Optical characterization and evaluation of the conduction band offset for ZnCdSe/ZnMgSe quantum wells grown on InP(001) by molecular-beam epitaxy

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Lattice matched ZnMgSe grown on InP is of considerable interest for its potential applications as a cladding layer due to the high band-gap energy (~3.6 eV) and for use in intersubband devices such as quantum cascade lasers. Several lattice matched $Zn_{0.5}Cd_{0.5}Se/Zn_{0.13}Mg_{0.87}Se$ quantum wells (QWs) were grown on InP (001) substrates. Emission ranging from the near UV to the visible spectral range was achieved by varying the thickness of the wells. The QW fundamental transition as function of the QW thickness was experimentally studied and modeled using an envelope calculation. The contactless electroreflectance measurements of a $Zn_{0.5}Cd_{0.5}Se/Zn_{0.13}Mg_{0.87}Se$ single QW yielded multiple transitions from the QW, allowing us to estimate the conduction band offset of this heterostructure to be as high as 1.12 eV.
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I. INTRODUCTION

Wide-band-gap II–VI $Zn_{(1-x)}Mg_xSe$ material has potential application as a cladding layer for optical devices in the blue region due to its wide direct band gap.[1] Recently, we have reported high crystalline quality zinc-blende $Zn_{(1-x)}Mg_xSe$ grown on InP (001) substrates by molecular-beam epitaxy (MBE).[2] The band gap of the $Zn_{(1-x)}Mg_xSe$ was tuned up to 3.62 eV by adjusting the Mg concentration (x). A nearly lattice matched $Zn_{0.15}Mg_{0.85}Se$ layer was grown on InP with a bandgap of 3.59 eV at 77 K. In addition, we have previously reported the growth of ZnCdSe (E_g ~2.1 eV)/ZnCdMgSe(E_g~2.8 eV) quantum well (QW) structures grown nearly lattice matched to InP substrates, and we found in that system, the conduction band offset is ΔE_c ~590 meV.[3]

In this article, we report the optical investigations of a series of ZnCdSe/ZnMgSe single QWs lattice matched to InP(001), with different QW layer thicknesses, exhibiting emission from the near-UV to the visible spectral range. We present the dependence of the QW emission wavelength with QW layer thickness. This is modeled using an envelope calculation. We also used contactless electroreflectance (CER) measurements, a modulation technique, to characterize the structures. From that measurement, we can observe higher order QW transitions, which allow us to obtain a good estimate of the anticipated large conduction band offset for this material system. A large conduction band offset is desired for application in intersubband devices such as quantum cascade lasers (QCLs) in order to address the present limitations of these devices.[4–10]

II. EXPERIMENT

The heterostructures were fabricated by MBE using a Riber 2300 system, which includes a chamber for the growth of As-based III–V materials and another for II–VI materials. The chambers are interconnected by UHV modules. Both the $Zn_{0.13}Mg_{0.87}Se$ barrier layers and the $Zn_{0.13}Mg_{0.87}Se/Zn_{0.53}Cd_{0.47}Se$ QWs were grown on InP(001) substrates. The InP substrate was deoxidized at ~490 °C under an As-flux impinging on the substrate. Then a ~0.1 μm InGaAs buffer layer was grown to smooth the surface and to adjust the surface stoichiometry. The sample was then transferred into the II–VI chamber. Prior to II–VI growth, the buffer was exposed to a Zn flux for 40 s. This was followed by growth of a 50 Å ZnCdSe interfacial layer at 170 °C. The temperature was then raised to 270 °C and the desired QW structures were grown. The beam equivalent pressure ratio of the group-VI/group-II fluxes was ~5–6. For the structures, ZnCdSe QW layer was sandwiched between two $Zn_{0.13}Mg_{0.87}Se$ barrier layers with thicknesses of 0.3 and 0.15 μm for the bottom and top barrier layer, respectively. The thickness of the well was varied between 6 and 60 Å. The growth was monitored *in situ* by reflection high-energy electron diffraction (RHEED). A streaky (2×1) RHEED pattern was observed during the growth indicating layer-by-layer growth, and Se-rich conditions. A 70-Å-thick cap layer of ZnCdSe or CdSe was used to avoid oxidation of the ZnMgSe layer. Low-temperature photoluminescence (PL) measurement was performed using the 325 nm line of a He-Cd

