Room-temperature band-edge photoluminescence from cadmium telluride

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Room-temperature photoluminescence (PL) spectroscopy of II-VI semiconductor alloys has been proposed as a useful tool for determination of spatial variations in alloy concentration and impurity concentration. However, the nature of the PL recombination can affect the emission peak energy, as well as line shape. These effects in the band-edge emission of the compound II-VI semiconductor CdTe are reported here. PL measurements at 300 K were recorded from (1) highly doped *n*-type CdTe films grown by molecular-beam epitaxy, (2) undoped high-resistivity ($\rho \sim 10^8-10^9$ Ω cm) bulk CdTe, and (3) as-grown nominally *p*-type ($\rho \sim 10^4-10^5$ Ω cm) bulk CdTe. The dependence of PL emission intensity and line shape over a range of excitation from 0.003–70 W/cm^2 was studied. As the excitation power density was increased, a redshift in PL peak position was observed from all samples. PL peak position, intensity, and line-shape analysis show the highly excitonic nature of the radiative recombination in these materials, even though the free-exciton binding energy in CdTe is about $\frac{1}{3}$ of kT at 300 K. In addition, the PL peak position can be more than 7 meV higher from *n*-type CdTe as compared to undoped CdTe.

I. INTRODUCTION

Photoluminescence (PL) spectroscopy has been widely used to characterize the quality of semiconductor bulk substrate materials and thin epitaxial layers grown for device structures. Although PL spectroscopy is usually performed at low temperatures in order to obtain spectral resolution of different emission lines, PL spectroscopy at room temperature has received increasing interest. Room-temperature PL mapping of band-edge emission and deeper defect-related emissions is proving to be a useful technique to characterize the homogeneity of the crystalline quality of III-V and group-IV semiconductor wafers.[1–3] Additionally, because the 300-K band-edge PL emission peak energy depends on the band gap of the semiconductor, alloy concentrations in ternary alloys such as $Al_xGa_{1-x}As$ and $Cd_{1-x}Zn_xTe$ can, in principle, be determined. The ability to probe alloy composition variations, for example, in $Cd_{1-x}Zn_xTe$ substrate wafers by a relatively simple, noncontact, optical technique is highly desirable. Efficient screening of these substrate materials for subsequent growth of the closely lattice-matched infrared detector material $Hg_{1-x}Cd_xTe$ could then be performed routinely.

An earlier examination of the usefulness of 300-K PL measurements in determining composition variations in $Cd_{1-x}Zn_xTe$ boules with low-Zn molar fraction reported that the measured PL emission peak energy depended on the sample conductivity as well as Zn concentration.[4] *n*- and *p*-type $Cd_{1-x}Zn_xTe$ samples with similar Zn molar fractions exhibited different room temperature PL emission peak energies. PL emission from *n*-type $Cd_{1-x}Zn_xTe$ samples occurred at higher energies than from *p*-type samples. The observed difference in PL emission peak energies was attributed to differences in Fermi levels, as modified by the relative populations of neutral acceptors. The 300-K PL emission in that earlier study of II-VI alloys[4] was thus attributed to band-to-band recombination, and excitonic effects were not accounted for. The free-exciton binding energy in $Cd_{1-x}Zn_xTe$ alloys, however, is essentially that of CdTe, since the exciton localization energy varies by only 3 meV over the entire range in composition from CdTe ($x=0$) to ZnTe ($x=1$). Evidence for the existence of free excitons in CdTe at room temperature has indeed been reported,[5] and excitonic contributions to the PL signal at 300 K from CdTe and $Cd_{1-x}Zn_xTe$ should be considered when evaluating room-temperature PL as a technique to determine alloy composition.

In this study, the binary compound semiconductor CdTe was selected in order to gain understanding of the general nature of room-temperature radiative recombination from this class of direct-band-gap II-VI semiconductors. By choosing the compound CdTe, variations in alloy concentration can thus be avoided in the analysis. The dependence of PL peak position on sample conductivity can be studied more closely, and the role of different radiative recombination processes can be established. Our study thus focused on the identification of the nature of the PL emission observed from CdTe at room temperature, and whether the emission peak energy could be directly related to the band-gap energy. Two important issues to be considered with our study are (1) what is the room-temperature band-gap energy in single-crystalline CdTe, and how precisely is that known; and (2) how will radiative emission (photoluminescence) energies be related to recombination (absorption) energies? These two points are reviewed first below.

There has been difficulty in precisely defining 300-K band gaps of semiconductors for many years. The band

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gap of CdTe at liquid-helium temperature has been well established as 1.606 eV; however, a wide range of 300-K E_g values has been obtained by a multitude of techniques. An early review of band-gap values reported for CdTe was made in 1978, giving values ranging from 1.49 to as high as 1.529 eV.[6] Absorption measurements generally gave the lower values due to the difficulty in defining the precise band edge, and the values depended greatly on the analysis chosen to interpret the optical data. It is interesting to note that two papers which established CdTe as a direct (rather than indirect gap) semiconductor presented careful experimental[7] and theoretical[8] analysis of optical-absorption data from liquid-helium temperatures up to room temperature. The experimental report of optical absorption at photon energies just below the transmission limit[7] emphasized the need for careful selection of high-purity samples with chemically polished surfaces, so that absorption due to impurities and defects did not mask the intrinsic absorption edge. Indeed, the data reported in this early work revealed absorption coefficient curves which followed a much steeper increase in α with photon energy at room temperature than had been reported prior to that time, thus revealing that indirect absorption processes could not explain the observed results. The companion paper which provided a theoretical treatment of the optical-absorption data[8] showed that phonon-assisted direct-exciton absorption could account quantitatively for the data recorded from these high-quality samples over the temperature range from 2 to 177 K. The contributions from $n > 1$ excited states of the exciton and one- and two-phonon processes (for $T > 80$ K) were shown to be necessary considerations to give excellent agreement with the experimental results. The analysis was further extended to suggest that strong exciton-phonon interactions in the polar II-VI semiconductors, such as CdTe, could explain the exponential tailing (Urbach's rule) of the absorption edge at even higher temperatures. Thus, as early as 1966, the dominant role of excitons in determining the optical properties of CdTe was considered.

