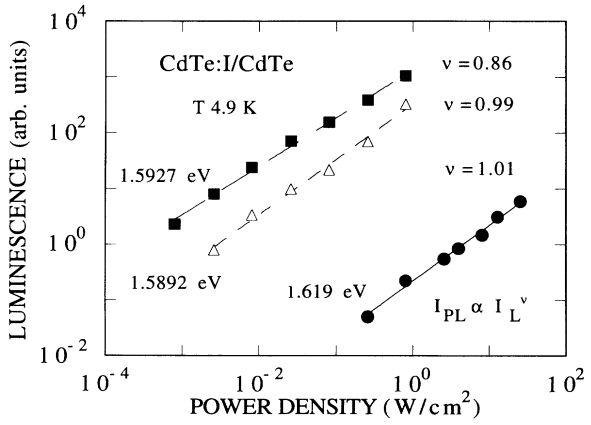

FIG. 2. Log (PL intensity) versus log (excitation power density) for n-type CdTe:I epilayer grown by molecular-beam epitaxy. Above-band-gap emission at 1.619 eV (black circles) increases at a slightly faster rate than (D^0,X) (black squares) or (A^0,X) (triangles) emission lines.

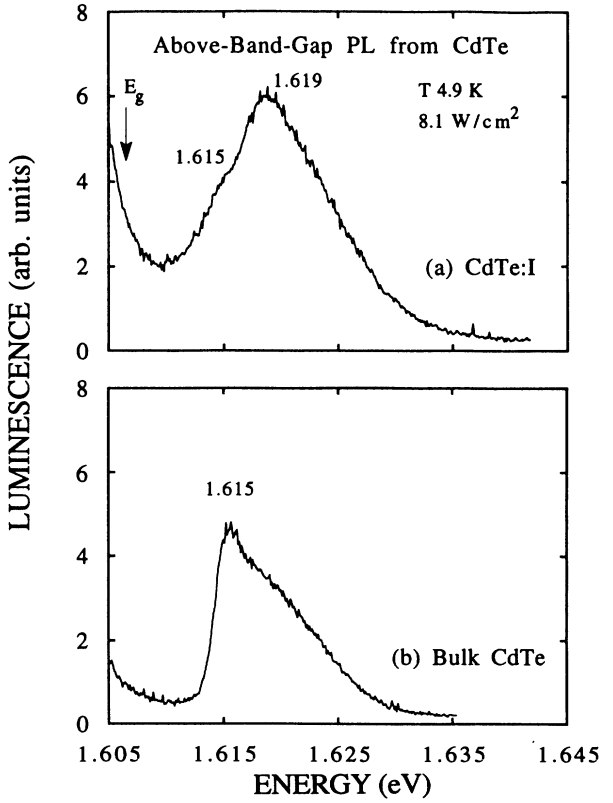

FIG. 3. Above-band-gap PL emission at 4.9 K from (a) n-type CdTe:I epilayer, and (b) nominally p-type as-grown bulk CdTe. Peak at 1.619 eV corresponds to phonon absorption related to (D^0,X) recombination. Peak at 1.615 eV corresponds to phonon absorption related to (A^0,X) recombination. Average exciton kinetic energy is 5 meV.

ed with a power density of 8.1 W/cm^2(514.5-nm line). Near-band-edge PL from the bulk CdTe is dominated by (A^0,X) emission at about 1.5892 eV. This (A^0,X) emission corresponds to the presence of sodium and/or lithium substitutional acceptor impurities, and is commonly resolved in liquid-helium PL from unintentionally doped bulk CdTe. The phonon-absorption PL could not be observed from all samples of bulk CdTe studied, and was dependent on sample surface quality.

As described above, the peak at 1.619 eV [Fig. 3(a)] corresponds to phonon-absorption exciton recombination related to the I_{Te} donors, with a contribution of 5 meV in kinetic energy. The small shoulder at 1.615 eV from the n-type epilayers becomes the dominant phonon-absorption band in the p-type bulk CdTe, due to the increased concentration of acceptor centers. The presence of the acceptor centers in the CdTe:I epilayers is believed to be due to impurity diffusion from the CdTe substrate.[6] Figure 3 shows clearly that the line shape and peak position of above-band-gap PL depend strongly on the conductivity of the sample.

The spectra shown in Fig. 3 are similar to the data reported from InP,[1,2] in that the phonon-absorption PL band is superimposed on a monotonically decreasing optical emission tail. The exciton-phonon emission from the InP in the earlier work was excited using 40 W/cm^2, which is much larger than the threshold needed to observe this exotic emission from CdTe. Our experimental study suggests that the exciton-phonon coupling which leads to increased density of anti-Stokes PL emission may be as large, or even larger, in CdTe than in InP.

In conclusion, we observe above-band-gap, phonon-absorption PL under nonresonant conditions from high-quality n-type CdTe:I epilayers and selected bulk CdTe samples. The above band-gap emission bands were observed at sample temperatures up to 30 K and with excitation power densities as low as 300 mW/cm^2. In order for phonon-absorption PL emission to be observed, a high density of phonons created through emission processes must be present. It is clear that in CdTe, which has a rather large electron-phonon coupling constant, the necessary threshold for phonon density can be achieved at rather low excitation power densities. Above-band-gap PL related to both (A^0,X) and (D^0,X) recombinations are observed clearly. Even though phonon emission bands of donor-related recombination are not observed in CdTe, there is clear evidence of phonon-absorption PL related to donor states. This momentum-conserving phonon-absorption radiative recombination process requires an average kinetic energy of 5 meV in CdTe.

The authors wish to thank the NSF/WV EPSCoR program for support of the work at West Virginia University. The film growth experiments at Georgia Tech were sponsored by the Wright Research and Development Center under Contract No. F33615-89-C-1066.

[1]F. Iikawa, C. Trallero-Giner, and M. Cardona, Solid State Commun. **79**, 131 (1991).

[2]C. Trallero-Giner, M. Cardona, and F. Iikawa, Phys. Rev. B **48**, 5187 (1933).

[3]J. I. Pankove, *Optical Processes in Semiconductor* (Dover, New York, 1971).

[4]P. J. Dean and D. C. Herbert, *Bound Excitons in Semiconductors,* edited by K. Cho, Excitons, Topics in Current Physics Vol. 14 (Springer-Verlag, Berlin, 1979).

[5]D. Rajavel and C. J. Summers, Appl. Phys. Lett. **60**, 2231 (1992).

[6]N. C. Giles, Jaesun Lee, D. Rajavel, and C. J. Summers, J. Appl. Phys. **73**, 4541 (1993).

[7]Jaesun Lee, N. C. Giles, D. Rajavel, and C. J. Summers, Phys. Rev. B **49**, 1668 (1993).

[8]P. J. Dean, G. M. Williams, and G. Blackmore, J. Phys. D **17**, 2291 (1984).

[9]Z. C. Feng, A. Mascarenhas, and W. J. Choyke, J. Lumin **35**, 329 (186).

[10]J. P. Noblanc, J. Loudette, and G. Duraffourg, J. Lumin **1&2**, 528 (1970).

[11]T. Taguchi, J. Shirafuji, and Y. Inuishi, Phys. Status Solidi B **68**, 727 (1975).

[12]T. Schmidt, K. Liscka, and W. Zulehner, Phys. Rev. B **45**, 8989 (1992).