

Optical Properties of Undoped and Iodine-Doped CdTe

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A comprehensive study of the properties of undoped and iodine-doped CdTe structures by photoluminescence (PL) and photoreflectance (PR) is reported. Undoped bulk CdTe and iodine-doped CdTe layers grown by metalorganic molecular beam epitaxy on (100)-oriented CdTe and (211)B-oriented GaAs substrates with electron concentrations ranging from 10^{14} to mid- 10^{18} cm^{-3} were included in this study. Lineshape modeling of 80K PL and PR spectra indicated the presence of both free exciton and donor-hole transitions at the higher doping levels. Strong PL and PR signals were also observed at room temperature. If only a single transition is considered for the analysis of the 300K spectra, the PL emission peak and the PR transition energy both exhibit a strong dependence on electron concentration for doped layers. However, lineshape modeling of the room-temperature spectra indicated the presence of multiple transitions consisting of free exciton and direct band-to-band transitions. The use of two transitions resulted in a constant value of bandgap over the entire range of conductivities studied. A strong correlation remained between the broadening of the PR and PL spectra and excess carrier concentration $N_D - N_A$. In addition, the E_1 transition energy measured by PR was found to vary dramatically with growth conditions.

Key words: CdTe, metalorganic molecular beam epitaxy (MOMBE), photoluminescence, photoreflectance

INTRODUCTION

Efficient n-type doping of CdTe has been accomplished using iodine as an anion dopant.^{1,2} Bright photoluminescence (PL) at low temperatures was obtained from a series of CdTe:I samples exhibiting room-temperature electron concentrations of $\sim 1 \times 10^{17}$ cm^{-3} .³ In the prior PL study, the shallow donor nature of substitutional I_{Te} was verified. Photoreflectance (PR) measurements were also previously reported for the same set of samples.⁴ The PL and PR spectroscopy studies have been extended in the present paper to include a series of samples displaying a wider range of conductivities.

CdTe:I epilayers were grown by MOMBE on (100)-

oriented CdTe and (211)B-oriented GaAs substrates at Georgia Tech. Electron concentrations ranged from 10^{14} to mid 10^{18} cm^{-3} at room temperature. Ethyliodide was used as the gas source for the dopant precursor. The films were grown at substrate temperatures ranging from 170 to 250°C using CdTe as the source material. Excess Cd was provided from a separate Cd source for various layers. A summary of layer parameters is given in Table I. A two micron CdTe buffer layer was grown on the GaAs substrates prior to deposition of the two lightly doped epilayers (A9307 and A9309). The thicknesses of the doped regions only are included in Table I. Hall effect, x-ray diffraction, PL, and PR measurements indicated that the epilayers were of high quality. Undoped bulk samples were included in our study for comparison. Photoluminescence measurements were recorded from the

