Interpretation of near-band-edge photoreflectance spectra from CdTe

Zhonghai Yu, S. G. Hofer, N. C. Giles, and T. H. Myers
Department of Physics, West Virginia University, Morgantown, West Virginia 26506-6315

C. J. Summers
Electro-Optics, Environment and Materials Laboratory, Georgia Tech Research Institute, Atlanta, Georgia 30332-0880
(Received 28 February 1994; revised manuscript received 15 February 1995)

A study of the mechanisms underlying the origin of near-band-edge photoreflectance (PR) in CdTe is reported. We find that multiple transitions, including excitons, must be considered to correctly interpret PR signals at 80 and 296 K near the E_0 energy in CdTe. Spectra were measured for both undoped and iodine-doped n-type CdTe. Comparisons with photoluminescence recombination energies and line shapes are made. Free exciton and donor-related transitions dominate the PR signal from CdTe at 80 K, while the 296-K PR spectra is primarily excitonic in nature, even in the n-type material.

The optical modulation technique of photoreflectance (PR) can provide accurate interband transition energies in bulk as well as thin-film single-layer and multilayer semiconducting structures.[1] A simple Lorentzian function[2] adequately represents the line shapes of most reflectance modulation spectra from bulk or thick layers of III-V semiconducting materials. This single-transition approach also works well for analysis of electroreflectance (ER) spectra of CdTe.[3-5] However, differentiated spectral ellipsometry, which does not utilize a strong electric field for modulation,yields measurements for bulk CdTe and bulk GaAs at 296 K that can only be explained by the inclusion of a significant Gaussian contribution to the dielectric function.[6] Confined or localized systems, such as excitons and quantum-well structures, result in a Gaussian contribution to the dielectric function at room temperature.[7] This paper presents a detailed analysis of PR signals about the E_0 gap in CdTe, and shows that single-transition analysis of PR is not always appropriate.

The nine CdTe samples used in this study were obtained from several sources, and represented a diversity of materials synthesis techniques. II-VI, Inc. (Saxonburg, PA) provided two undoped bulk (100)- and (211)-oriented samples chemically polished with Br:methanol. Martin Marietta Electronics Laboratory provided an undoped (211)B-oriented CdTe layer grown on (211)B GaAs by molecular-beam epitaxy (MBE). Four iodine-doped ($n \sim 1\times10^{17}$ cm^{-3}) (100) CdTe:I layers on (100) CdTe and two lightly doped ($n \leq 1\times10^{15}$ cm^{-3}) (211)B CdTe:I layers on (211)B GaAs were grown by metalorganic MBE at Georgia Tech. The undoped (211)B CdTe/GaAs (Ref. 8) and doped CdTe:I epilayers[9] were previously shown to be high quality. The back surface of the samples was left unpolished to prevent complications due to electroabsorption effects resulting from back-surface reflection.[10]

The sweeping PR technique described by Shen and Dutta[11] was used to minimize the effect of the significant photoluminescence (PL) present during measurements. The probe source consisted of a 100-W tungsten lamp and $\frac{1}{4}$-m monochromator. The modulating light consisted of 1–5 mW/cm^2 of a 514.5-nm argon-ion laser line passed through an acousto-optic modulator operating at 200 Hz. Data were taken at 80 and 296 K. The PL spectra were obtained using a standard experimental setup described elsewhere.[12] Analysis of PR spectra was performed using a nonlinear least-squares fitting routine using standard line shapes described in a recent review.[1]

Measurements at 80 K resulted in two distinctly different types of PR spectra, differing by about a factor of 10 in signal strength. Figure 1(a) shows the PR spectra obtained from the undoped bulk (211) sample, representative of the weaker signal observed. Similar PR spectra

