Journal of Electronic Materials, Vol. 24, No. 5, 1995

Reflectance and Photoreflectance for *In-Situ* Monitoring of the Molecular Beam Epitaxial Growth of CdTe and Hg-Based Materials

ZHONGHAI YU, M.A. MATTSON, and T.H. MYERS

Department of Physics, West Virginia University, Morgantown, WV 26507

K.A. HARRIS,* R.W. YANKA, and L.M. MOHNKERN

Martin Marietta Electronics Laboratory, Syracuse, NY 13221

L.C. LEW YAN VOON and L.R. RAM-MOHAN

Department of Physics, Worcester Polytechnic Institute, Worcester, MA 01609

R.G. BENZ II, B.K WAGNER, and C.J. SUMMERS

Physical Sciences Laboratory, Georgia Tech Research Institute, Atlanta, GA 30332

Epitaxial growth of Hg-based semiconductors by molecular beam epitaxy (MBE) and metalorganic MBE (MOMBE) has progressed sufficiently to shift emphasis to the control of factors limiting the yield of both materials and devices. This paper reports on an *ex-situ* study to evaluate the suitability of reflectance and photoreflectance (PR) as *in-situ* characterization techniques for the growth of CdTe and HgCdTe. Photoreflectance yields information about CdTe layers, with largest utility for doped and multi-layer structures. However, caution must be taken in interpretation of the spectra since the near-bandedge PR spectra consists of multiple transitions and the E_1 transition energy is very sensitive to the sample history. Photoreflectance appears to be of limited utility for HgCdTe single layer growth with x<0.4. However, reflectance measurements of the E_1 peak can be used to determine composition in HgCdTe single layers with an accuracy $\Delta x = \pm 0.01$, which can be useful for growth control. A tight binding model was used to calculate the E_1 peak energy as a function of bandgap for HgCdTe and HgTe/CdTe superlattices. Comparisons are made with experimental observations. Surface interdiffusion in HgTe-CdTe superlattices was probed using reflectance measurements.

Key words: HgCdTe, *in-situ* characterization, molecular beam epitaxy (MBE), metalorganic molecular beam epitaxy (MOMBE), reflectance, photoreflectance

INTRODUCTION

Significant progress has been made in the growth of HgCdTe alloy and HgTe/CdTe superlattice (SL) epitaxial layers by molecular beam epitaxy (MBE) and metalorganic MBE (MOMBE). High quality HgCdTe and HgTe/CdTe SL with properties suitable for infrared (IR) detector fabrication have been demonstrated.[1,2] Emphasis has shifted to evaluating and controlling critical factors during growth that limit the yield of both materials and devices.

Photoreflectance (PR) spectroscopy is a powerful tool for characterization of semiconductor materials and quantum well structures. Photoreflectance signals are observed at elevated temperatures in III-V semiconductors,[3] indicating that PR may be suitable as an *in-situ* monitoring technique during growth. Reflectance spectroscopy has been used for many years as a standard characterization technique for semiconductors. This *ex-situ* study assesses the utility of reflectance and PR as *in-situ* growth characterizations for CdTe and Hg-based MBE. Efforts concentrated on two key areas. The first area was an assess-

(Received October 30, 1993; revised August 19, 1994)
*Present address: II-VI, Inc., Saxonburg, PA 16056.

