

# Optical characterization of intersubband transitions in $\text{Zn}_x\text{Cd}_{1-x}\text{Se}/\text{Zn}_{x'}\text{Cd}_{y'}\text{Mg}_{1-x'-y'}\text{Se}$ multiple quantum well structures by contactless electroreflectance

H. Lu,<sup>a)</sup> A. Shen,<sup>b)</sup> W. Charles,<sup>a),b)</sup> I. Yokomizo,<sup>b)</sup> and M. C. Tamargo<sup>a),c)</sup>

*Department of Chemistry, The City College of the City University of New York, New York, New York 10031*

K. J. Franz and C. Gmachl

*Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544*

M. Muñoz

*Department of Physics, University of South Florida, Tampa, Florida 33620*

(Received 5 September 2006; accepted 8 November 2006; published online 15 December 2006)

Contactless electroreflectance was measured at room temperature to characterize a wide range of the possible optical transitions in  $\text{Zn}_x\text{Cd}_{1-x}\text{Se}/\text{Zn}_{x'}\text{Cd}_{y'}\text{Mg}_{1-x'-y'}\text{Se}$  multi-quantum-well structures grown by molecular beam epitaxy. Based on these measurements, the authors predict and then verify the anticipated intersubband transition energies. They investigate a representative  $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{Se}/\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$  structure, for which the  $E1$ - $E2$  transition energy is predicted to be 178 meV ( $6.97\ \mu\text{m}$ ). Intersubband absorption using Fourier transform infrared spectroscopy exhibits a peak at 180 meV ( $6.89\ \mu\text{m}$ ), in excellent agreement with the contactless electroreflectance measurements. © 2006 American Institute of Physics. [DOI: 10.1063/1.2405385]

Devices based on intersubband (ISB) transitions, such as quantum cascade lasers and quantum well infrared photodetectors (QWIPs), are of great interest due to their potential advantages over interband devices in the infrared range.<sup>1-3</sup> Intersubband devices are usually made from multiple quantum well (MQW) structures and need a large band discontinuity to achieve operation at shorter wavelength and higher temperatures. Multiple quantum well structures made of wide band gap II-VI materials  $\text{Zn}_x\text{Cd}_{1-x}\text{Se}/\text{Zn}_{x'}\text{Cd}_{y'}\text{Mg}_{1-x'-y'}\text{Se}$  are very promising candidates for short-wave midinfrared ISB device applications due to their large tunable band discontinuity.<sup>4-6</sup>

Modulated reflectance measurements are useful methods for understanding the physical properties of MQW and superlattice materials.<sup>7-10</sup> Contactless electroreflectance (CER) is a modulated technique<sup>11,12</sup> that measures the reflectivity changes produced by the presence of a periodic modulating electric field. This technique enables one to observe many band-to-band transitions besides the  $E1$ - $H1$  transition. Therefore the ISB transition energies can be estimated. While modulation techniques have previously been used to characterize complex structures, including device structures such as heterojunction bipolar transistors (HBTs) and high electron mobility transistors (HEMTs),<sup>13</sup> we only found one report<sup>9</sup> used to characterize ISB structures. Our study shows that by using CER we can accurately determine the ISB transition energy, and the result is confirmed by ISB absorption measured by Fourier transform infrared (FTIR) spectroscopy.

In this work, the MQW sample, which is similar to the active region of a QWIP structure, was grown by molecular beam epitaxy (MBE) on a semi-insulating InP (001) substrate using a dual-chamber MBE system with one chamber

for III-V materials growth and another for growth of II-VI compounds. Oxide desorption of the substrate was performed in the III-V chamber under As flux. After growth of a lattice-matched InGaAs buffer layer ( $\sim 0.1\ \mu\text{m}$ ), the sample was transferred to the II-VI chamber and the InGaAs surface was exposed to a Zn flux for 20 s, followed by the growth of a  $\text{ZnCdSe}$  buffer layer ( $\sim 100\ \text{\AA}$ ) at  $170\ ^\circ\text{C}$ . These steps for adjusting the III-V/II-VI interface improve the quality of the epitaxial layers.<sup>14-16</sup> Then the substrate temperature was raised to  $270\ ^\circ\text{C}$  to grow the II-VI MQW structure using a VI/II beam equivalent pressure ratio of about 3.7. The structure in this study has ten periods of  $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{Se}/\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$  QWs sandwiched between two  $\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$  layers. The nominal thicknesses of the well and the barrier are 50 and  $140\ \text{\AA}$ , respectively. The structure was capped by a  $90\ \text{\AA}$  CdSe cap layer to avoid the oxidation. The growth rates ( $0.55\ \mu\text{m}/\text{h}$  for the ternary and  $1.35\ \mu\text{m}/\text{h}$  for the quaternary) and a doping level of  $10^{18}/\text{cm}^3$  were determined from calibration layers. The excellent material quality of these II-VI MQW samples, consistent with the device design requirements, has been previously demonstrated.<sup>17</sup>

Sample quality was established by x-ray diffraction (XRD) and photoluminescence (PL). The interband transitions in this sample were determined using CER.<sup>11</sup> The  $E1$ - $E2$  intersubband transition was estimated and confirmed by FTIR measurement at room temperature (RT).