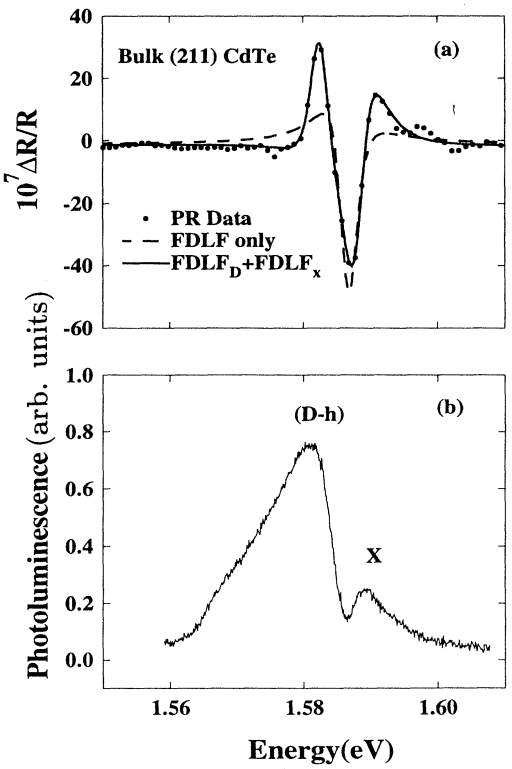

FIG. 1. PR and PL spectra from undoped bulk (211) CdTe at 80 K. (a) PR line-shape analysis using a single transition (dashed line) gives a poor fit, while that using two transitions (solid line) yields energies of 1.582 (donor) and 1.587 eV (free exciton). (b) The PL spectrum clearly shows the donor-hole (D,h) and free exciton (X) recombination.

were recorded for the undoped and low-doped (211)*B* CdTe/GaAs samples. Analysis of the PR spectra using only the third derivative of a Lorentzian function (TDLF) suitable for direct band-to-band transitions yielded an extremely poor fit and indicated a transition energy of 1.586 eV, significantly lower than the 80-K band-gap energy for CdTe of $\sim 1.598 \pm 0.002$ eV.[13,14] Using the first derivative of a Lorentzian function (FDLF) appropriate for confined systems at low temperatures, such as excitons or impurities,[1] resulted in the fit shown in Fig. 1(a) (dashed line) which does not adequately fit the measured line shape or result in a reasonable transition energy. An adequate fit could only be obtained by using two FDLF's with transition energies of 1.582 ± 0.001 and 1.587 ± 0.001 eV. The resulting line shape [solid line, Fig. 1(a)] is in excellent agreement with experiment. Analysis of the PR spectra from the CdTe/GaAs layers resulted in the same two transition energies within the 1-meV uncertainty. The relative strengths of the two transitions were nearly equal in all the samples exhibiting weak PR signal. The transitions were quite sharp, with broadening parameters Γ of 3.4 and 2.6 meV, for the 1.582- and 1.587-eV transitions, respectively.

PL from the same CdTe samples identifies the mechanisms underlying the two transitions observed in the 80-K PR spectra. The 80-K PL spectrum recorded from the (211) bulk CdTe sample, shown in Fig. 1(b), contains two emission bands with maxima at 1.581 ± 0.002 and 1.588 ± 0.002 eV. The origin of this emission was determined by tracking the PL over the range 4.2 to 80 K. By starting from well-known transitions at 4.2 K,[12] this approach unambiguously determined that the peak at 1.588 eV corresponds to free exciton (X) recombination, while donor-hole recombination gives the emission at 1.581 eV, in agreement with previous studies.[13,14] Comparison between PL and PR indicates that the two transitions producing the PR signal correspond to free exciton and donor-hole transitions. Both these transitions are confined systems, in agreement with the PR line-shape analysis. Additionally, the ~ 5-meV energy separation found between the two PR transitions is consistent with the 10-meV exciton binding energy[15] and the 13–15-meV ionization energy observed for shallow donors in CdTe.[16] The PR and PL transition energies are also consistent with the small temperature dependence (less than 1 meV between 4 and 80 K) predicted for free exciton and donor-hole transitions, as compared to the approximately $\frac{1}{2}k_B T$ dependence expected for direct band-to-band and electron-acceptor transitions.[17]