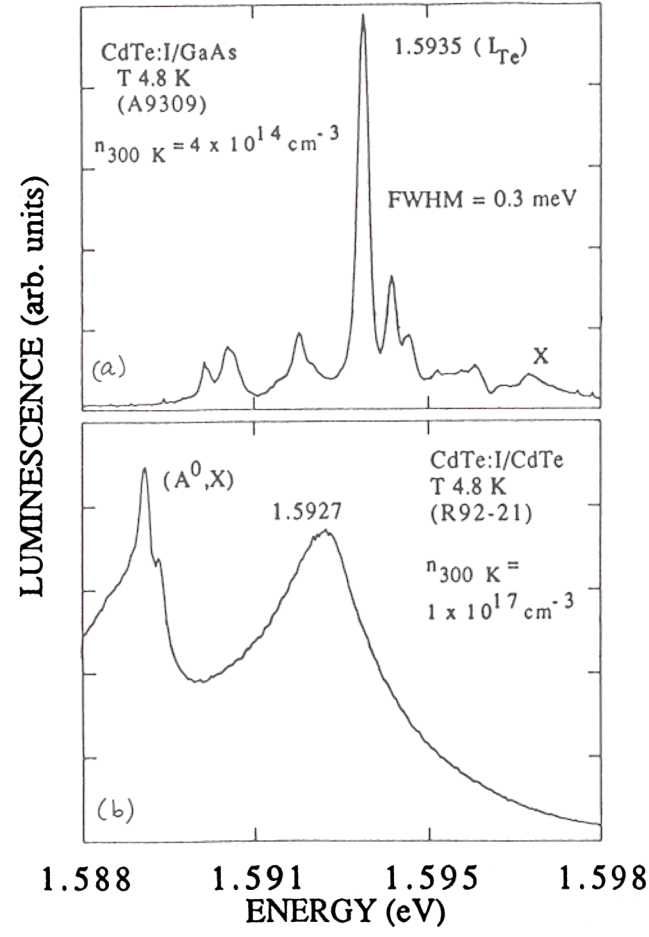


Fig. 1. Representative 4.8K PL spectra recorded under 500 mW/cm² excitation (argon ion laser, 514.5 nm) from (a) low-doped epilayer grown on a GaAs substrate showing (D⁰, X) at 1.5935 eV, and (b) heavily doped CdTe:I grown on bulk CdTe substrate.

samples at 4.8, 80K, and room temperature (~300K). Photoreflectance data was taken at 80, 296, and 363K. The PL³ and PR⁴ experimental setups have been described elsewhere.

Representative liquid-helium temperature PL spectra recorded from the iodine-doped epilayers are shown in Fig. 1 for emission immediately below the bandgap energy. The luminescence was excited using an incident power density of 500 mW/cm². Figure 1a is the emission recorded from the lowest doped epilayer which had a room-temperature excess electron concentration, $N_D - N_A$, of 4.4×10^{14} cm⁻³. Sharp bound-exciton lines were observed with the dominant emission corresponding to donor-bound exciton recombination (D⁰, X) at 1.5935 eV, consistent with the shallow donor nature of I_{Te}.³ The free-exciton recombination, which normally is seen at 1.5954 eV in bulk or homoepitaxially grown CdTe, was observed at 1.5966 eV in Fig. 1a. This increase in free-exciton emission energy of 1.2 meV is believed to be related to residual strain due to the thermal expansion mismatch between the CdTe epilayer and the GaAs substrate upon cooling to 4.8K.

An estimate of the I_{Te} donor ionization energy E_D can be made from the (D⁰, X) emission energy in the

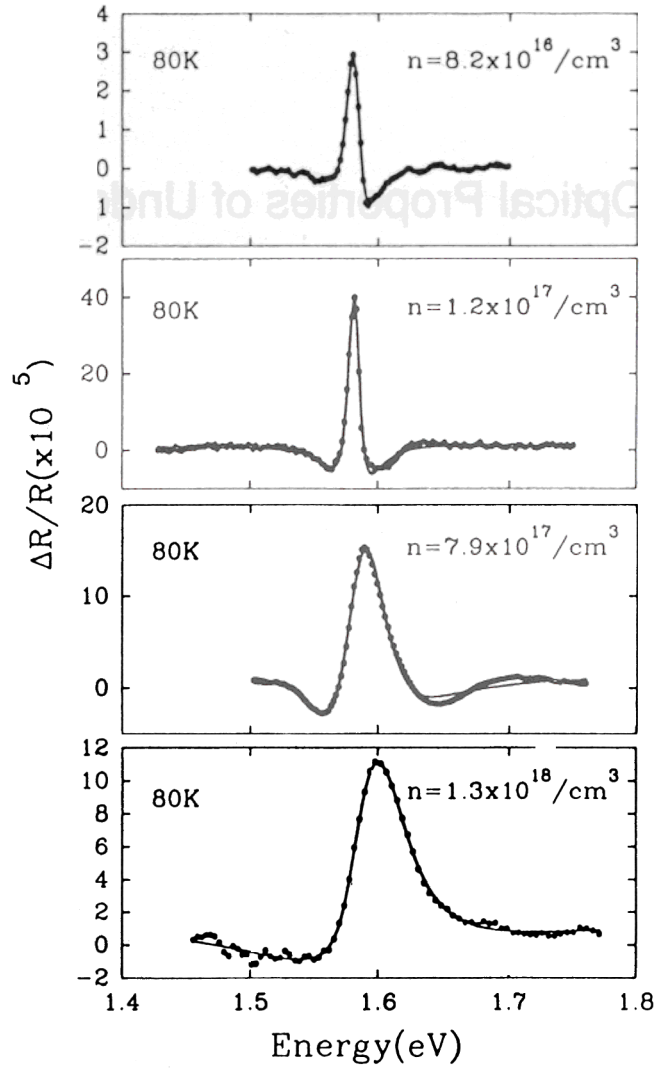


Fig. 2. Photoreflectance at 80K from CdTe:I/CdTe epilayers with varying carrier concentrations. A two-transition fit using two FDLF (solid line) reproduces the PR data (dots) very well. The two transitions are the iodine donor-hole transition at ~1.582 eV and the free exciton at ~1.588 eV.