By the late 1970s, a reliable 300-K band-gap value for CdTe was considered to be 1.529 eV, which was obtained by tracking the direct $n = 1$ exciton energy up to temperatures of about 200 K using piezoreflectance spectroscopy, and then extrapolating to room temperature and adding the free-exciton binding energy.[9] Since that time, dramatic improvements in the purity and crystalline quality of CdTe have been achieved, and further refining of the exact band-gap value has been provided by a range of other modulated reflectance techniques. Photoreflectance spectroscopy has yielded room-temperature band-gap values between 1.505 and 1.515 eV for polycrystalline CdTe films, and a value of 1.513 eV for high-quality single-crystalline bulk CdTe.[10] Electrolyte electroreflectance (EER) spectroscopy has yielded a room-temperature CdTe band-gap value of 1.511 ± 0.005 eV.[11] EER studies performed more recently on CdTe thin films and bulk samples yielded an average band-gap value of 1.512 ± 0.003 eV, with a value of 1.513 eV obtained from a noncontact polished surface of a bulk CdTe single crystal.[12] From these recent studies, much of the uncertainty in the value of the CdTe 300-K band gap has now been eliminated, and most groups agree with a band-gap value of 1.51 eV. The two separate studies performed on high-quality bulk CdTe samples[10,12] give support to the more precise value of 1.513 eV, which we chose to use in our analysis.

The second point to be addressed deals with the question of how radiative peak emission energies are related to the actual electronic recombination energies. It is important to note that few reports of 300-K PL from CdTe have been made. Until recently, commercially available bulk CdTe substrate materials were not likely to exhibit PL emission above about 200 K, explaining the absence of room-temperature PL as a technique to determine room-temperature band gaps. Dramatic improvements in the material quality and control of the point defect structure have now proved the opposite to be true; commercially available bulk CdTe substrates are now routinely of sufficiently high quality to allow detection of 300-K PL; thus the increasing interest in using room-temperature PL mapping to determine alloy composition in ternary II-VI semiconductors.

A review of luminescence emission line shapes for a variety of recombination processes has been reported[13] and is included in Sec. III B of this paper. At liquid-helium temperatures, the emission and recombination energies correspond closely in value for most common radiative emissions. However, at temperatures above 80 K, the discrepancy between the radiative emission peak energy and the recombination energy in CdTe can be several meV or greater. PL arising from direct band-band (e,h) recombination will exhibit an emission peak displaced to *higher* energy than the band-gap value E_g, thus a comparison between absorption or modulated reflectance measurements and PL measurements must be made carefully. The photon energy at which (e,h) luminescence emission amplitude is a maximum corresponds to $E_g + kT/2$ (k is Boltzmann constant) assuming vector conservation. If wave-vector conservation can be ignored, band-band recombination gives PL emission peaks at photon energies which can be as high as $2kT$ above the band-gap energy. This effect has been included in studies of narrow-gap II-VI $Hg_{1-x}Cd_xTe$ alloys,[14,15] where an energy shift of $2kT \sim 50$ meV at room temperature thus represents a sizable fraction of the actual band gap.

There is also a difference in the luminescence peak emission energy related to exciton recombination and the actual recombination (or absorption) energy; however, this energy shift is *opposite* that of (e,h) recombination. PL emission due to $n = 1$ free-exciton recombination will occur at *lower* energies than the actual recombination energy,[13] thus giving rise to what is commonly referred to as a "Stokes" shift. Indeed, comparison between excitonic absorption and emission at low temperatures generally reveals a small shift in energy. Thus one method to establish quickly whether PL emission at room temperature is (e,h) or excitonic is to note first whether the emission peak energy is higher or lower than the band-gap value.

By choosing to study the room-temperature PL observed from CdTe, the band-gap energy at 300 K

($E_g = 1.513$ eV) and the free-exciton binding energy ($\varepsilon_B = 10$ meV) are known to within about 1 meV. Our study includes both undoped and intentionally n-type doped samples; thus the dependence of PL peak position on sample conductivity can be studied more closely, and the role of different radiative recombination processes can be established. As mentioned above, strong exciton-optical-phonon coupling in CdTe is known to play a large role in determining the shape of absorption spectra; however, a detailed consideration of exciton–optical-phonon coupling in radiative emission at high temperatures (300 K) has not been reported. The results of this work can readily be applied to understanding the nature of the room-temperature PL in the important ternary alloy $Cd_{1-x}Zn_xTe$ because the difference between the nature of PL emission in CdTe and $Cd_{1-x}Zn_xTe$ alloys will be small for the low Zn concentrations which are used as substrates for Hg-based epitaxially grown II-VI infrared detector structures.

II. EXPERIMENTAL DETAILS

The CdTe samples investigated in this PL study cover a range of conductivities. The samples include n-type iodine-doped CdTe epilayers ($n_{300\ K} \sim 10^{17}$ cm^{-3}) grown by molecular-beam epitaxy (MBE), and undoped CdTe grown by the vertical Bridgman technique (manufactured by II-VI, inc.). The heavily doped n-type CdTe:I films were grown by MBE using ethyliodide as the gas source for the dopant precursor on bulk 2° off (001) CdTe substrates at substrate temperatures from 170 to 250 °C.[16–18] These heavily doped films exhibited room-temperature electron concentrations between 9.3×10^{16} and 1.3×10^{17} cm^{-3}. The low-temperature PL emission from these doped epilayers has been reported previously.[19] The chemipolished surfaces of the bulk samples produce bright PL signals from the bulk samples at low temperature.