The heavily doped CdTe:I layers and the (100) bulk CdTe sample exhibit 80-K PR spectra with an overall increase in signal strengths of about ten times. Figure 2(a) contains a representative spectrum from a CdTe:I epilayer ($n_{300\,\mathrm{K}} \sim 1 \times 10^{17}$ cm^{-3}). In contrast to the lightly doped samples, a reasonable fit to the PR data was obtained with a single FDLF, yielding a transition energy of 1.581 ± 0.001 eV. Note that this energy value agrees with the lower transition energy in the CdTe/GaAs and (211) bulk CdTe samples. The 78-K PL spectrum obtained from the same epilayer is shown in Fig. 2(b). The peak at 1.581 eV clearly dominates the spectrum and has been

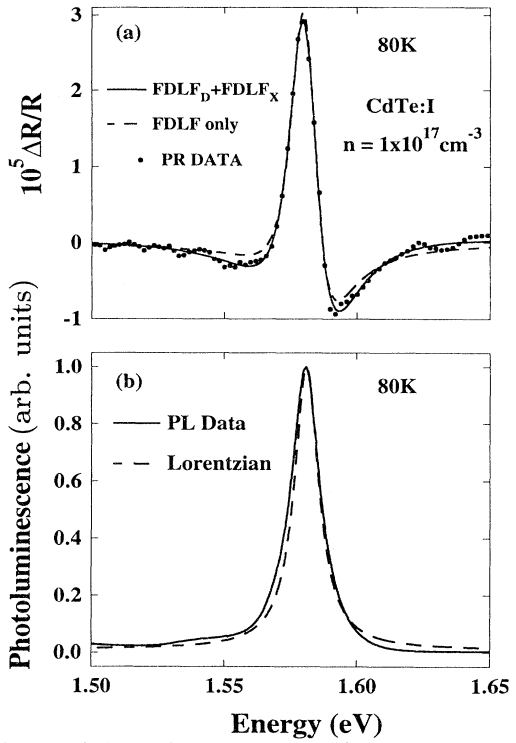

FIG. 2. PR and PL spectra from CdTe:I epilayer ($n \sim 1 \times 10^{17}$ cm^{-3}) at 80 K. (a) PR line-shape analysis with only the (D,h) transition (dashed line), and the improved fit obtained with a contribution from free excitons (solid line). (b) PL dominated by (D,h) emission at 1.581 eV, and the predicted PL spectrum (dashed line) generated using parameters from PR analysis.

shown to originate from the iodine-related donor-hole transition.[12] Using the 1.581-eV transition energy and the 10.2-meV broadening parameter obtained from the PR analysis, a normalized PL spectrum was predicted (dashed line) based on a simple Lorentzian absorption profile. This excellent agreement identifies the 1.581-eV signal as due to the iodine-related (I_{Te}) donor-hole transition in the intentionally doped samples.

A slightly improved fit to the PR spectrum in Fig. 2(a) could be obtained using two FDLF's (solid line). The best fit to the PR spectra indicated transition energies of 1.581 and 1.586 ± 0.002 eV, with the second transition again indicating the presence of free excitons. The larger uncertainty in the exciton transition energy is due to its smaller *relative* contribution to the overall signal in the heavily doped layers. Surprisingly, the excitonic contribution to the 80-K PR signal was essentially the same strength for the entire set of CdTe samples. The factor of 10 increase in overall PR signal in the heavily doped samples is due solely to the increase in magnitude of the shallow donor contribution.

Analysis of the PR spectra obtained from the CdTe samples at 296 K was less straightforward. A representative PR spectra is shown in Fig. 3, with the experimental data represented by the solid diamonds. The line shapes were invariant with changing illumination intensity, indicating that the PR signal was in the low-field regime. A reasonable approach is to assume that the room-