lowest doped CdTe:I epilayer once the strain-shift in the X emission is taken into account. Fluorine ($E_D = 13.71$ meV) and chlorine ($E_D = 14.48$ meV) donors in bulk CdTe produce bound exciton lines at 1.59314 and 1.59296 eV, respectively.⁵ After subtracting the 1.2 meV shift due to strain in our CdTe/GaAs epilayer, the normalized energy for the iodine (D⁰, X) is 1.5923 eV, resulting in an estimate of the iodine E_D in the range from 14.5–15 meV. Thus, a consistent decrease in bound exciton emission energy (and increase in E_D) is predicted with increasing atomic number for these halogen species.

The PL spectrum from a more heavily doped epilayer grown on a CdTe substrate is shown in Fig. 1b. The broad donor-related PL band is centered around 1.5927 eV. Note that the (D⁰, X) line cannot be clearly resolved in this case but is consistent with a 14.5–15 meV value for E_D . Acceptor-bound exciton (A⁰, X) emission was also detected at 1.589 eV. As reported earlier,³ the (A⁰, X) emission lines can be separately resolved in

high resolution scans as transitions due to Cu (1.5895 eV), Ag (1.5885 eV), and Li and/or Na (1.5892 eV) acceptor impurities in the CdTe:I/CdTe epilayers. Figure 1a shows that Cu contamination is absent when GaAs substrates are used. Our study indicates that diffusion of acceptor impurities from II-VI substrates into the epilayer during growth remains a problem.

Both PR and PL measurements were made at 80K. Two types of PR spectra were observed which differed by about a factor of ten in signal strength, as discussed elsewhere.⁴ The weaker signal was only obtained from low-doped samples ($n \leq 1 \times 10^{15} \text{ cm}^{-3}$) and clearly consisted of the superposition of two transitions with energies at 1.582 and 1.588 eV. The mechanisms underlying the two transitions were determined through a comparison with the PL spectrum of the same CdTe taken at 78K. The PL spectrum consisted of two peaks with maxima near 1.581 and 1.589 eV. By tracking CdTe PL edge emission peaks from 1.6K to higher temperatures, Giles⁶ has shown that the peak at 1.589 eV corresponds to a free-exciton transition, while the emission at 1.581 eV is associated with a donor-hole transition. Thus, the two overlapping PR signals are due to donor-hole and free-exciton transitions with energies of about 1.582 eV (donor) and 1.588 eV (exciton).

At 80K, the edge PL emission from the more heavily iodine-doped samples broadened to a single bright peak occurring at about 1.581 eV, varying only slightly with doping concentration. This emission occurs significantly below the 80K bandgap of CdTe (~ 1.598 eV). A similar result was observed for the PR measurements. Photoreflectance spectra from samples with different doping levels are shown in Fig. 2. Analysis of the 80K PR lineshape assumed only the first derivative of a Lorentzian function (FDLF), appropriate for confined systems such as excitons at low temperatures.⁷ While the dielectric function of an impurity-band transition has been described by a more complex dielectric function,⁸ the PR signal in Fig. 2 was adequately fit using a FDLF for extracting transition energies. A two-transition analysis was performed where both exciton and donor transitions were considered based on the results obtained for the less heavily doped samples. The PR spectra of the more heavily doped samples was dominated by the donor-hole transition with a relative contribution about ten times larger than that of the exciton contribution. Lightly doped or undoped samples exhibited contributions from donors and excitons at comparable intensities.