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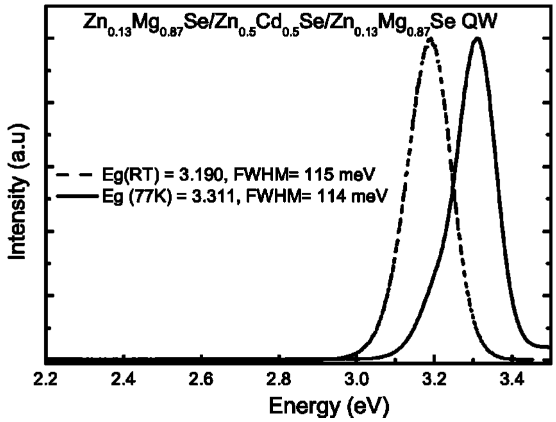

FIG. 1. Room-temperature and 77 K PL spectra of a nearly lattice matched $Zn_{0.13}Mg_{0.87}Se/Zn_{0.53}Cd_{0.47}Se$ QW structure exhibiting near-UV visible emission.

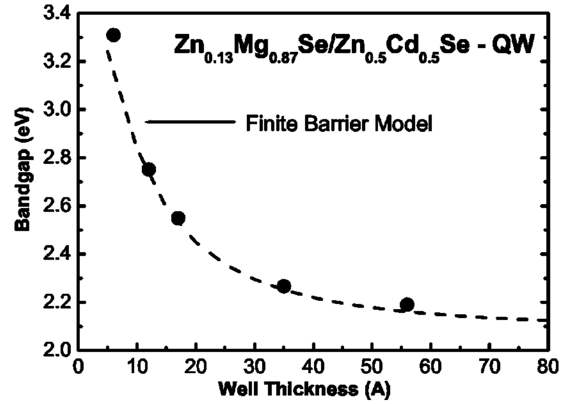

FIG. 2. Band gap as a function of QW thickness for a series of $Zn_{0.13}Mg_{0.87}Se/Zn_{0.53}Cd_{0.47}Se$ QW structures.

laser. To study the conduction band offset we have used CER.[11] CER measures the changes in the optical reflectance of the material induced by a modulating electric field, giving rise to sharp, differential-like spectra in the region of the transitions. CER utilizes a condenser-like system consisting of a front wire grid electrode with a second metal electrode separated from the first electrode by insulating spacers, which are ~0.1 mm larger than the sample dimension. We placed the sample between these two capacitor plates and achieved electromodulation by applying an ac voltage of 1.2 kV, 200 Hz across the electrodes.

III. RESULTS AND DISCUSSION

The PL spectra at room temperature and at 77 K of a $Zn_{0.5}Cd_{0.5}Se/Zn_{0.13}Mg_{0.87}Se$ single QW structure grown lattice matched to InP(001) are shown in Fig. 1. The thickness of the QW for this structure was ~6 Å. A very strong PL emission was observed in the near-UV region at 3.31 eV at 77 K and at 3.190 eV at room temperature. No deep-level emission was observed. The full widths at half-maximum (FWHM) of the PL emission lines were measured to be 114 meV at 77 K and 115 meV at room temperature, respectively. The FWHM of the PL emission is almost the same at room temperature and 77 K (and even at 9 K), which is attributed to dominant interface broadening effects due to the very narrow well.