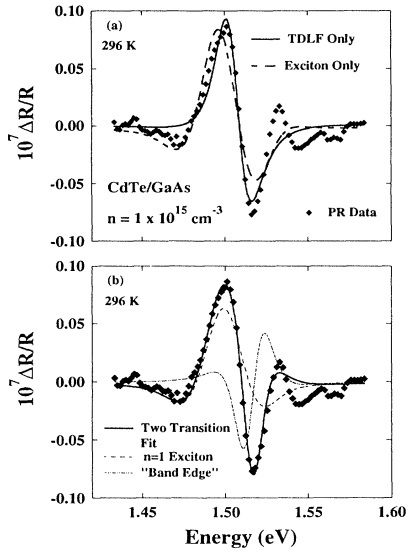

FIG. 3. PR from the CdTe:I/GaAs epilayer at 296 K. (a) PR line-shape analysis with a single band-to-band (solid line) or exciton (dashed line) transition results in a poor fit to the data. (b) A two-transition fit which includes an exciton transition and a general Lorentzian function representing near-edge transitions. The relative contributions are indicated.

temperature PR signal is dominated by direct band-to-band (e,h) transitions. However, the line shape resulting from the use of the appropriate TDLF, also shown in Fig. 3(a), does not adequately fit the structure observed both above and below the main PR transition. In addition, the use of the TDLF line shape resulted in a transition energy of 1.504 eV with $\Gamma=31$ meV. This transition energy is about 7–9 meV lower than reported E_g values obtained from electroreflectance measurements of bulk CdTe, which indicated 296-K E_g values of 1.513 eV,[3] 1.511 ± 0.005 eV,[4] and 1.513 ± 0.003 eV,[5] and a recent PL study that indicated a room-temperature band-gap value of about 1.513 eV.[18] The value of Γ from the PR analysis was also about *twice* that reported in the ER studies. This was surprising since other studies on this sample indicated improved material quality. Applying the single transition TDLF fit to the 296-K PR spectra recorded from all the samples included in our study also resulted in transition energies ranging from 1.504 to 1.510 eV. This large variation in energy cannot be explained by the experimental uncertainty.

We then considered the line shape appropriate for excitonic transitions at room temperature, which is the first derivative of the dielectric function suitable for a Gaussian absorption profile (FDGF).[1] The FDGF fit to the data shown in Fig. 3(a) yields a transition energy of 1.504 eV. This transition energy is consistent with the expected band gap of about 1.514 eV, in agreement with earlier reports, if the PR transition is indeed excitonic. The FDGF fit gives better agreement than a single TDLF at energies below the main PR transition. However, this single-transition line shape does not adequately fit either of the large extrema or the structure seen at energies above the main PR transition.

A recent analysis of room-temperature PL spectra measured from a subset of the same CdTe epilayers and similar bulk substrates reports that the PL line shape is reproduced by using a combination of free exciton ($n=1$ and 2 states) and continuum band-to-band radiative transitions.[18] Thus we included the $n=2$ exciton state in our analysis. One additional parameter, the relative strength of the contribution of the excited state, was added in this step as the energy separation from the ground state was fixed at 7.5 meV, consistent with the simple hydrogenic model.[15] Unfortunately this indicated a strength for the $n=2$ exciton state comparable to or larger than the $n=1$ state, in direct conflict with the predictions of the effective-mass theory of exciton transitions first proposed by Elliot[19] or experimental measurements of free exciton absorption profiles.[20] Inclusion of the $n=2$ exciton level with the approximately one-eight relative strength predicted by the simple effective-mass theory resulted in a line shape essentially indistinguishable from that based only on the $n=1$ level.

The next step is to consider continuum band-to-band transitions. This approach is complicated by two factors. First, whenever excitonic effects are present, the TDLF for direct band-to-band (e,h) transitions is no longer valid. As pointed out by Elliot,[19] excitonic states merge smoothly with the continuum transition, thereby altering the nature of the dielectric function. Second, it has been reported that while excitonic effects dominate the PR spectra of GaAs and other III-V semiconductors[21] up to 300 K, only direct band-to-band transitions are present at higher temperatures. Thus there must be a transition region where both effects are present, with the magnitudes of each contribution depending on the individual sample history.