The samples were excited at 300 K with the 514.5-nm single-line output from a Laser Ionics model 552A argon-ion laser. PL data were taken with incident power densities from 0.003 to 70 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. Low-temperature (5-K) PL measurements were also recorded from the three types of samples chosen for this study to allow evaluation of the different point defects involved in radiative recombination, and to identify the dominant impurity centers in the undoped bulk CdTe substrate material.

III. RESULTS AND DISCUSSION

PL spectra from CdTe at room temperature is composed of a single broad peak at an energy close to the band-gap energy. In order to obtain information about different point defects (vacancies, interstitials, and impurities), low-temperature PL experiments must be performed. In this study, the three types of samples have different point defect structures (and different conductivities), which could influence the nature of the 300-K PL. Thus liquid-helium PL was first performed on the samples to obtain baseline information of the types of defect centers in each of the samples which would give rise to radiative recombination, and which could thus influence the 300-K PL emission.

A. Photoluminescence data

Figure 1 shows representative near-band-edge PL emission spectra at 5 K from (a) n-type doped CdTe:I grown by MBE, (b) undoped high-resistivity ($\rho \sim 10^9$ Ω cm) bulk CdTe subject to a post-growth Cd anneal, and (c) as-grown nominally p-type bulk CdTe substrate material. In Fig. 1(a), the dominant PL edge emission occurs at 1.593 eV. This emission band is related to the 14-meV donor, I_{Te}. The sharp PL emission peak at 1.5892 eV is identified as an acceptor-bound exciton recombination (A^0,X) related to the substitutional acceptors Na_{Cd} and/or Li_{Cd}. In that same emission region are (A^0,X) lines due to Cu_{Cd} and Ag_{Cd} impurity centers.[19]

In sharp contrast to the spectrum recorded from the n-type material, the liquid-helium PL spectra from the

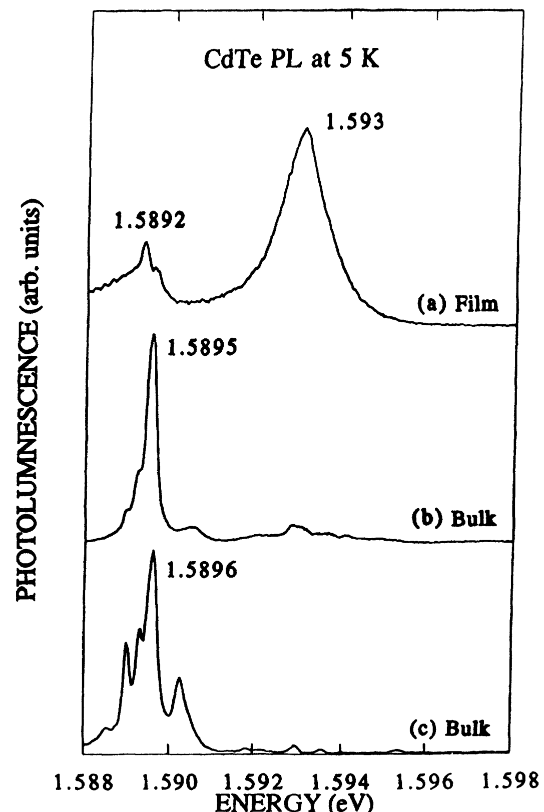

FIG. 1. Representative near-band-edge PL emission spectra at liquid-helium temperature (5 K) from (a) n-type CdTe:I film grown by MBE; (b) undoped high-resistivity bulk CdTe; and (c) as-grown nominally p-type bulk CdTe. PL amplitudes have been normalized.

bulk CdTe are dominated by (A^0,X) recombination. As shown in Fig. 1(b), the PL spectrum from the high-resistivity bulk CdTe is dominated by an (A^0,X) emission line at 1.5895 eV. The full width at half maximum (FWHM) of the PL line is only 0.32 meV. The measured emission energy of 1.5895 eV agrees with the earlier identification of (A^0,X) recombination related to the Cu_{Cd} acceptor in bulk CdTe.[20] In Fig. 1(c), the PL spectrum from the as-grown bulk CdTe shows several (A^0,X) recombination lines. The emissions occurring at 1.5896, 1.5893, 1.5889, and 1.5885 eV, agree with the emission energies related to the substitutional acceptors Cu_{Cd}, Na_{Cd}, and/or Li_{Cd}, P_{Te}, and Ag_{Cd}, respectively.[20] The low amplitude feature at higher energies in both Figs. 1(b) and 1(c) are due to shallow donors (1.592–1.594 eV) and free-exciton recombination.

The free-exciton (X) recombination line which is typically seen at 1.596 eV in CdTe was not resolved in the low-temperature PL spectra recorded from the n-type CdTe:I films. The donor-related emission at 1.593 eV exhibits a high-energy tail which extends above the X recombination energy under high excitation power densities. The bulk CdTe samples, however, typically show a low amplitude free-exciton emission band as well as several orders of phonon replicas of free-exciton recombination (X-1LO, X-2LO, X-3LO). The one-phonon recombination line (X-1LO) in bulk CdTe is usually of a larger signal amplitude than the zero-phonon line due to the strong self-absorption which reduces the intensity of the 1.596-eV band. It was noted, however, that phonon replica emission bands of the free-exciton recombination were not observed in the spectra recorded from the n-type films, even though phonon replicas of (A^0,X) emission lines were observed from both the n-type and nominally p-type samples. It appears then that at low temperature the coupling between free excitons and optical phonons giving rise to PL emission bands is weak in the n-type MBE-grown films.