The XRD measurements showed that the  $\text{ZnCdMgSe}$  barrier and the  $\text{ZnCdSe}$  QW layers were nearly lattice matched to the InP substrate, with  $\Delta a/a = 0.25\%$  and  $\Delta a/a = -0.19\%$ , respectively. The thickness of one period ( $200\ \text{\AA}$ ) was calculated from the satellite peaks. The  $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$  quantum well had a composition of  $x = 0.50$  and was doped with Cl (using  $\text{ZnCl}_2$  as dopant source) to  $10^{18}/\text{cm}^3$ . The ZnSe and CdSe contents in the  $\text{Zn}_{x'}\text{Cd}_{y'}\text{Mg}_{1-x'-y'}\text{Se}$  were  $x' = 0.20$  and  $y' = 0.19$ , respectively, corresponding to a band gap of 3.1 eV at 77 K, which was further confirmed by PL

<sup>a)</sup>Also at: the Graduate Center of CUNY, New York.

<sup>b)</sup>Also at: the Grove School of Engineering of CCNY, New York.

<sup>c)</sup>Author to whom correspondence should be addressed; electronic mail: tamar@sci.ccny.cuny.edu

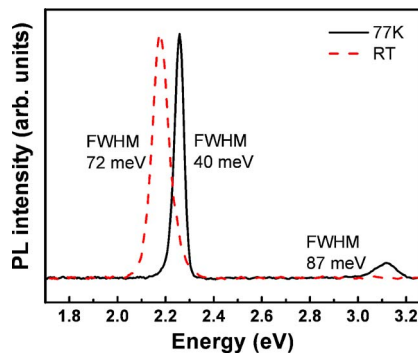


FIG. 1. (Color online) PL emission spectra at 77 K and at room temperature (RT). The peak at 3.1 eV of the 77 K spectrum is the emission from the  $\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$  barrier, which is quenched at room temperature. The FWHMs of the MQW emission peaks are 40 and 72 meV for 77 K and RT, respectively.

measurement (see Fig. 1) at 77 K and room temperature using the 325 nm line of a He–Cd laser as source.

The CER measurements were taken at room temperature from 2.0 to 3.2 eV using a 150 W xenon-arc lamp. The sample was placed in a condenserlike system consisting of a front wire grid electrode with a second metal electrode separated from the first by insulating spacers. Electromodulation was achieved by an ac voltage of 1 kV (peak to peak), 200 Hz across the electrodes. A photovoltaic Si detector and reflective optics were used to collect the light reflected by the sample. The FTIR measurements were performed using a Nicolet Nexus-870 FTIR spectrometer equipped with a liquid-nitrogen ( $\text{LN}_2$ )-cooled HgCdTe detector.

Intense and narrow PL emission peaks from the MQWs were observed at 549 nm (2.26 eV, 77 K) and 569 nm (2.18 eV, RT), as shown in Fig. 1, with no trace of deep level emissions. The peak at  $\sim 398$  nm (3.11 eV) of the 77 K spectrum is the emission from the  $\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$  barrier, which was quenched at room temperature. The full widths at half maximum (FWHMs) of the MQW peaks are 40 meV at 77 K and 72 meV at room temperature, an evidence of excellent material quality.

The CER spectrum of this MQW sample measured at room temperature is shown in Fig. 2 (solid line). The transition energies were obtained using a fit (shown by the dashed line) based on the first derivative of a Gaussian line shape, due to the bound origin of the transitions.<sup>7,8</sup> The arrows in

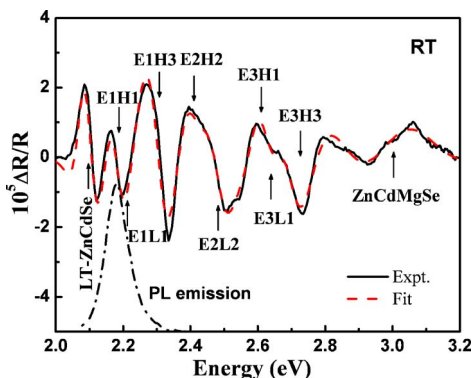


FIG. 2. (Color online) CER spectrum at room temperature (RT). The solid line represents the experimental data. The dashed line is a fit based on the first derivative of a Gaussian line shape, yielding the energies indicated by the arrows. The PL emission measured at room temperature, used to identify the  $E1H1$  transition, is also shown.