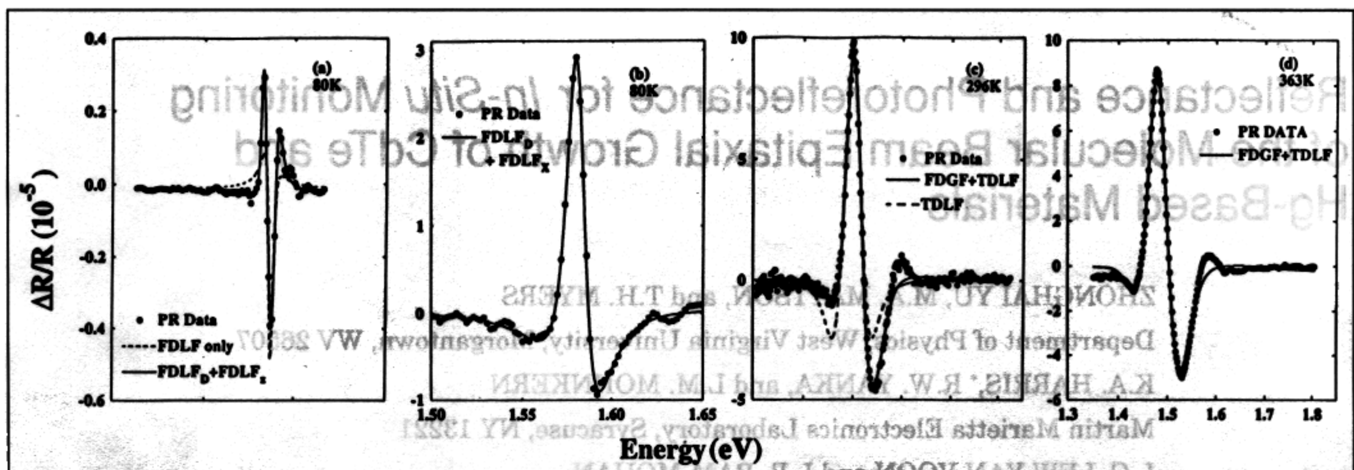

Fig. 1. Photoreflectance of CdTe. Plot (a) represents an 80K spectrum representative of undoped CdTe while plots (b), (c), and (d) are representative of iodine doped CdTe at 80, 296, and 363K, respectively.

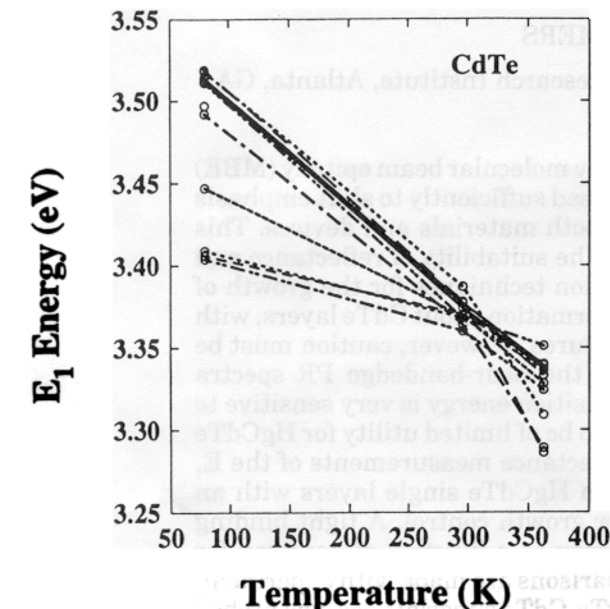

Fig. 2. E_1 transition energies of CdTe measured by photoreflectance. A wide spread in the transition energies was observed.

ment of the accuracy with which reflectance and PR measurements can determine composition during growth, allowing small corrections to be made in alloy composition or SL layer thicknesses thereby improving reproducibility. Second, a determination was made whether these techniques can provide an independent measure of the growth temperature, a very critical parameter in Hg-based MBE.

EXPERIMENTAL

During this study, PR and reflectance measurements were made on bulk and thin film CdTe, single layers of HgCdTe grown by MBE and MOMBE, and HgTe/CdTe superlattices. II-VI, Inc. (Saxonburg, PA) provided samples of undoped bulk (100) and (211)-oriented CdTe. The surface of the bulk CdTe was chemically polished with Br:methanol using a technique developed for MBE growth. An undoped (211)B CdTe/(211)B GaAs layer, a (211)B HgCdTe/CdTe layer, and six (211)B HgTe/CdTe superlattices grown by MBE were provided by Martin Marietta Electronics Laboratory. Four iodine doped (100) CdTe/CdTe layers and two (211)B HgCdTe/CdTe layers grown by metalorganic MBE were provided by the Physical Sciences Laboratory at Georgia Tech Research Institute. The epilayers were high quality as determined by transmission electron diffraction (TEM), Hall effect and double crystal x-ray diffraction measurements.