The room-temperature PL signal from CdTe is significantly broader than the edge emission lines observed at liquid-helium temperature. Representative spectra from the n-type thin films and bulk material are shown in Fig. 2. The difference in emission energies of about 0.1 eV between Figs. 1 and 2 is due to the band-gap narrowing which occurs in CdTe as the temperature is raised to 300 K. The PL signal from the MBE-grown epilayers is still quite strong at 300 K. The spectrum shown in Fig. 2(a) from the n-type CdTe:I film was excited using an incident power density of only 8 mW/cm^2. The PL signal shown in Fig. 2(b) from the high-resistivity bulk CdTe sample was excited using 70 W/cm^2. The undoped nominally p-type CdTe [of Fig. 1(c)] exhibited room-temperature PL emission essentially identical to that of the high-resistivity bulk material, and so is not shown separately here. It is important to note that PL emission from the bulk samples included in our study could not be detected with our apparatus for power densities below about 3 W/cm^2. Although the PL emission intensity from the thin film represented by the curve shown in Fig. 2(a) is about 400 times smaller than that observed from the bulk sample [Fig. 2(b)], a *much* weaker

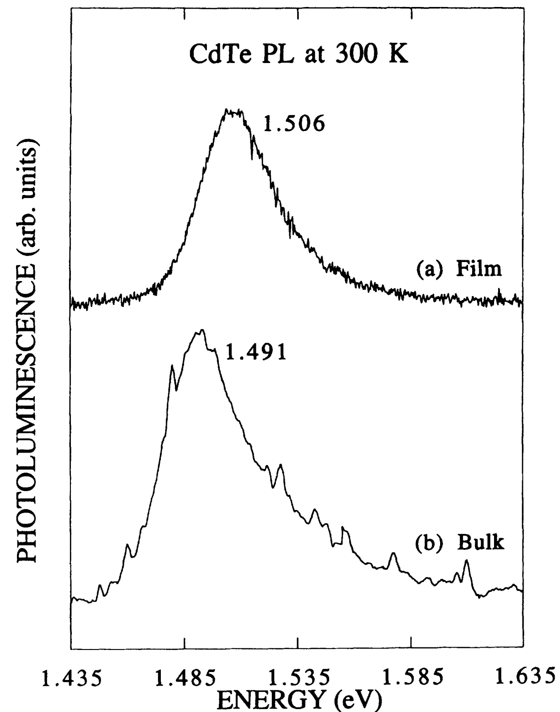

FIG. 2. Representative 300-K PL from (a) n-type CdTe:I film under excitation of 8 mW/cm^2 and (b) high-resistivity bulk CdTe under excitation of 70 W/cm^2. PL amplitudes have been normalized.

(8750 times) excitation probe beam was used. This attests to the high quality of the MBE-grown epilayers.

The general line shapes of the 300-K PL emission shown in the two curves of Fig. 2 are similar; however, the peak of the emission band from the MBE-grown epilayers occurs at a higher energy than for the bulk samples. Recall that a similar dependence of peak energy on sample conductivity was observed for bulk $Cd_{1-x}Zn_xTe$ with low Zn concentration.[4] The PL emission peak energy for the CdTe:I film occurs at 1.506 eV [Fig. 2(a)] and for the high-resistivity bulk CdTe occurs at 1.491 eV [Fig. 2(b)]. Note that these PL emission peak energies are both *less than* the 1.513-eV band-gap value obtained from photoreflectance and electroreflectance measurements from bulk CdTe,[10,12] and are thus not solely due to band-band (e,h) recombination which would be shifted to a peak emission energy greater than E_g. However, the PL emission bands from both samples exhibit high-energy tails which do extend well above the band-gap energy. As discussed below, this high-energy contribution to the PL line shape is believed to be due to conduction-band electron–valence-band hole recombination (e,h), and thus should show the appropriate temperature dependence. The PL emission peak energies decreased with increasing excitation for all three types of samples.

The 300-K PL emission bands from the n-type CdTe:I films were relatively narrow. The emission band shown in Fig. 2(a) exhibits a FWHM of only 39 meV. An earlier report of luminescence characteristics of these n-type epilayers included a room-temperature spectrum excited

with 300 mW/cm^2 exhibiting a FWHM of 43 meV.[19] The FWHM for the emission band from the bulk CdTe in Fig. 2(b) exhibits a FWHM of 46 meV under the increased excitation of 70 W/cm^2. The measured FWHM for band-edge PL from the three types of CdTe samples included in this study was indeed seen to increase with excitation power density.

To understand the nature of the room-temperature PL emission from CdTe and, thus, to determine the reason for the varying peak position due to excitation power density and sample conductivity, a systematic study of the PL emission amplitude, emission peak energy, and line shape was made over the excitation power range from 3 mW/cm^2 to 70 W/cm^2. Figure 3 shows the dependence of PL peak emission amplitude on the excitation power density at 300 K from the three types of CdTe samples. As mentioned above, the CdTe:I films exhibited a much brighter PL signal than the bulk CdTe substrates. Therefore, the spectrometer slit settings were reduced during the data acquisition from the CdTe:I films (curve *a*). Although Fig. 3 shows that the PL emission from the *n*-type films is brighter than the bulk samples, the relative brightness is actually much larger when the spectrometer slit settings are accounted for. The PL emission from the bulk CdTe samples could not be detected with an excitation power density below about 3 W/cm^2 (curves *b* and *c*). To make a direct comparison between the relative PL intensities from the CdTe:I epilayers and bulk material, PL experiments were performed with identical spectrometer slit settings at selected values of power density. For example, using 5 W/cm^2 from the argon laser, the PL peak intensity from the CdTe:I will be $\sim$1000 times brighter than from the bulk CdTe substrates.