We believe that the CdTe samples investigated in this study are in this intermediate region. We applied a two-transition fit, based on an excitonic transition and a single additional transition to mimic all the near-edge transitions. The functional form of this near-edge transition is not easily obtained, as it would be a mixture of discrete excitonic and continuum band-to-band transitions. Thus we decided to use a Lorentzian function as the second transition and to allow the program to obtain the best fit for the critical-point exponent, m, as well as the other parameters. Other groups often use a similar approach to minimize numerical calculation; for example, the TDLF for a two-dimensional critical point (with $m=3$) is commonly used to mimic the more rigorously correct but numerically tedious FDGF line shape for excitonic transitions above 77 K.[1] The $n=2$ exciton transition was neglected as its inclusion had little effect in fitting.

The two-transition least-squares fit to the PR data resulted in an exciton transition energy and broadening parameter of 1.504 eV and 13 meV, respectively. This transition energy agrees with that obtained using a single exciton transition and, as importantly, agrees with the values obtained in the independent PL measurement.[18] The best-fit near-edge transition yielded a transition energy of 1.513 eV, broadening parameter of 16 meV, and an exponent of 3.28. Note that this transition energy is within 1 meV of the band-gap energy (1.514 eV) indicated by the exciton value and the broadening parameter is

comparable to the previous ER studies. The exponent indicates that the transition cannot be represented by a TDLF suitable for a three-dimensional critical point (with $m=\frac{5}{2}$), but is a more complex function with a probable Gaussian nature. The line shape resulting from the two-transition fit is shown in Fig. 3(b), along with the relative contributions from each transition. While this procedure does not completely reproduce the PR spectral line shape, it provides evidence of the presence of at least two transitions, an excitonic and near-edge transition. To test the robustness of the presence of two transitions, we fixed m at values ranging from 2 to 4, and repeated the least-squares fitting. The exciton transition energy remained 1.504 for all fits, with a broadening parameter of 13 meV. The near-edge transition energy varied slightly, from 1.515 ($m=2$) to 1.513 ($m=4$), with broadening parameter values ranging from 12 to 19 meV, respectively. The agreement between the transition energies for the various fits is a reflection that transition energies can be closely determined if a reasonable function is chosen for the form of the dielectric constant. Note that the near-edge broadening parameter changes with m, but in all cases remains comparable to the values reported in the ER studies.[5]

Additional observations are explained by the presence of excitonic contributions. The excitonic contribution explains the Gaussian component of the dielectric function measured previously by ellipsometry.[6] Inclusion of both excitonic and near-edge contributions in the analysis of the PR spectra from all nine samples resulted in the *same* E_0 energy, 1.514±0.002 eV. Indeed, the spread in energies that results from a single-transition analysis of 296-K PR data can be explained solely by differences in the relative strengths of the two contributions from the variety of samples included in our study. Similar results were obtained for all nine samples investigated, indicating that excitonic contributions dominate the PR spectra in low-doped and n-type doped CdTe. Importantly, excitonic contributions must be considered in analysis of room-temperature PR and PL line shapes to obtain a consistent band-gap energy on the *same* samples. A recent study uses room-temperature PR to assess the quality of thin (2000 Å) CdTe grown on GaAs.[22] The E_0 values, determined only to the nearest 10 meV by considering a single transition, are in general agreement with the values reported here. It is interesting that the E_0 values determined for the best two samples differed by 30 meV with corresponding large broadening parameters. It is conceivable that multiple transitions are also present in these layers.

In conclusion, a detailed analysis of near-band-edge PR spectra from CdTe indicates the presence of donor, free exciton, and continuum band-to-band transitions in CdTe. The near-band-edge PR spectra at 80 K contain a superposition of excitonic and shallow-donor-related transitions. At room temperature, both excitonic and near-edge continuum transitions must be considered, resulting in both Gaussian and Lorentzian contributions to the dielectric function. Analysis of PR spectra yields values for the band gap of CdTe as 1.598±0.002 eV at 80 K and 1.514±0.002 eV at 296 K. By using the two-transition analysis, the same band-gap energy is obtained for all the room-temperature PR spectra. As importantly, this band-gap energy is in agreement with PL analysis and prior electroreflectance measurements.