The CdTe samples exhibited significant photoluminescence (PL) during the PR measurements. To minimize the effect of the PL, a "sweeping" PR technique similar to that described by Shen et al.[4] was used. Light passing from a tungsten lamp through a 1/4-meter monochromator served as the probe source. The modulating light was provided by passing the 514 nm line of an argon ion laser through an acousto-optic modulator operating at 200 Hz. The power density at the sample ranged between 1 to 5 mW/cm². The reflected light was directed into a photomultiplier tube, with the resultant signal being deconvoluted into ac and dc signals using a lock-in amplifler and dc voltmeter for subsequent acquisition and analysis. A narrow bandwidth active bandpass filter was placed before the lock-in to further reduce noise. The minimum detectable ΔR/R was ~5×10^{-8}. All operations were under computer control. The samples were mounted in a simple dewar system for PR measurements, and data was taken at 80, 296, and 363K. Reflectance measurements were made at room temperature using an Olis-14 dual beam spectrophotometer. The measured reflectance was referenced to a calibrated sapphire window.

CdTe

Photoreflectance measurements in CdTe were made for near bandedge transitions and for the E_1 transition. Two distinctly different types of near-bandedge PR spectra were measured at 80K, as shown in Fig. 1. The relatively weak spectrum shown in Fig. 1a was representative of all undoped low carrier concentra-

tion samples and represents a superposition of a free exciton transition and a donor-hole transition.[5] In contrast, as illustrated by Fig. 1b, the iodine-doped layers and the undoped (100) bulk CdTe sample exhibited a strong signal dominated by the transition identified as the donor-hole transition. The fit to the PR spectra for doped samples was significantly improved if the excitonic transition was also included. The only fixed parameter in the least-squares fitting procedure was the choice of a first derivative of a Lorentzian as the functional form (FDLF) for the fit as appropriate for confined systems such as excitons and donors at low temperature.[6] Other choices for the functional form did not result in an adequate fit to the data. Both types of spectra indicated an exciton energy of 1.586±0.002 eV and donor-hole transition energy of 1.581±0.002 eV which implies an 80K bandgap of 1.596±0.002 eV.

Interestingly, only the samples exhibiting the strong donor-hole PR signal at 80K had a measurable PR signal at 296 and 363K. The PR signal at higher temperatures, as shown in Figs. 1c and 1d, consisted of a superposition of both excitonic and direct band-to-band transitions at 1.504±0.002 eV and 1.514±0.002 eV at 296K and 1.483±0.002 eV and 1.493±0.002 eV at 363K, respectively. This analysis is discussed in more detail in another paper presented at this workshop[7] and is consistent with the results of a recent photoluminescence study[8] indicating that excitons play a significant role at room temperature. The multiple transitions complicate interpretation and give an inherent uncertainty of up to 7 meV in any analysis of the spectra assuming only a single transition. For example, assuming only the third derivative of a Lorentzian functional form (TDLF) appropriate for band-to band transitions results in a bandgap energy of 1.507 eV. As shown in Fig. 1c, use of only a TDLF resulted in a poor fit to the data on both sides of the main figure. A significantly better single transition fit is obtained when the first derivative Gaussian function (FDGF) suitable for excitonic transitions[6] at high temperatures is also included. The multiple transition fits also yield values for the bandgap more consistent with previous electroreflectance and photoluminescence measurements.[8–11] If the near-bandedge PR signal for CdZnTe consists of similar multiple transitions, this could lead to an uncertainty in x-value of about 1%. It is also important to note that both in the as-grown samples and the chemically polished substrates, the only samples which exhibited a measurable high temperature PR signal also had an appreciable donor-hole signal at 80K. Thus, an appreciable room-temperature or above PR signal may be a signature of high levels of impurities in the substrates. This latter effect warrants more investigation.