Note that the relative rate of increase in PL emission amplitude for the *n*-type CdTe:I epilayer differs from the

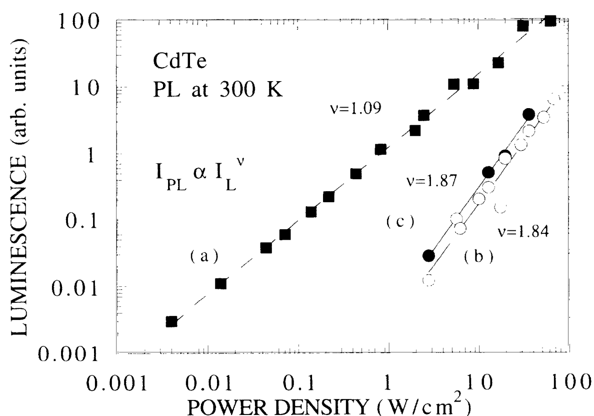

FIG. 3. Log (PL intensity) versus log (excitation power density) for (curve *a*) *n*-type CdTe:I film grown by MBE; (curve *b*) high-resistivity bulk CdTe; and (curve *c*) nominally *p*-type bulk CdTe. Curve *a* was recorded using reduced spectrometer slit settings. Under equivalent excitation, PL amplitude from *n*-type films was measured to be $\sim$1000 times brighter than the PL signal from bulk samples. Using $I_{PL} \sim I_L^{\nu}$, *n*-type CdTe:I films show $\nu \sim 1$ dependence, while bulk CdTe shows $\nu \sim 1.8-1.9$ dependence.

rate of increase for the bulk samples. Thus the *ratio* of PL peak intensity from *n*-type CdTe:I to bulk CdTe decreased as the excitation power density increased. The dependence of near-band-edge PL emission intensity on exciton power density is typically observed to follow the relation

$$I_{PL} = C I_L^{\nu} , \quad (1)$$

where I_{PL} is the measured luminescence signal amplitude, C is a proportionality constant, I_L is the laser power density on the sample surface (laser power often used instead of power density), and ν is an exponent describing the rate at which the PL intensity increases with excitation power.[21-23] The exponent ν depends on the nature of the radiative recombination. Thus different recombination channels will be described by different values of ν. Recently, a model has been presented which gives excellent agreement with experimental observations and relates the value of ν with free-exciton, bound-exciton, and free-to-bound transitions at low temperatures.[24]

For the PL data shown in Fig. 3, the following values were obtained from Eq. (1): $\nu=1.09$, 1.84, and 1.87 for curves *a*, *b*, and *c*, respectively. Recall that at low temperature, the two types of bulk CdTe samples included in this study exhibit quite different luminescence emission [Figs. 1(b) and 1(c)]. The radiative recombination at 300 K is, however, essentially the same for these two bulk materials. The unintentionally doped bulk CdTe exhibits a rate of increase in PL emission intensity which follows $\nu=1.8-1.9$, and is significantly different from that for the highly conducting *n*-type doped epilayers ($\nu \sim 1$). That the recombination processes are different in the bulk material as compared to the thin films is not surprising, and agrees with the observation that the peak positions are measurably different (see comparison in Fig. 2).

For the 300-K PL peak energy from a direct-band-gap semiconductor to be less than the band-gap energy, either excitonic or impurity-related processes should still be dominant in the radiative recombination. Impurity-related recombination, such as (D,h) or (e,A) transitions, will be characterized by $\nu<1$, in disagreement with our experimental observations. Bound-exciton recombination about neutral centers is not believed to be a significant contribution either since exciton binding energies to most identified defects and impurities in CdTe are on the order of 2–7 meV. According to the model presented in Ref. 24, the intensity of free-exciton recombination can follow a dependence on excitation with the value of ν between 1 and 2 depending on the recombination processes in the sample. A value of $\nu=1$ applies when exciton recombination dominates in a direct-band-gap semiconductor. A value of $\nu=2$ applies when only a small portion of the free-electron-hole pairs form excitons, while most photoexcited carriers recombine via defect states of donors and acceptors. Further, if neither donor-acceptor nor exciton recombination dominates, the linear and quadratic contributions to ν are of equal magnitude and curved log(PL) vs log(power density) plots will result. Note in Fig. 3 that the excitation power is varied by over four orders of magnitude for the spectra recorded from the *n*-

type film. No deviation in the linearity of the log-log plot is seen. Although the data recorded from the bulk CdTe represents a variation in excitation by only slightly less than two orders of magnitude, again no deviation in linearity is observed. The study of PL emission amplitude on excitation power density reveals that the rate of increase observed from the n-type CdTe:I ($\nu \sim 1$) is consistent with the case where exciton recombination dominates. On the other hand, the PL emission from the bulk CdTe samples ($\nu \sim 1.8-1.9$) follows the dependence of free-exciton emission exhibited when most photoexcited electrons recombine via defect states (nonradiative). The much brighter PL signal from the n-type films is also consistent with this interpretation.