Figure 2 shows the results of the two-transition lineshape fits to the 80K PR spectra for the heavily doped CdTe:I samples. In all cases, the two-transition least-squares fit (solid line) provided for almost complete reproduction of the PR data (dots). The donor-hole transition occurred at 1.581 ± 0.001 eV for all doping levels and is consistent with the PL measurements. The energy difference between the two transition energies (exciton and donor) was consistently

found to be $5 \text{ meV} \pm 1 \text{ meV}$. Since the ground state energy of the exciton is 10 meV, this indicates a donor energy E_D of ~ 15 meV, which is consistent with the liquid helium temperature PL measurement. Note also in Fig. 2 that the PR transition broadens with increasing carrier concentration. Broadening of comparable magnitude was observed in the PL spectra.

Bright PL at room temperature was observed from the CdTe:I samples. As reported previously,⁹ the signal intensity from the CdTe:I epilayers with $n = 1 \times 10^{17} \text{ cm}^{-3}$ was ~ 1000 times larger than that obtained from a piece of bulk CdTe normally used as a PL standard. In the present study, the magnitude of the 300K PL signal increased with increasing doping level. Both the position of the PL peak and the full-width-at-half-maximum (FWHM) of the emission peak were found to depend on carrier concentration, as shown in Fig. 3 (solid dots). Note the shift in PL emission peak energy from 1.507 to 1.523 eV. However, the origin of the peak shift cannot be understood in terms of a single band-to-band transition. Even for the highest doping level, the PL emission peak energy is still too low to be attributed to conduction band valence band (e, h) recombination. The 300K bandgap of CdTe is about 1.513 eV, and the (e, h) emission should peak about $1/2 kT$ higher in energy.^{9,10}

Room-temperature PR spectra taken near the band edge also indicated a strong dependence on electron

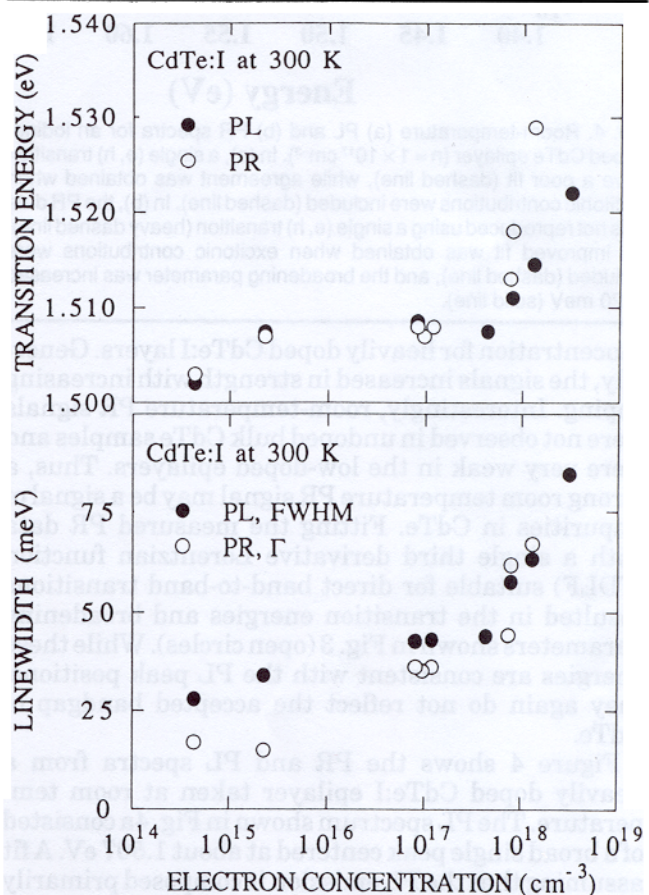


Fig. 3. Apparent transition energy and linewidth of PL and PR measurements as a function of carrier concentration in iodine-doped CdTe.