The E_1 transition was also measured, and appeared to consist of a single, narrow transition. The PR spectrum was thus analyzed in the conventional fashion for the E_1 transition, as a third derivative of a Lorentzian function appropriate for a two-dimensional transition. The surprizing results obtained for E_1 are displayed in Fig. 3. This figure shows the measured E_1 energy as a function of temperature for 13 samples. A very broad range of energies was observed at 80K, with the spread in energies becoming less pronounced as the temperature was raised. However, a distinct spread in the measured E_1 energies remained up to 363K. As discussed in more detail in another paper at this workshop,[7] the E_1 energy depends on many factors related to the sample's history. Certainly, this observation of a wide variation for E_1 in the current diverse set of samples allows a better understanding of the spread in reported E_1 values for CdTe reported in the literature, a spread which has been much larger than can be explained by the inherent precision of the measurements themselves.[9,12,13] Unfortunately, this spread limits the utility of this measurement for determining growth parameters such as substrate temperature. The samples which exhibited the least bowing in the E_1 energy as a function of temperature still had a slope at high temperatures that ranged form 0.54 to 0.62 meV/K. Without *a priori* knowledge of this slope for a given substrate, this uncertainty limits an independent determination of the substrate temperature to about ±10°C. Thus, while PR measurement of the E_1 energy in CdTe can be used as a general diagnostic of surface temperature, it appears that other techniques, such as the observation of Te-condensation by reflection high energy electron diffraction (RHEED) reported by Rajavel et al.[14] provide a better independent determination of substrate temperature. However, since the E_1 energy depends on the sample's growth param-

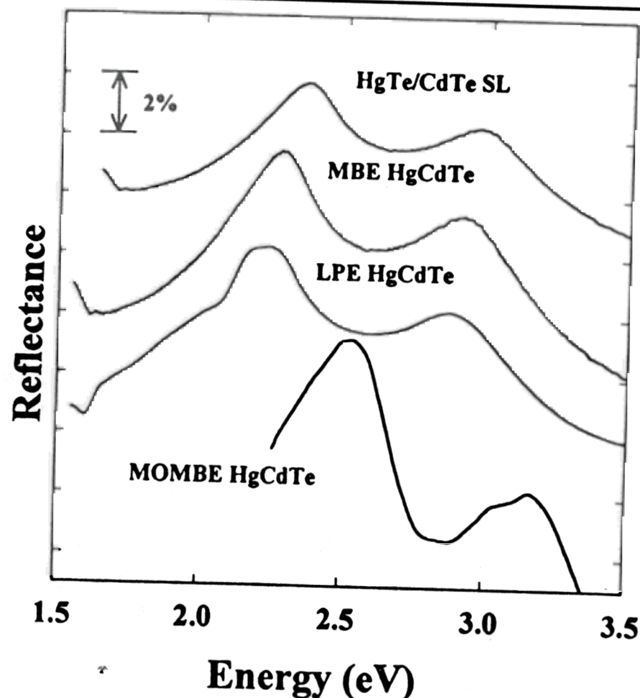

Fig. 3. Reflectance spectra from HgCdTe grown by MBE, MOMBE, and LPE and a spectrum from a HgTe/CdTe SL. The MBE and LPE samples have a nominal x-value of 0.22, while the MOMBE sample has a nominal x-value of 0.43.

