

Zn$_x$Cd$_{1-x}$Se/Zn$_x$Cd$_{1-x}$Mg$_{1-x}$Se multi-quantum well structures for intersubband devices grown by MBE

H. Lu$^{1,2}$, A. Shen$^1$, M. Muñoz$^3$, M. N. Perez-Paz$^{1,2}$, M. Sohel$^{1,2}$, S. K. Zhang$^4$, R. R. Alfano$^{1,2,4}$, and M. C. Tamargo$^{1,2}$

$^1$ The City College of New York, 138th Street and Convent Avenue, New York, 10031, USA
$^2$ The Graduate Center of CUNY, 365 Fifth Avenue, New York, 10016, USA
$^3$ Virginia Commonwealth University, 1020 West Main Street, Richmond, 23284, USA
$^4$ Institute for Ultrafast Spectroscopy and Lasers, and New York State Center for Advanced Technology for Ultrafast Photonic Materials and Applications, 138th Street and Convent Avenue, New York, 10031, USA

Received 14 September 2005, revised 25 January 2006, accepted 26 January 2006
Published online 3 March 2006

PACS 78.55.Et, 78.66.Hf, 78.67.De, 81.05.Dz, 81.15.Hi

Quantum well infrared photodetectors (QWIPs) from wide bandgap II–VI compounds are promising as high quantum efficiency detectors in the mid-IR. A series of Cl-doped Zn$_x$Cd$_{1-x}$Se/Zn$_x$Cd$_{1-x}$Mg$_{1-x}$Se multiple-quantum-wells (MQW) with different quantum well (QW) thicknesses have been grown by MBE lattice-matched to InP substrates. The high material quality of the samples was demonstrated by X-ray diffraction (XRD), steady-state photoluminescence (PL), and time-resolved photoluminescence (t-PL) measurements. Contactless electroreflectance (CER) measurements were performed to investigate high order transitions within the QWs. From these transitions, intersubband transition energies were predicted and compared with the theoretical calculations, a very useful result for device design. Our results indicate that this material system is very promising for intersubband device applications such as QWIPs operating in the 3–5 µm region.

© 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction

Devices, such as quantum well infrared photodetectors (QWIPs) based on intersubband absorption involving transitions within the same band, are attracting increased attention due to their rapid carrier relaxation time, large tunability of the transition wavelength and appreciable transition dipole moments [1]. A distinguishing feature of QW infrared detectors is that they can be implemented in chemically stable wide bandgap materials as a result of the use of intersubband transitions in contrast with interband devices typically made from HgCdTe. Compared with the well-developed GaAs/AlGaAs IR detectors for applications in the 8–14 µm spectrum range, QWIPs operating at wavelengths of 3–5 µm, and even 1.55 µm, need a QW system with a much larger band discontinuity. A II–VI semiconductor material system recently investigated in our lab, Zn$_x$Cd$_{1-x}$Se/Zn$_x$Cd$_{1-x}$Mg$_{1-x}$Se MQWs is very promising for fabricating this kind of devices due to its large tunable wide bandgap (2.1–3.6 eV). R-G-B full-color LEDs and optically pumped lasers have been demonstrated by this material system [2]. According to our recent research accomplishments, the conduction band offset of this system has been determined to be as large as 1.12 eV [3], which satisfies the requirement of a large band discontinuity for QWIPs working at the
near-infrared (IR) and mid-IR ranges. It’s important to note that unlike the usual devices based on interband transition, the QW structures in these devices must be doped in order to provide sufficient intersubband absorption.

In this work, heavily doped (>10^{18}/cm^3) ZnCdSe/ZnCdMgSe MQW structures were grown lattice-matched to InP substrates and characterized by X-ray diffraction, steady state photoluminescence (PL) and time-resolved PL measurements. Contactless electroreflectance (CER) studies were performed from which the intersubband transition energies were estimated.