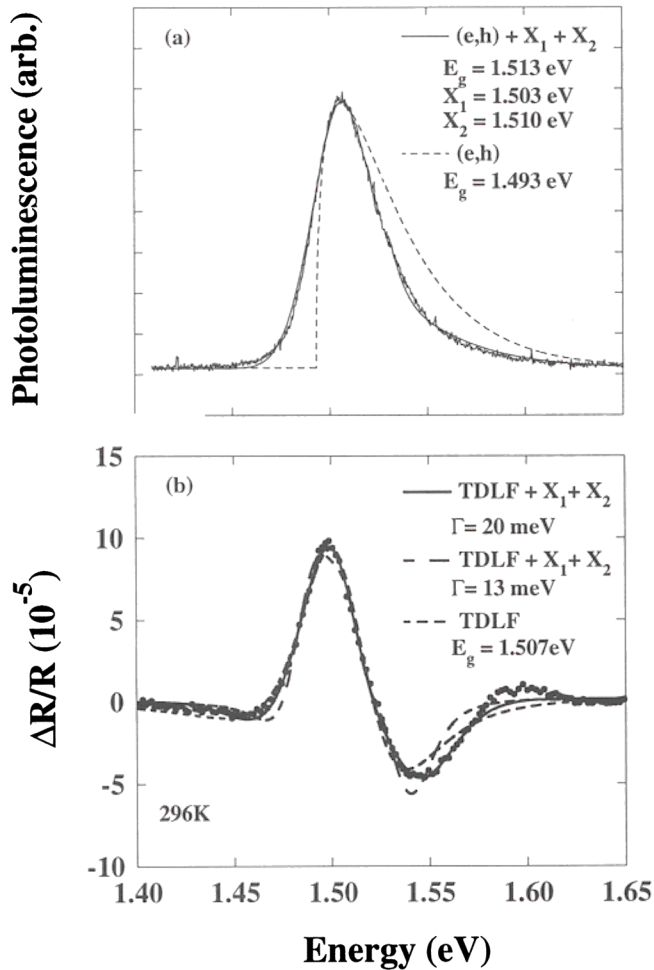


Fig. 4. Room-temperature (a) PL and (b) PR spectra for an iodine-doped CdTe epilayer ($n = 1 \times 10^{17} \text{ cm}^{-3}$). In (a), a single (e, h) transition gave a poor fit (dashed line), while agreement was obtained when excitonic contributions were included (dashed line). In (b), the PR data was not reproduced using a single (e, h) transition (heavy dashed line). An improved fit was obtained when excitonic contributions were included (dashed line), and the broadening parameter was increased to 20 meV (solid line).

concentration for heavily doped CdTe:I layers. Generally, the signals increased in strength with increasing doping. Interestingly, room-temperature PR signals were not observed in undoped bulk CdTe samples and were very weak in the low-doped epilayers. Thus, a strong room temperature PR signal may be a signal of impurities in CdTe. Fitting the measured PR data with a single third derivative Lorentzian function (TDLF) suitable for direct band-to-band transitions resulted in the transition energies and broadening parameters shown in Fig. 3 (open circles). While these energies are consistent with the PL peak positions, they again do not reflect the accepted bandgap of CdTe.

Figure 4 shows the PR and PL spectra from a heavily doped CdTe:I epilayer taken at room temperature. The PL spectrum shown in Fig. 4a consisted of a broad single peak centered at about 1.507 eV. A fit assuming that the PL emission is composed primarily of (e, h) recombination is shown by the dashed line in Fig. 4a. The fit to the data is poor and a bandgap of