As the excitation power density is increased, the 300-K PL emission peak energy from the bulk samples and n-type films exhibits a redshift (Fig. 4). The filled squares represent data from the n-type CdTe:I (curve a) and the empty and filled circles represent the high resistivity and nominally p-type bulk CdTe, respectively (curve b). As the excitation power density is increased, the PL peak positions shift to lower energy, and the FWHM values of all three types of samples increases. Localized heating at the sample surface due to the increased energy in the probe beam was initially considered the cause of the redshift. However, similar excitation studies were performed at liquid-helium temperatures where the energy positions of sharp bound-exciton recombination lines could be monitored to reveal changes in sample temperature. No change in bound-exciton emission energies was observed for excitation power densities as high as 50 W/cm^2, thus the shift to lower emission peak energy is believed to be related to the nature of the recombination processes contributing to the detected emission band.

The PL peak position from the n-type CdTe:I decreased with excitation power from 1.506 to 1.498 eV (Fig. 4). The two types of bulk CdTe substrates exhibit the same general trend to lower emission peak energies,

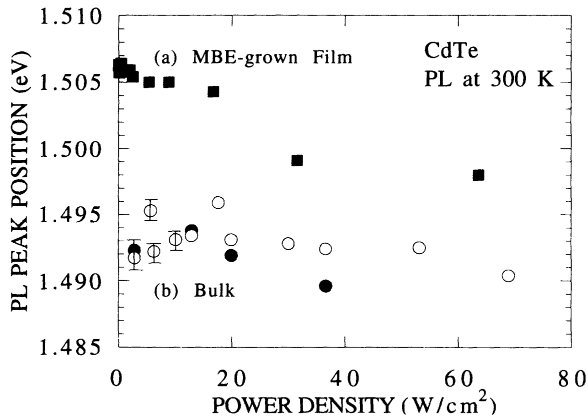

FIG. 4. Excitation power dependence of 300-K PL emission peak energy from CdTe. PL peak energy depends on the sample conductivity type. Filled squares represent n-type CdTe:I; empty circles represent high-resistivity bulk CdTe; and filled circles represent the nominally p-type as-grown bulk CdTe. Uncertainty in the emission peak energy from high-ρ bulk CdTe due to weak signal intensity is given by error bars in curve b.

although the decrease is not as great as that observed in the thin films. Note that over the entire excitation range studied, the PL peak position of the n-type CdTe:I is from 7 to 14 meV higher in energy than that of the bulk CdTe, yet is still *less than* the band-gap energy of CdTe at room temperature. The PL peak positions of the high-resistivity bulk CdTe agree closely with those of the p-type bulk CdTe. Note that if the room-temperature PL from the CdTe samples was dominated by (e,h) recombination, an increasing excitation power density should produce a blueshift in emission peak energy, which is opposite to what is observed.

B. PL line-shape analysis

To understand the differences in the nature of the PL emission from the thin films and bulk samples, and thus to identify the causes of the different ν values (Fig. 3) and different emission peak energies (Fig. 4), an analysis of PL line shape was performed. Recall from power dependence studies that the characteristic signature of impurity recombination is absent. Band-to-band (e,h) recombination will account for the observed high-energy tail in the PL spectra. Excitonic contributions (ground state and first excited state) will provide emission peak energies at below-band-gap energies. The individual contributions to these luminescence recombination bands are given by the expressions below,[11] in order of decreasing emission energy: Band to band (e,h),

$$I_{\rm PL} = A\sqrt{h\nu - E_g}\, e^{-(h\nu - E_g)/kT} ; \tag{2a}$$

$X, n=2$ excited state,

$$I_{\rm PL} = B e^{-(h\nu - E_{x2})^2/2\sigma^2} ; \tag{2b}$$

$X, n=1$ ground state,

$$I_{\rm PL} = C e^{-(h\nu - E_{x1})/kT} e^{-(h\nu - E_{x1})^2/2\sigma^2} . \tag{2c}$$

where $h\nu$ is the emitted photon energy, E_g is the band gap of CdTe, E_{x1} and E_{x2} are the ground state $(n=1)$ and first excited state $(n=2)$ free-exciton recombination energies, σ is the temperature-dependent standard deviation for the Gaussian excitonic line shapes, k is the Boltzmann constant, T is absolute temperature in degrees Kelvin, and A, B, and C are constants. Using a value of $E_g = 1.513$ eV and the free-exciton binding energy of 10 meV in CdTe, the exciton recombination energies are $E_{x1} = 1.503$ eV and $E_{x2} = 1.5105$ eV. The emission peak energy for the $n=1$ ground-state X_1 emission band, however, is displaced to lower energy relative to the actual recombination energy.[11] At $T = 300$ K, this lowering in emission peak energy is predicted by Eq. (2c) to be about $\frac{1}{2}\sigma$. As stated earlier, band-to-band (e,h) recombination [Eq. (2a)] produces an emission band which peaks in energy at a value of about $\frac{1}{2}kT$ *higher* than E_g.

We also considered PL contributions due to the strong exciton-phonon coupling in II-VI semiconductors. Recall that at low temperatures, many orders of phonon replicas of the free-exciton emission can typically be observed in PL spectra from bulk CdTe. The line-shape

contributions due to X-1LO and X-2LO recombination processes are described below:[11]

X-1LO,

$$I_{\rm PL}=D(h\nu-E_{x1\rm LO})^{1.5}e^{-(h\nu-E_{x1\rm LO})/kT}\ ; \quad (3a)$$

X-2LO,

$$I_{\rm PL}=E\sqrt{h\nu-E_{x2\rm LO}}\,e^{-(h\nu-E_{x2\rm LO})/kT}\ . \quad (3b)$$

$E_{x1\rm LO}$ is the radiative emission energy associated with recombination of the free exciton involving one longitudinal-optical (LO) phonon for momentum conservation. Similarly, $E_{x2\rm LO}$ is the energy associated with free exciton recombination involving two LO phonons. The LO-phonon energy in CdTe is 21.3 meV. D and E in the expression above are constants obtained through curve fitting.