Table I. Parameters Used in the ETBM Calculation

	77K	300K
E_0(HgTe)	−0.271 eV	−0.167 eV
E_1(HgTe)	2.21 eV	2.12 eV
E_0(CdTe)	1.596 eV	1.529 eV
E_1(CdTe)	3.44 eV	3.31 eV

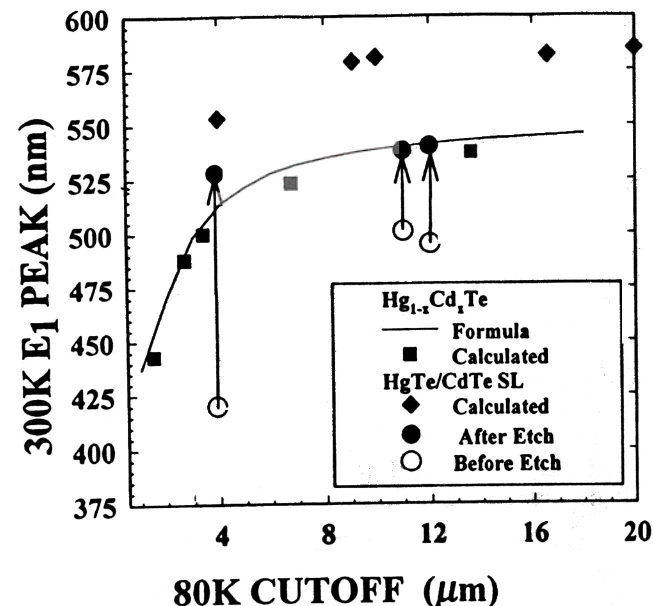

Fig. 4. E_1 transition energy as a function of cutoff wavelength for HgCdTe and HgTe/CdTe SL. Experimental measurements are compared to results predicted by ETBM calculations. For HgCdTe, the ETBM calculations are compared to the formula by Raccah[16] based on electrolyte electroreflectance measurements.

eters, E_1 energies can be determined that correspond to the desired materials properties. Thus, the E_1 energy can serve as a process check. Deviation from this point during growth would indicate deviation from the desired characteristics.

A strong PR signal was easily observed in all of the doped CdTe layers. Variations in the PR signal with doping concentration and other growth parameters are discussed in another paper in this proceedings.[7] However, in all cases, the magnitude was virtually unchanged in going from 296 to 363K. This indicates that PR measurements in doped layers should be quite feasible at the growth temperatures. When proper interpretation is given to the spectra, PR will be a useful tool for investigating doped single layers and multi-layer structures based on CdTe.

HgCdTe AND HgTe/CdTe SUPERLATTICES

A photoreflectance signal was *not* observed for any of the HgCdTe single layers or HgTe/CdTe superlattices at room temperature or above, to the measurement limit of our system. This is consistent with earlier measurements of PR in undoped HgCdTe[13,15] which reported quite small signals at 80K. Only undoped layers with bandgaps corresponding to wavelengths larger than 4 μm were investigated. Highly doped multi-layer structures or single layers of shorter wavelength were not investigated. It is conceivable that either shorter wavelengths or the presence of strong electric fields at the junction/interfaces in doped structures will yield a PR signal during growth. However, the current result indicates that PR will be of limited value for the growth of undoped and single layers of Hg-based materials for long wave IR applications.

The E_1 transition can also be observed in reflectance measurements. Reflectance measurements made at room temperature as a function of energy for three samples of HgCdTe are compared in Fig. 2. The relatively sharp spectra from the MBE and MOMBE samples allowed a reproducible determination of the peak position to within ±0.5 nm, which corresponds to ±3 meV at these wavelengths. Shown for comparison is the reflectance spectrum obtained from a liquid phase epitaxy (LPE) sample. The relatively broad E_1 peak measured for this particular sample was representative of that measured for many samples from various sources and indicates a spread in x-value over the 1 cm linear dimension of our reflectance beam, precluding accurate peak determination. Thus, reflectance measurement also provides a measure of sample uniformity. By using expressions such as that given by Raccah et al.[16] which experimentally relate the E_1 energy at room temperature to x-value, the x-value can be determined to ±0.01. While this is not the accuracy desired in final control of cutoff wavelength, it is certainly accurate enough to serve as a coarse process check. The next step needed to fully implement this measurement during growth is an accurate determination of the shift in E_1 energy with temperature for HgCdTe. Again, as with the E_1 transition in CdTe, measurement of the E_1 reflectance peak in HgCdTe may best serve as an indicator of when growth has deviated from the desired conditions.