A set of samples having QW thicknesses ranging from 6 to 60 Å was grown and their PL spectra were measured. The PL emission peak energy as a function of QW layer thickness is plotted in Fig. 2. The dashed line is the fit obtained by considering a finite barrier model where the upper and lower boundary is dictated by the band gap of the lattice matched ZnMgSe (3.52 eV) and ZnCdSe materials (2.1 eV), with a conduction band offset of 80% of the band-gap discontinuity. This offset estimate is based on the CER results presented below. An excellent fit between the experimental results and calculated values was observed indicating a good QW behavior.

Figure 3 shows the room-temperature CER measurement of a $Zn_{0.53}Cd_{0.47}Se/Zn_{0.13}Mg_{0.87}Se$ single QW with a nominal thickness of ~35 Å. The notation $EnH(L)m$ in Fig. 3 indicates that the transitions are from the nth conduction subband to the mth valence subband of heavy (H) or light (L) hole character, respectively. A CdSe cap layer was used for this structure in order to avoid overlap between the CER signal of the QW and the cap layer. The energies corresponding to the observed transitions were obtained using a fit, shown by the dashed line, based on the first derivative of a Gaussian line shape.[12,13] The signal at 1.69 eV corresponds to the CdSe cap layer, which also exhibits the typical Franz-Keldish oscillations. The transitions of the ZnMgSe barrier layer cannot be seen due to the limit of the CER apparatus at high energies.

The transitions in the range of 2.2–2.8 eV correspond to five QW transitions. Using an envelope approximation calculation[14,15] we determined the energy transitions in our QW structure as a function of the conduction band offset (ΔE_c). The calculation also predicts a QW layer thickness of 33.6 Å, which agrees with the nominal experimental value (35 Å). The value for the band-gap energy of the barrier

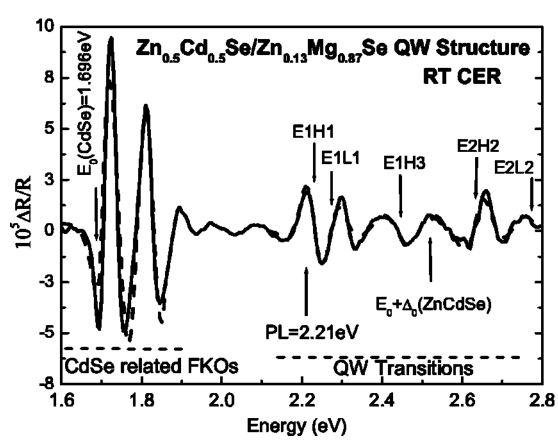

FIG. 3. Room-temperature CER spectrum of a $Zn_{0.13}Mg_{0.87}Se/Zn_{0.53}Cd_{0.47}Se$ QW structure where the solid line represents the experimental $\Delta R/R$ spectrum and the dashed lines are fits yielding the energies indicated by the arrows.

TABLE I. Comparison of the experimental (fit from CER) and calculated (envelope calculation) values of the interband transition energies of a $Zn_{0.13}Mg_{0.87}Se/Zn_{0.53}Cd_{0.47}Se$ QW structure.

Transitions	Fit from CER (eV)	Envelope calculation (eV)
E1H1[a]	2.228	2.229
E1L1[a]	2.272	2.269
E1H3	2.448	2.444
$E_0+\Delta_0$ (ZnCdSe)	2.521	2.525 exp. (Ref. 3)
		2.522 calc. (Ref. 16)
E2H2	2.635	2.624
E2L2	2.777	2.780

[a]E=electron; H=heavy hole; L=light hole.