Using the expressions given in Eqs. (2) and (3) above, the general line shapes of the PL data recorded from n-type CdTe:I and bulk CdTe samples under both low and high excitation power densities were reproduced. Representative results are shown in Fig. 5. The best fit was obtained using a value of $\sigma=13$ meV for both n-type epilayers and bulk samples over the entire range of power densities. The experimental data are represented by the solid curves, and the curve fits obtained from our line-shape analysis are represented by the dashed lines.

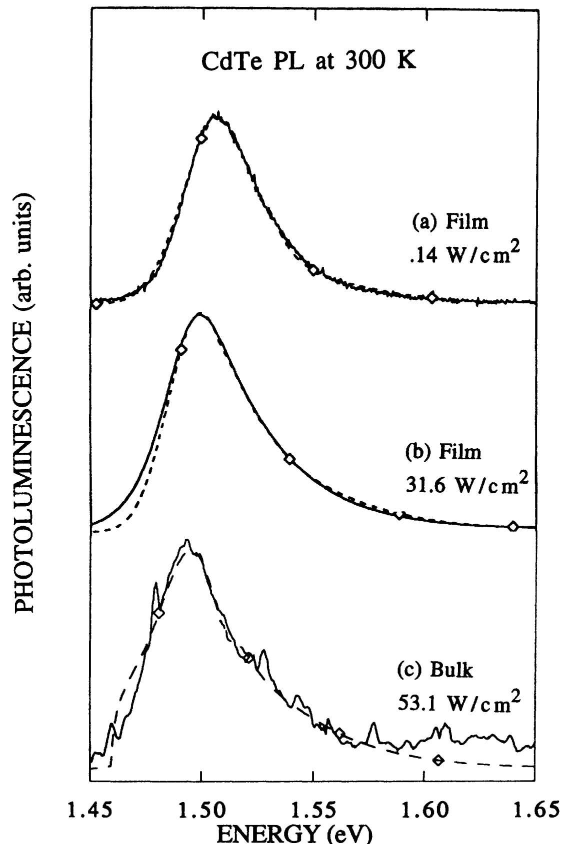

FIG. 5. Room-temperature PL and line-shape analysis for (a) CdTe:I film under low-power excitation of 0.140 W/cm^2; (b) CdTe:I film under high power excitation of 31.6 mW/cm^2; and (c) high-resistivity bulk CdTe under high-power excitation of 53.1 W/cm^2. Solid lines represent PL data, and dashed lines curve fitting. A strong excitonic contribution is used to obtain curve fits. Emission peak energies all lie below the CdTe band gap.

In Fig. 5(a), the PL data from the CdTe:I is recorded under a relatively low excitation power density of 140 mW/cm^2, while the data shown in Fig. 5(b) was recorded using 31.6 W/cm^2. We reproduced the PL emission from the n-type films using contributions from (e,h), X_1, and X_2 recombinations only. Recall that at low temperatures, evidence of exciton-phonon emission was absent in the PL data from CdTe:I. Our 300-K PL line-shape analysis which did not include multiphonon processes is thus consistent with this observation. The redshift in emission peak energy for higher excitation powers was obtained by a slight variation in the relative strengths of the contribution from the ground state X_1 and excited state X_2. Under low excitation power density, the X_2 emission dominates over X_1 recombination, thus yielding a higher emission peak energy. Recall that the excited $n>1$ exciton states had to include in the early theoretical analysis[8] of absorption spectra. Under high excitation power densities, the X_1 contribution at slightly lower energy becomes dominant. The relative contributions to the overall PL emission shown in Fig. 5(a) are 1:3.3:1.7 for the (e,h):X_2:X_1 processes, respectively. In Fig. 5(b), the relative contributions the PL emission are 1:0.9:2.3 for the (e,h):X_2:X_2 processes. The (e,h) contribution was found to be less than the X_1 contribution over the entire power density range investigated, which is consistent with an emission peak energy of less than E_g. From Eq. (1), values of $\nu=1.17$, 1.01, and 1.24 were obtained for (e,h), X_2, and X_1 recombinations, respectively.

Band-filling effects (due to iodine doping) on the (e,h) recombination were ignored in our analysis since 10^{17} cm^{-3} is still below the level for degenerately doped CdTe. For doping levels where band filling should be considered the (e,h) emission peak shifts to about kT (or even as high as $2kT$) above E_g, instead of the $\frac{1}{2}kT$ shift which results from the expression in Eq. 2(a) due to nonconservation of wave vector. Although we obtained excellent agreement with the experimental data using the expression from wave-vector conservation, if we allow for nonconserving transients, then the relative contribution of (e,h) to the overall PL signal is reduced even further in our analysis.

To reproduce the PL emission from the bulk CdTe samples, a contribution with peak emission energy *less than* X_1 must be considered. The dominant contribution to the overall PL emission, however, is excitonic in origin in order to explain the rate of increase in signal intensity with excitation power density ($\nu=1.8-1.9$). The rate of increase observed in the experimental data does not agree with an identification of impurity level-to-band recombination. An alternative explanation includes phonon-related processes. As the incident excitation power density is increased, the population of excitons with nonzero kinetic energy will increase. Recombination of excitons with $\mathbf{k}$ close to zero requires one- and two-phonon (and

higher-order) processes for momentum conservation. The curve fit shown in Fig. 5(c) for bulk CdTe under 53.1 W/cm^2 excitation is composed of contributions from (e,h), X_1, and X_1-2LO processes. Using the expressions given in Eqs. (2) and (3), the X_1-1LO contribution is superimposed with the X_1 emission band, and so was left out of the analysis. The relative contributions to the PL emission shown in Fig. 5(c) are 1:2.8:1.3 for the (e,h):X_1:X_1-2LO processes, respectively. The best curve fit is obtained when (e,h) contributions are again less than excitonic contributions.