HgTe/CdTe SL continue to be of interest.[2] A calculation of the E_1 energy vs bandgap by Ritze et al.[17] for HgTe/CdTe SL suggested that, for 10 to 12 μm cutoff, measurement of the E_1 energy may be a better predictor of bandgap for the SL than for the equivalent alloy. The initial measurements of the E_1 peak position for several SL also supported a more pronounced variation of the E_1 energy with bandgap than is found for HgCdTe. Thus, a more detailed study of the E_1 transition in HgTe/CdTe SL was undertaken using reflectance measurements.

An empirical tight-binding method (ETBM), which has been described in detail elsewhere,[18] was used to calculate E_1 as a function of bandgap energy. For the present calculations, the parameters listed in Table I were used. Calculations were first made for the E_1 energy as a function of bandgap for the alloy, HgCdTe. As shown in Fig. 4, excellent agreement was found between the results of this calculation and the experimentally measured values of E_1 for HgCdTe. The values were obtained by linear interpolation of the tight-binding parameters of the constituents which corresponds to the virtual crystal approximation.

Deviation between experiment and theory away from the endpoints can thus be understood since this approach leads to practically no bowing in the E_0 and E_1 energies.

A valence band offset of –350 meV was assumed between HgTe and CdTe for the SL calculations. The barrier layers were taken to be $Hg_{0.1}Cd_{0.9}Te$ in order to reflect the actual composition in the samples. The calculations were done for the (100) growth direction assuming growth on a CdTe substrate. Strain effects are included by fitting the bulk energy shift and splitting of the HgTe to the respective a and b deformation potentials. For example, dE_0/dP = 12.meV/kbar[19] and $E_{1h}-E_{hh}$ = 22 meV[20] for a CdTe substrate. Since the calculations were to be compared to samples grown in the (211) direction, first order corrections were made to the bandgap energies based on k·p calculations. The calculated results are summarized in Table II and compared with that for HgCdTe in Fig. 4. The trend in E_1 as a function of cutoff wavelength is very similar to that observed for HgCdTe, exhibiting essentially the same curvature.

Also shown in Fig. 4 are measured values of E_1 determined for the HgTe/CdTe SL using reflectance. It can be seen that the initial values for the SL disagree quite significantly with the predicted values. It was noticed that the measured E_1 values corresponded closely to that expected for the resulting HgCdTe if the layers were completely interdiffused. However, an interpretation of complete interdiffusion strongly conflicted with IR photoluminescence and TEM measurements made on the same SL.

The SL were then etched in a sequence of steps using a Br-methanol solution. About 0.25 μm was removed per step, and reflectance measurements were repeated after each etch step. The absorption coefficient of a HgTe/CdTe SL has values greater than 5×10^4 cm^{-1} at the E_1 energy.[21] Thus, the reflectance measurement samples a depth approximately equal to the etch step. The E_1 peak initially shifted quite dramatically toward longer wavelength with etch depth and then remained stable at a fixed wavelength after removal of about 0.5 μm. This effect was observed on all the superlattices and can be interpreted as interdiffusion of the SL at the front surface. The interdiffusion is not caused by the sample temperature during growth, or the SL would exhibit more severe interdiffusion near the substrate. Indeed, comparison of front-side and through the substrate photoluminescence indicates little change in bandgap throughout a relatively thick SL,[2] indicating minimal interdiffusion in the initial layers grown. Evidence of significant interdiffusion has not been observed in as-grown SL by transmission electron microscopy.