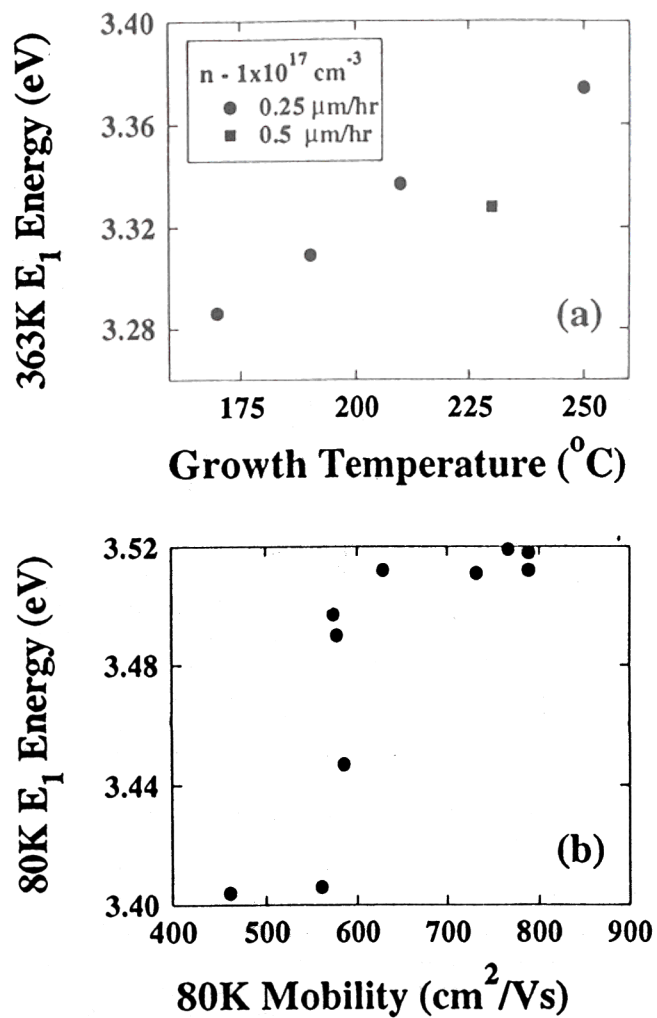


Fig. 5. Correlation of the E_1 energy with (a) sample growth temperature, and (b) electron mobility.

1.493 eV is obtained which is far below the accepted value of 1.513 eV for CdTe at 300K. As discussed below, the 1.493 eV energy also disagrees significantly with the PR result. By including recombination bands due to the ground X_1 ($n = 1$) and first excited state X_2 ($n = 2$) of the free exciton, the PL emission curve was reproduced quite accurately (solid line).

A TDLF fit to the PR spectrum in Fig. 4b yields a transition energy of 1.507 eV. Note that the TDLF lineshape yields a poor fit to the data. Based on the PL results above, the PR data was analyzed using a combination of band-to-band transition (TDLF) and the first derivative functional forms appropriate for a Gaussian absorption profile (FDGF) expected for excitonic transitions at room temperature.⁷ While not correct when excitonic contributions are significant, as in quantum well structures or at low temperatures, earlier PL studies⁹ indicate that CdTe at room temperature is in a regime where both effects are comparable. Both the ground state and the first excited state of the exciton were used. The values obtained from the PL analysis for the transition energies ($E_g = 1.513 \text{ eV}$, $X_1 = 1.503 \text{ eV}$, and $X_2 = 1.5105 \text{ eV}$) and the PL broadening parameter of the exciton transitions ($\Gamma =$

13 meV) were used as fixed parameters for this analysis. The fitting consisted primarily of determining the relative contribution of each transition. The result of this fit is also shown in Fig. 4b and resulted in an improvement over that obtained from a single band-to-band transition alone. By allowing the broadening parameter to vary, the PR data could be exactly reproduced with $\Gamma = 20$ meV. In both cases, the relative contribution of the (e, h):X₁:X₂ transitions was 1:1:1.5. The remarkable agreement between PL, which probes the imaginary part of the dielectric function, and PR, which probes the real part, clearly indicates that excitonic contributions to both signals are important at room temperature.

When both band-to-band and excitonic transitions were considered, all of the PR spectra could be accurately reproduced using a single value of the bandgap energy regardless of carrier concentration. This analysis yielded a 296K bandgap energy of 1.514 ± 0.002 eV for CdTe. The apparent shift in the transition energy for the PR and PL spectra shown in Fig. 3 reflects the varying contributions from the (e, h) and X transitions. Excitonic contributions were comparable to (e, h) transitions for low doping, while higher doping increased the relative (e, h) contribution.

One use of PR is to determine alloy composition through measurement of the bandgap. The present analysis indicates that the near-band-edge signal in CdTe consists of at least two overlapping transitions. Different surface preparations, crystal quality, or doping levels may affect the relative contribution of each transition, resulting in a shifting of the transition energy obtained by assuming only one transition. Such a shift was observed in the study by Vazquez-Lopez et al.¹¹ for PR of CdTe. Thus, PR analysis for room-temperature bandgap determination relying on only one transition has an inherent uncertainty of as much as 7 meV in CdTe and care must be exercised in the use of such an analysis. Such an uncertainty, for example, would result in an absolute error in x of