TABLE I. Experimental and calculated interband energies.

Transition	Calculation (eV)	PL (eV)	RT CER (eV) ( $\pm 0.005$ )
LT-ZnCdSe		2.105 (RT)	2.098
$E1H1$	2.181	2.179 (RT)	2.183
$E1L1$	2.205		2.205
$E1H3$	2.300		2.306
$E2H2$	2.405		2.412
$E2L2$	2.496		2.483
$E3H1$	2.606		2.608
$E3L1$	2.630		2.633
$E3H3$	2.725		2.726
Barrier		3.113 (77 K)	3.000

Fig. 2 indicate the values resulting from the fit, which are also presented in Table I. The notation  $EnH(L)m$  represents the transition from the  $n$ th conduction subband to the  $m$ th valence subband of heavy ( $H$ ) or light ( $L$ ) hole character, respectively. The assignments were done according to the following considerations. First, the signal at 3.0 eV was assigned to the  $\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$  barrier by comparison to the 77 K PL emission from the barrier, which was observed at 3.1 eV, considering that the thermal energy shift from 77 K to room temperature is about 100 meV. The signal at 2.1 eV was assigned to the  $\text{Zn}_{0.50}\text{Cd}_{0.50}\text{Se}$  grown lattice matched to the InP substrate according to previous reports.<sup>18</sup> Comparing the PL emission spectrum at room temperature, included in Fig. 2 and in Table I, we assign the CER transition at 2.183 eV to the  $E1H1$  transition.

To assign the remaining transitions, a calculation was performed based on the envelope function approximation, considering that the QW was doped.<sup>19,20</sup> The values for the effective masses and spin-orbit splitting were obtained from a linear interpolation of the binary values.<sup>4</sup> Following the previously reported values,<sup>4,5</sup> we have assumed that the conduction band offset is 80% of the band gap difference between the barriers and wells. A QW thickness of 52 Å is obtained from this calculation, which agrees well with the designed thickness of 50 Å. The identified transitions correspond to the symmetry allowed ( $n=m$ ) and symmetry forbidden but parity allowed ( $n=m\pm 2, 4, \dots$ ) transitions. As seen in Table I, the calculation agrees well with the measured values. From these data, the  $E1$ - $E2$  ISB transition energy can be estimated to be 178 meV, which corresponds to a wavelength of  $\sim 6.97$   $\mu\text{m}$ . By decreasing the QW thickness and increasing the barrier band gap, the ISB transition could be easily tuned into a shorter wavelength range of 3–5  $\mu\text{m}$ .<sup>6</sup>

The predicted value of the  $E1$ - $E2$  transition was confirmed by FTIR absorption measurements. For the ISB absorption measurement, the sample was polished to obtain a multiple-pass geometry (see inset of Fig. 3). The FTIR spectra including the transmittance spectra of  $S$ -polarized light and  $P$ -polarized light and the spectrum of  $P$  polarized over  $S$ -polarized absorbance are shown in Fig. 3. An absorption peak at 180 meV (6.89  $\mu\text{m}$ ) is clearly observed which is strongly polarization dependent. The FWHM is 20.8 meV and the ratio of  $\Delta E/E_{\text{peak}}$  is  $\sim 11\%$ . This suggests that the absorption is due to the bound-to-bound ISB transition  $E1$ - $E2$ . From the  $P$ -polarized transmittance spectrum we estimate absorption of more than 11% for this sample, which

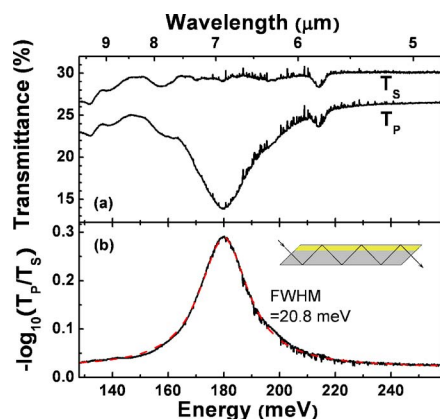


FIG. 3. (Color online) FTIR spectra at room temperature (RT). (a) Spectra of the transmittance of  $S$ -polarized light ( $T_S$ ) and  $P$ -polarized light ( $T_P$ ). (b) Absorbance of the sample obtained by taking minus logarithm of  $T_P$  over  $T_S$ . The inset indicates the multiple-pass geometry used in the measurement. An absolute absorption value of 11% is estimated from  $T_P$  by subtracting the peak at 14% from the base line at 25%.

contains only ten QWs, also attesting to the high material and structural quality. Comparison between the FTIR result (180 meV) and the CER prediction (178 meV) indicates excellent agreement. An important conclusion is that a nondestructive technique such as CER may be used to accurately predict ISB transition energies of devicelike structures in place of FTIR absorption, which is a destructive measurement that requires complex sample preparation.