A detailed study of HgTe/CdTe SL interdiffusion by Kim et al.[22] has indicated that a significantly higher interdiffusion coefficient occurs near the surface of a SL as compared to the bulk, most likely due to surface generation of defects or vacancies. This effect was measured in SL annealed at elevated temperatures without an equilibrium Hg overpressure. It is conceivable that similar conditions, deviating from equilibrium, occur during cooldown after growth. If the interdiffusion is indeed an artifact of the growth cooldown conditions, suitable changes can eliminate the problem. It should be noted that the rapid change in bandgap implied by the dramatic change in E_1 with etch depth would not show up in a PL measurement, and so was not detected. Indeed, the measurement of the E_1 reflectance peak has proven to be a useful tool for evaluating surface interdiffusion in HgTe/CdTe SL. One SL has been selected to monitor for an extended period of time to look for surface interdiffusion at room temperature.

A typical reflectance spectrum for a HgTe/CdTe SL after etching was shown in Fig. 3. This is the first report of E_1 and $E_1 + \Delta_1$ transition energies for HgTe/CdTe SL that are different from that observed for HgTe.[17,23] Values of E_1 measured for the etched SL are included in Fig. 4 as a function of measured SL cutoff wavelength. Interestingly, the values agree quite closely with that observed for HgCdTe. This result indicates that using measurements of the E_1 peak to determine the cutoff wavelength is possible for HgTe/CdTe SL. However, if a trend can be inferred from three points, the E_1 peak of the HgTe/CdTe SL exhibits less variation with wavelength than found for HgCdTe.

CONCLUSION

This paper reports on an evaluation of the suitability of reflectance and photoreflectance as *in-situ* characterization techniques for the growth of Hg-based materials. Photoreflectance can yield information about CdTe layers, with largest utility for doped and multi-layer structures. However, caution must be taken in interpretation of the spectra. The near-bandedge PR spectra appears to consist of multiple transitions while the E_1 transition energy is very sensitive to the sample history. The latter precludes using measurement of the E_1 transition energy to determine sample temperature without prior knowledge of the sample.

Photoreflectance appears to be of limited utility for

Table II. Calculated and Measured Values of E_0 and E_1 for Various HgTe/CdTe SL

Layer HgTe (Å)	Thick. CdTe (Å)	Calculated E_0 @ 80K (μm)	Calculated E_1 @ 296K (nm)	Measured E_0@ 80K (μm)	Measured E_1@ 296K (nm)
39	36	9.1	579	—	—
42	45	11.3	581	11.5	540
48	26	20.0	585	—	—
49*	26*	—	—	11	538
45	26	16.6	582	—	—
19	≈23	4.0	553	—	—
19	24	—	—	3.9	528

*These layer thicknesses were not measured directly, but inferred from growth conditions.

Hg-based alloy and single layer growth. However, reflectance measurements of the E_1 peak can be used to determine composition in HgCdTe single layers with an accuracy $\Delta x = \pm 0.01$, which is useful for growth control. For precise process control, however, the higher precision obtainable with ellipsometry or wavelength difference spectroscopy is desirable. A tight binding model was used to calculate the E_1 peak energy as a function of bandgap for HgCdTe and HgTe/CdTe superlattices. The SL were found to have essentially the same E_1 energy at a given cut-off wavelength as HgCdTe. Surface interdiffusion in HgTe-CdTe superlattices was probed using reflectance measurements.

ACKNOWLEDGMENTS

We want to thank J.R. Meyer of the Naval Research Laboratory for many useful discussions. The reflectance and PR measurements performed at West Virginia University (WVU) were supported by the U.S. Air Force Wright Laboratory Materials Directorate under contract number F33615-90-C-5922 (contract monitor L.E. Brown) and by the NSF/West Virginia EPSCoR program. One of us (THM) also acknowledges support from a WVU Senate Research Grant. The ETBM calculations at WPI was supported by the Strategic Defense Initiative of the Innovative Science and Technology Office administered by the US Naval Research Laboratory under Grant No. N00014-91-K-2027LRR.