Although the curve-fitting results for the bulk CdTe are not as satisfactory as the fitting for the CdTe:I epilayers, the redshift in peak position can be reproduced by allowing the contribution from phonon processes to increase more rapidly with excitation power. That is, the X_1-2LO emission has a higher ν value than X_1. This behavior is consistent with what we have observed recently from bulk CdTe at liquid-helium temperatures. Multiphonon PL processes of exciton recombination (X-1LO and X-2LO) increase in signal intensity at a faster rate than the zero-phonon exciton emission bands. Our results suggest that for processes related to free-exciton recombination, which occurs at energies are still strongly self-absorbed in the sample, the phonon bands at room temperature also increase more rapidly with laser power.

Although we obtained convincing evidence that the room-temperature PL observed from high-quality CdTe samples was indeed highly excitonic, it is worthwhile to consider the 300-K PL in terms of (e,h) recombination alone, if only to determine the error introduced when neglecting excitonic contributions. Therefore, we analyzed PL emission from the CdTe:I films which, you will recall, exhibit higher emission peak energies over the entire range of excitation power densities employed and thus give the best agreement with the model of (e,h) recombination. At low excitation powers, a band-gap value of 1.494 eV was needed in order to reproduce a PL emission peak energy of about 1.507 eV. This E_g value is 19 meV lower than the most reliable E_g value at present. In addition, using this low value of E_g gave an unsatisfactory fit to the high-energy tail, which you notice is reproduced quite well in Fig. 5. Further, (e,h) recombination could not explain the observed emission peak energy shift to lower energies with increasing excitation. Therefore, the experimental data give no support to the interpretation of room-temperature PL as being due solely to band-band recombination processes. Quite the opposite conclusion is obtained, for we find that the dominant contribution to the PL emission is due to the radiative recombination associated with the $n=1$ exciton in both n-type and bulk materials. No evidence for impurity-related recombination was observed. The difference in emission peak energies is caused by the strong exciton–optical-phonon coupling which shifts the emission peak to lower energies in bulk CdTe.

IV. CONCLUSIONS

PL studies at room temperature from the direct-gap semiconductor CdTe show that the emission peak energy can vary significantly depending on sample conductivity. Our study agrees with the observations made earlier,[4] however; we include exciton and exciton-phonon processes in our analysis. The nature of the PL emission from both CdTe:I epilayers and bulk undoped CdTe, however, is found to be highly excitonic at 300 K, with the main contribution arising from direct-exciton recombination. In addition, the emission energy depends strongly on incident excitation power, such that a redshift of several meV occurs with increasing excitation. Both the power dependence data and line-shape analysis show the highly excitonic nature of radiative recombination in these materials.

In our doped n-type CdTe:I films, the emission occurs at higher energy and is several orders of magnitude brighter than from chemipolished surfaces of CdTe. The radiative recombination is primarily excitonic (ground and excited states) in the epilayers, and the power dependence follows the characteristic rate of increase for direct-band-gap semiconductors when exciton recombination is dominate ($\nu \sim 1$). The PL emission from the bulk CdTe samples occurred at lower emission peak energy, and the power dependence follows the rate of signal intensity increase characteristic of direct-band-gap semiconductors when only a small portion of the free-electron-hole pairs form excitons, and most photoexcited carriers recombine via defect states of donors and acceptors. However, no evidence of these defect states was observed from the near-band-edge PL at room temperature, and we conclude that recombination involving these defect states is thus primarily nonradiative.

The need to include exciton-phonon coupling in the line-shape analysis of room-temperature PL reported here is consistent with the strong exciton-phonon coupling we observe at low temperature in PL spectra from bulk CdTe. This strong coupling, which is characteristic of II-VI semiconductors, is also responsible for the lack of direct observation of excitons in room-temperature absorption spectroscopy from bulk CdTe, in addition to the smearing out between the exciton density of states and the band-edge continuum. In order to observe distinct room-temperature absorption peaks due to excitons in II-VI semiconductors, quantum-well structures are required, as has been demonstrated for the $Cd_{1-x}Zn_xTe$/CdTe system,[25,26] where the increased localization provided by the confinement in real space further increases the Coulomb interaction between electron and hole and the steplike density of states allows resolution of exciton absorption about the different quantized subbands. With the ability to identify discrete exciton energies at room temperature from high-quality quantum-well structures, it should be possible to determine from these microstructures if PL emission at room temperature is excitonic. Recall that exciton emission peak energies occur at lower energies than the corresponding absorption (recombination) energies. In fact, experimental verification of this "Stokes" shift has already been observed at low temperature in the $Cd_{1-x}Zn_xTe$/CdTe system.[27]

Because the 300-K PL emission peak energy from different CdTe sample can vary by over 7 meV, the use-

fulness of using only the emission peak energy to determine band gaps in ternary alloys seems doubtful. For example, a 1.0-meV shift in band-gap energy at 300 K represents the difference between 4.00% and 4.16% zinc in $Cd_{1-x}Zn_xTe$.[28] If, however, the dependence of PL emission intensity and peak position on incident excitation power density is also established, then a more accurate interpretation of the nature of the 300-K recombination can be made. The PL emission from CdTe occurs consistently at energies below the band gap at room temperature. In $Cd_{1-x}Zn_xTe$, where the free-exciton binding energy is comparable to CdTe, the nature of radiative recombination processes is expected to be similar. Thus room-temperature PL mapping spectra of the ternary alloy must be carefully interpreted in order to extract accurate band-gap values. A relative determination of changes in alloy composition, however, would be more easily obtained from 300-K PL studies.

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