The authors want to thank II-VI, Inc. (Saxonburg, PA) and Martin Marietta Electronics Laboratory (Syracuse, NY) for supplying samples, and L. E. Halliburton of West Virginia University for providing equipment used in the PR measurements. One of us, T.H.M., acknowledges useful conversations in analyzing PR line shapes with R. Anderson of the University of Maryland. This work was supported in part by the NSF/WV EPSCoR program.

[1]O. J. Glembocki and B. V. Shanabrook, in *Spectroscopy of Semiconductors,* edited by D. Seiler and C. Littler, Semiconductors and Semimetals Vol. 36 (Academic, New York, 1992).
[2]D. E. Aspnes and J. E. Rowe, Phys. Rev. B **5**, 4022 (1972).
[3]C. Vasquez-Lopez, H. Navarro, Raul Aceves, M. C. Vargas, and Cornelius A. Menezes, J. Appl. Phys. **58**, 2066 (1985).
[4]P. M. Amirtharaj, F. H. Pollak, J. R. Waterman, and P. R. Boyd, Appl. Phys. Lett. **41**, 860 (1982).
[5]W. S. Enloe, J. C. Parker, J. Vespoli, T. H. Myers, R. L. Harper, and J. F. Schetzina, J. Appl. Phys. **61**, 2005 (1987).
[6]J. W. Garland, H. Abad, M. Viccaro, and P. M. Raccah, Appl. Phys. Lett. **52**, 1176 (1988).
[7]O. J. Glembocki and B. V. Shanabrook, Superlatt. Microstruct. **3**, 235 (1987).
[8]Jeffrey S. Gold, T. H. Myers, N. C. Giles, K. A. Harris, L.M. Mohnkern, and R. W. Yanka, J. Appl. Phys. **74**, 6866 (1993).
[9]D. Rajavel and C. J. Summers, Appl. Phys. Lett. **60**, 2231 (1992).
[10]H. Roppischer, N. Stein, U. Behn, and A. B. Novikov, J. Appl. Phys. **76**, 4340 (1994).
[11]H. Shen and M. Dutta, Appl. Phys. Lett. **57**, 587 (1990).
[12]N. C. Giles, Jaesun Lee, D. Rajavel, and C. J. Summers, J. Appl. Phys. **73**, 4541 (1993).
[13]N. C. Giles, Ph.D. thesis, North Carolina State University, 1987.
[14]N. C. Giles, K. A. Bowers, R. L. Harper, Jr., S. Hwang, and J. F. Schetzina, J. Cryst. Growth **101**, 67 (1990).
[15]See, for example, Kenneth Zanio, in *Cadmium Telluride,* edited by R. K. Willardson and A. C. Beer, Semiconductors and Semimetals Vol. 13 (Academic, New York, 1978).
[16]J. M. Francou, K. Saminadayar, E. Molva, and J. L. Pautrat, in *Proceedings of the 13th International Conference on Defects in Semiconductors, Coronado, CA, 1984,* edited by L. C. Kimerling and J. M. Parsey, Jr. (Metallurgical Society of AIME, Warrendale, PA, 1985), p. 1213.
[17]See, for example, H. B. Bebb and E. W. Williams, in *Transport and Optical Phenomena,* edited by R. K. Willardson and A.C. Beer, Semiconductors and Semimetals Vol. 8 (Academic, New York, 1972).
[18]Jaesun Lee, N. C. Giles, D. Rajavel, and C. J. Summers, Phys. Rev. B **49**, 1668 (1994).
[19]R. J. Elliot, Phys. Rev. **108**, 1384 (1957).
[20]See, for example, D. D. Sell, Phys. Rev. B **6**, 3750 (1972).
[21]H. Shen, S. H. Pan, F. H. Pollak, M. Dutta, and T. R. AuCoin, Phys. Rev. B **36**, 9384 (1987).
[22]M. Melendez-Lira, I. Hernandez-Calderon, D. W. Niles, and H. Hochst, Appl. Phys. A **58**, 219 (1994).