about 1% in Cd_{1-x}Zn_xTe.¹²

The E₁ transition in CdTe was also measured by PR and appeared to consist of a single, narrow transition in each sample. The PR spectrum was thus analyzed in the conventional fashion for the E₁ transition, as a third derivative of a Lorentzian function appropriate for a two-dimensional transition. The E₁ energy for 13 samples was measured as a function of temperature. A very broad range of energies, differing by as much as ~100 meV was observed at 80K. The spread in energies became less pronounced as the temperature was raised; however, a distinct spread in the measured E₁ energies remained up to 363K. This spread in energy was much larger than expected from the width of the transition (~40 meV) and did not appear to be the result of multiple transitions. The E₁ energy does appear to be related to the sample's characteristics and growth history. As shown in Fig. 5a, a distinct trend in E₁ energy measured at 363K occurs with growth temperature. The E₁ energy depends on more than just the growth temperature. As shown in the figure, a different growth rate resulted in a shift in the E₁ energy from the expected value. A correlation also apparently exists between the 80K E₁ energy and electron mobility, as shown in Fig. 5b.

It should be noted that discrepancies exist for the value of the E₁ energy in the literature for CdTe. Most studies have involved a single sample and the variation in the values of E₁ between the studies is larger than expected from the inherent precision of the measurement techniques. This study, with its variety of samples, reproduces most of the values reported for E₁. Indeed, the E₁ energy appears to be unique to each sample of CdTe depending on its prior history.

SUMMARY

Photoluminescence measurements made at liquid helium temperatures allowed determination of the iodine donor ionization energy E_d to be 14.5–15 meV. Photoreflectance and PL spectra taken at 80K in-

Table I. Growth Conditions, Room Temperature Electron Concentrations and Mobilities, and X-Ray Diffraction (Selected Samples Only) FWHM for the CdTe:I Epilayers Included in This Study

| Sample | Growth Temp. (°C) | Cd (Torr) × 10 ⁻⁷ | Thickness (μm) | n at 300K × 10 ¹⁵ (cm ⁻³) | μ at 300K (cm ² /V·s) | X-ray (FWHM arc-s) |
|--------|-------------------|------------------------------|----------------|--|----------------------------------|--------------------|
| R91-8 | 230 | 4.0 | 3.5 | 3100 | 461 | 100 |
| R91-35 | 230 | 0.7 | 3.8 | 1300 | 577 | — |
| R91-3 | 230 | 3.5 | 3.4 | 790 | 585 | 80 |
| R91-12 | 230 | 4.0 | 2.0 | 750 | 573 | — |
| R91-2 | 230 | 3.5 | 2.8 | 440 | 560 | 100 |
| R91-24 | 170 | 0.4 | 2.0 | 130 | 789 | 50 |
| R91-21 | 210 | 0.4 | 1.9 | 120 | 795 | 40 |
| R91-9 | 230 | 0 | 2.4 | 110 | 767 | 100 |
| R91-22 | 250 | 4.0 | 2.1 | 96 | 732 | 50 |
| R91-25 | 190 | 0.4 | 2.4 | 93 | 789 | 60 |
| R91-13 | 230 | 3.2 | 1.7 | 82 | 629 | 60 |
| A9307 | 250 | 0 | 12.6 | 2.3 | 580 | — |
| A9309 | 250 | 0 | 12.6 | 0.44 | 280 | — |

Beam equivalent pressures for excess Cd source included.

licated the presence of both excitonic and donor related transitions. At the higher doping levels, both PR and PL measurements are dominated by the donor-hole transition occurring at 1.581 eV. The relative broadness of the transition correlated with carrier concentration. At 300K, the near-edge PL emission peak energy and PR transition energy both exhibited a strong dependence on electron concentration for doped layers if only a single band-to-band transition is considered for the PL and PR spectra measured. However, detailed lineshape modeling of room-temperature PL and PR spectra reveals that a strong excitonic component remains, even though the exciton binding energy in CdTe (10 meV) is only about $1/3$ of $k_B T$ at room temperature. The best fit to the data is obtained using multiple transitions consisting of the free exciton (X_1 and X_2) and a direct band-to-band transition. This analysis indicates a constant value of bandgap over the entire range of conductivities studied. The relative strengths of the transitions differ according to doping concentration and film quality. The emission peak shift is due to the varying relative strength of excitonic recombination as compared to free electron-hole recombination.

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