In summary, a  $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{Se}/\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$  MQW structure was grown having excellent material quality, consistent with the requirements of midinfrared ISB devices. Using CER and envelope function approximation calculations, the ground state and higher order transitions were observed and identified. From this, the  $E1$ - $E2$  ISB transition energy was estimated as 178 meV. This value was confirmed by FTIR absorption measurements, which gave a peak value at 180 meV. The excellent agreement between these two techniques shows that CER can be used to investigate structural, optical, and electronic properties of these complex structures, including prediction of the ISB transition energy. The wide band gap II-VI material system presented here has

been previously proposed as a candidate for ISB devices working in the  $3\sim 5\ \mu\text{m}$  range.

This work was supported by NSF Grant No. EEC-0540832 through MIRTHERC, NASA Grant No. NCC-1-03009, and the Center for Analysis of Structures and Interfaces (CASI). Special thanks to S. K. Zhang, R. R. Alfano, and D. Crouse for helpful discussions and support. One of the authors (K.J.F.) acknowledges the support of the NSF Graduate Research Fellowship Program.

<sup>1</sup>*Intersubband Transitions in Quantum Wells: Physics and Device Applications I and II*, Semiconductors and Semimetals Vols. 62 and 66, edited by H. C. Liu and F. Capasso (Academic, San Diego, 2000).

<sup>2</sup>B. F. Levine, J. Appl. Phys. **74**, R1 (1993).

<sup>3</sup>C. Gmachl, F. Capasso, D. L. Sivco, and A. Y. Cho, Rep. Prog. Phys. **64**, 1533 (2001).

<sup>4</sup>M. Muñoz, H. Lu, X. Zhou, M. C. Tamargo, and F. H. Pollak, Appl. Phys. Lett. **83**, 1995 (2003).

<sup>5</sup>M. Sohel, X. Zhou, H. Lu, M. N. Perez-Paz, M. Tamargo, and M. Muñoz, J. Vac. Sci. Technol. B **23**, 1209 (2005).

<sup>6</sup>H. Lu, A. Shen, S. Y. Song, H. C. Liu, S. K. Zhang, R. R. Alfano, M. C. Tamargo, and M. Muñoz, Appl. Phys. Lett. **89**, 131903 (2006).

<sup>7</sup>F. H. Pollak and H. Shen, Mater. Sci. Eng., R. **10**, 275 (1993).

<sup>8</sup>O. J. Glembocki and B. V. Shanabrook, in *The Spectroscopy of Semiconductors*, Semiconductors and Semimetals Vol. 36, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1992), p. 221.

<sup>9</sup>P. A. Dafesh, J. Appl. Phys. **71**, 5154 (1992).

<sup>10</sup>G. Sek, J. Misiewicz, K. Regiński, and J. Muszalski, Vacuum **48**, 283 (1997).

<sup>11</sup>F. H. Pollak, *Group III Nitride Semiconductor Compounds* (Clarendon, Oxford, 1998), pp. 158–181.

<sup>12</sup>M. Cardona, *Modulation Spectroscopy* (Academic, New York, 1969).

<sup>13</sup>Y. S. Huang and F. H. Pollak, Phys. Status Solidi A **202**, 1193 (2005).

<sup>14</sup>S. P. Guo and M. C. Tamargo, *II-VI Semiconductor Materials and Their Applications* (Taylor & Francis, New York, 2002), Vol. 12.

<sup>15</sup>L. Zeng, B. X. Yang, M. C. Tamargo, E. Snoeks, and L. Zhao, Appl. Phys. Lett. **72**, 1317 (1998).

<sup>16</sup>L. Zeng, S. P. Guo, Y. Y. Luo, W. Lin, M. C. Tamargo, H. Xing, and G. S. Cargill III, J. Vac. Sci. Technol. B **17**, 1255 (1999).

<sup>17</sup>H. Lu, A. Shen, M. Muñoz, M. N. Perez-Paz, M. Sohel, S. K. Zhang, R. R. Alfano, and M. C. Tamargo, Phys. Status Solidi B **243**, 868 (2006).

<sup>18</sup>T. Holden, P. Ram, F. H. Pollak, J. L. Freeouf, B. X. Yang, and M. C. Tamargo, Phys. Rev. B **56**, 4037 (1997).

<sup>19</sup>G. Bastard and J. A. Brum, IEEE J. Quantum Electron. **QE-22**, 1625 (1986).

<sup>20</sup>G. Bastard, *Wave Mechanics applied to Semiconductor Heterostructures* (Les Editions de Physique, Paris, France, 1988).