2 Experimental details and results

The details of the molecular beam epitaxy (MBE) system used and the growth of these II–VI materials were described elsewhere [4]. The MQW samples used in this work were grown on n-type InP (001) substrates and consisted of a lattice-matched InGaAs buffer layer (~0.1 µm), a ZnCdSe interfacial layer (~100 Å) and the II–VI MQW structures. The MQW structures, with different QW thicknesses, had 10 periods of Zn_{0.2}Cd_{0.2}Mg_{0.6}Se/Zn_{0.5}Cd_{0.5}Se QWs sandwiched between 5000 Å (bottom) and 1000 Å (top) Cl-doped Zn_{0.5}Cd_{0.5}Se contact layers. The bandgap of the Zn_{0.2}Cd_{0.2}Mg_{0.6}Se barriers had been controlled to be about 3.0 eV. The growth rates of the quaternary and ternary layers were 1.0 µm and 0.55 µm per hour, respectively. The VI/II beam equivalent pressure ratio was about 3.5. This procedure has been shown to achieve epilayers with high crystalline quality and low defect density [4]. Thickness-calibration samples were grown during the same run. The ZnCdMgSe barrier and the QW layers were almost lattice-matched to the InP substrate, with \( \Delta a/a = 0.2\% \) and \( \Delta a/a = -0.2\% \), respectively. The mismatch of the QW layer was calculated from the X-ray data of a thick layer of ZnCdSe. In order to perform CER studies, MQW structures with the same compositions for QWs and barriers were grown on semi-insulating InP substrates without the bottom (5000 Å) and top (1000 Å) contact layers, on the same day as the QWIP structures.

All the MQW structures were doped by chlorine, obtained with a ZnCl\textsubscript{2} source, which is the typical n-type dopant for wide bandgap II–VI materials. The free carrier concentration was obtained by Hall Effect measurements and the doping level was on the order of 10^{18}/cm\textsuperscript{3}. Electrochemical Capacitance Voltage profiles also showed that the net carrier \((N_D - N_A)\) concentration in QWs region was in the range of 10^{18}/cm\textsuperscript{3}, which meets the requirement of device design.

For the purpose of device fabrication it is essential to establish the material quality. X-ray diffraction (XRD) measurements were used to characterize the structural properties of the samples. Clear satellite peaks were observed for all the samples. From the spacing of the satellite peaks, the periodicity of the MQWs can be accurately determined. Figure 1 shows a double crystal XRD rocking curve of one MQWs structure. Three satellite peaks were observed. A periodicity of 90 Å calculated from the XRD data.

![Fig. 1 Double crystal XRD rocking curve of a MQW sample. Inset shows the clear thickness fringes.](image-url)
agrees well with the designed value, indicating very good control of the growth. The appearance of clear thickness fringes, evident in the inset, is an indication of excellent crystalline quality of the sample.

All the MQW samples were characterized by steady state PL measurements using the 325 nm line of a He–Cd laser as an excitation source. Strong and sharp interband photoluminescence emission was observed for all the samples, as shown in Fig. 2. The inset (a) of Fig. 2 shows the PL emission peak energy as a function of QW thickness. The solid line is the theoretical calculation of $E_{1H1}$ transition energies based on the transfer matrix technique [5]. Very good agreement was obtained between the experimental values and the theoretical predictions. The FWHM of the PL emission decreases with increasing well thickness (inset (b) of Fig. 2), which is expected since thicker wells are less sensitive to the interface roughness. For our samples, even the one with the thinnest well has a FWHM less than 70 meV.