REFERENCES

1. J.M. Arias, J.G. Pasko, M. Zandian, S.H. Shin, G.M. Williams, L.O. Bubulac, R.E. DeWames and W.E. Tennant, *J. Electron. Mater.* (1993).
2. R.W. Yanka, K.A. Harris, L.M. Mohnkern, A.R. Reisinger and T.H. Myers, *J. Electron. Mater.* (1993).
3. H. Shen, *SPIE Proc.: Modulation Spectroscopy,* 1286, 125 (1990).
4. H. Shen and M. Dutta, *Appl. Phys. Lett.* 57, 587 (1990).
5. Zhonghai Yu, S.G. Hofer, N.C. Giles, T.H. Myers, D. Rajavel and C.J Summers, submitted to *Phys. Rev. B*.
6. A recent review of photoreflectance pertinent to confined systems can be found by O.J. Glembocki and B.V. Shanabrook, *Semiconductors and Semimetals,* vol. 36, (New York: Academic Press, 1992).
7. N.C. Giles, Jaesun Lee, T.H. Myers, Zhonghai Yu, R.G. Benz, II, B.J. Wagner and C.J. Summers, *J. Electron. Mater.* (24), 693 (1995).
8. Jaesun Lee, N.C. Giles, D. Rajavel, and C.J. Summers, *Phys. Rev.* B 49, 1668 (1994).
9. W.S. Enloe, J.C. Parker, J. Vespoli, T.H. Myers, R.L. Harper and J.F. Schetzina, *J. Appl. Phys.* 61, 2005 (1987).
10. C. Vasquez-Lopez, H. Navarro, Raul Aceves, M.C. Vargas and Cornelius A. Menezes, *J. Appl. Phys.* 58, 2066 (1985).
11. P.M. Arnirtharaj, F.H. Pollak, J.R. Waterman and P.R. Boyd, *Appl. Phys. Lett.* 41, 860 (1982).
12. A. Ksendov, F.H. Pollak and O.K. Wu, *Sol. State Comm.* 70, 963 (1989).
13. P.M. Amirtharaj, J.H. Dinan, J.J. Kennedy, P.R. Boyd and O.J. Glembocki, *J. Vac. Sci. Technol.* A4, 2028 (1986).
14. D. Rajavel, F. Mueller, J.D. Benson, B.K. Wagner, R.G. Benz, II and C.J. Summers, *J. Vac. Sci. Technol.* A8, 1002 (1990).
15. A. Ksendzov, F.H. Pollack, P. M. Amirtharaj and J.A. Wilson, *J. Cryst. Growth* 86, 586 (1988).
16. P.M. Raccah, *J. Vac. Sci. Tech.* A1, 1587 (1983).
17. M. Ritze, R. Enderlein, D. Schikora, O. Goede and W. Heimbrodt, *Supperlattices and Microstructures* 9, 351 (1991).
18. Lok C. Lew Yan Voon, L.R. Ram-Mohan, H. Luo and J.K. Furdyna, *Phys. Rev.* B47, 6585 (1993).
19. H.H. Cheong, J.H. Burnett, W. Paul, P.M. Young, Y. Lansari and J.F. Schetzina, *Semicon. Sci. Technol.* 8, S58 (1993).
20. Schulman and Chang, *Phys. Rev.* B33, 2594 (1986).
21. T.H. Myers, J.R. Meyer and C.A Hoffman, *Quantum Wells and Superlattices for Long-Wavelength Infrared Detectors* (Boston, MA: Artech House, Inc, 1993).
22. Y. Kim, A. Ourmazd and R.D. Feldman, *J. Vac. Sci. Technol.* A8, 1116 (1990).
23. P.P. Chow and D. Johnson, *J. Vac. Sci. Tech.* A3, 67 (1983).