$E_0=3.52$ eV, was obtained from the PL measurements. Other parameters used in this calculation, such as the effective masses for ZnMgSe are unknown. In order to estimate these unavailable parameters we have used a linear interpolation scheme. The details of this approach can be found in Ref. 4. The values obtained using this scheme were the mass of the electron, $m_e=0.22$, mass of the heavy hole and light holes are $m_{hh}=0.76$, $m_{lh}=0.31$ respectively, and the split orbit parameter $\Delta_0=0.44$ eV.[16] The results are summarized in Table I. A very good agreement was obtained between the experimental and calculated transitions for $\Delta E_c=80\%$ of the band-gap discontinuity (ΔE_0), which yields $\Delta E_c=1.12$ eV. Assuming that the separation between electron subbands in the QW can be as high as 70% of the ΔE_c, one can anticipate that emission energies from QCLs made with these structures may approach 1.55 μm showing a potential application of this material system in QCLs and other intersubband devices for optical communications applications.

IV. CONCLUSION

In conclusion, we have grown a series of nearly lattice matched ZnCdSe/ZnMgSe QW structures on InP substrates. By varying the QW thickness, low-temperature PL emission in the range from 2.19 to 3.31 eV was obtained from these QW structures. Intense PL band-edge emission with the absence of deep levels was obtained both at room temperature and 77 K, indicating good optical quality. The CER measurements exhibiting several QW transitions were identified using an envelope approximation. These assignments are consistent with a very large conduction band offset of ~1.12 eV for this QW system. We suggest that lattice matched ZnCdSe/ZnMgSe QWs grown on InP may be an excellent candidate for applications in intersubband devices for optical communications and other devices where a large conduction band offset of 1.12 eV is desirable.

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[1]H. Okuyama, K. Nakano, T. Miyajima, and K. Akimoto, Jpn. J. Appl. Phys. **30**, L1620 (1991).
[2]M. Sohel, M. Muñoz, and M. C. Tamargo, Appl. Phys. Lett. **85**, 2794 (2004).
[3]M. Muñoz, H. Lu, X. Zhou, F. H. Pollak, and M. C. Tamargo, Appl. Phys. Lett. **83**, 1995 (2003).
[4]C. Gmachl, H. M. Ng, and A. Y. Cho, Appl. Phys. Lett. **79**, 1590 (2001).
[5]C. Gmachl, H. M. Ng, S. N. G. Chu, and A. Y. Cho, Appl. Phys. Lett. **77**, 3722 (2000).
[6]B. H. Yang, D. Zhang, Rui Q. Yang, C. H. Lin, S. J. Murry, and S. S. Pei, Appl. Phys. Lett. **72**, 2220 (1998).
[7]R. Q. Yang, B. H. Yang, D. Zhang, C. H. Lin, S. J. Murry, H. Wu, and S. S. Pei, Appl. Phys. Lett. **71**, 2409 (1997).
[8]R. Akimoto, K. Akita, F. Sasaki, and T. Hasama, Appl. Phys. Lett. **81**, 2998 (2002).
[9]R. Akimoto, K. Akita, F. Sasaki, and S. Kobayashi, Appl. Phys. Lett. **80**, 2433 (2002).
[10]M. Göppert, M. Grün, C. Maier, S. Petillon, R. Becker, A. Dinger, A. Storzum, M. Jörger, and C. Klingshirn, Phys. Rev. B **65**, 115334 (2002).
[11]F. H. Pollak, in *Group III Nitride Semiconductor Compounds*, edited by B. Gil (Clarendon, Oxford, 1998), p. 158.
[12]O. J. Glembocki and B. V. Shanabrook, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York 1992), Vol. 36, p. 221 (1992).
[13]F. H. Pollak and H. Shen, Mater. Sci. Eng., R. **10**, 275 (1993).
[14]G. Bastard and J. a. Brum, IEEE J. Quantum Electron. **QE-22**, 1625 (1986).
[15]G. Bastard, *Wave Mechanics Applied to Semiconductor Heterostructures* (Les Editions de Physique, Paris, 1988).
[16]T. Holden, P. Ram, F. H. Pollak, J. L. Freeouf, B. X. Yang, and M. C. Tamargo, Phys. Rev. B **56**, 4037 (1997).