Temperature-dependent time-resolved photoluminescence ($\tau$-PL) spectroscopy was used to characterize the radiative recombination in these MQW samples. The second harmonic radiation at 400 nm was obtained from a mode-locked tunable Ti-Sapphire laser (Spectra Physics Tsunami), which was used as the excitation source. The time evolution of the luminescence was recorded in 2000 picoseconds by a streak camera (Hamamatsu Model C5680) with a typical temporal resolution of 10 ps. The temporal profiles of the PL at five different temperatures are shown in Fig. 3 for one of the samples. It can be seen that the PL traces decay exponentially with time, and can be well described by a first order exponential equation, $I(t) = I_0 e^{-t/\tau_{\text{PL}}} + C$, where $I$ is the PL intensity at time $t$, $I_0$ is the maximum PL intensity at $t = 0$, $\tau_{\text{PL}}$ is the PL decay time and $C$ represents noise level. The decay time was plotted as a function of temperature and shown in the inset of Fig. 3. The square symbols present the experimental data and the straight line is a linear fit of the data. The temperature dependence remained linear, an indication of pure free carrier recombination process, up to 230 K and only dropped a little near room temperature. This indicates that the nonradiative recombination processes are negligible. Based on these characteristics we conclude that the quality of Zn$_x$Cd$_{1-x}$Se/Zn$_x$Cd$_y$Mg$_{1-x-y}$Se MQW samples meets the requirements of QWIP device applications.

The interband transitions in these structures were estimated using CER, which is a modulated technique that measures the changes in the optical reflectance of the material with respect to a modulating electric field. The experimental details and principles of CER are described in Ref. [6].

The CER measurement was performed on a sample in which only the MQWs ($d_{\text{QW}} = 52$ Å) region was doped n-type. No highly doped top and bottom contact layers were used because these layers would dramatically broaden and weaken the transition features of the CER spectrum. We chose to present a
CER spectrum for a sample with thicker QW in order to demonstrate as many transitions as possible. The solid line in Fig. 4 is the CER spectrum measured at RT. The transition energies were obtained using a fit, shown by the dashed line, based on the first derivative of a Gaussian line shape [7, 8]. The arrows in Fig. 4 indicate all the values resulting from the fit, which are also presented in Table 1. 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 from the barrier ZnCdMgSe was assigned to the signal at 3.0 eV by comparison to the 77 K PL signal from the barrier, which was observed at 3.1 eV, and considering that the thermal shift from 77 K to RT is about 100 meV. The signal at ~2.08 eV was assigned to the transition of ZnCdSe grown lattice-matched to the InP substrate at low temperature (see growth details). It is also the reason for the broadening of the peak of the E1H1 transition at 2.183 eV. The assignment of the E1H1 transition of the MQW region was done by comparison to the RT PL data.

In order to assign the remaining transitions a calculation was performed considering the QW doping based on the envelope function approximation [9]. The parameters used in this calculation were obtained from reference [10]. As seen in Table 1, the calculation agrees well with the measured transitions when the parameter $Q = \Delta E_c/\Delta E_0$ is equal to 0.80, which is in good agreement with the $Q_c$ values reported in reference 10 (0.82 ± 0.02). From this data, the E2–E1 intersubband transition energy can be estimated to be 185 meV, which corresponds to a photocurrent of the QWIP at a wavelength of ~6.7 µm. By decreasing the QW thickness, the intersubband transition can be easily tuned into the 3–5 µm wavelength range.

Table 1  Experimental and calculated interband energies of the MQW structure.

<table>
<thead>
<tr>
<th>transition</th>
<th>calculation (eV)</th>
<th>PL (eV)</th>
<th>CER (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LT-ZnCdSe</td>
<td>2.098</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E1H1</td>
<td>2.182</td>
<td>2.176</td>
<td>2.183</td>
</tr>
<tr>
<td>E1L1</td>
<td>2.203</td>
<td></td>
<td>2.205</td>
</tr>
<tr>
<td>E1H3</td>
<td>2.299</td>
<td></td>
<td>2.306</td>
</tr>
<tr>
<td>E2H2</td>
<td>2.407</td>
<td></td>
<td>2.412</td>
</tr>
<tr>
<td>E2L2</td>
<td>2.484</td>
<td></td>
<td>2.483</td>
</tr>
<tr>
<td>E3H1</td>
<td>2.608</td>
<td></td>
<td>2.608</td>
</tr>
<tr>
<td>E3L1</td>
<td>2.630</td>
<td></td>
<td>2.633</td>
</tr>
<tr>
<td>E3H3</td>
<td>2.726</td>
<td></td>
<td>2.726</td>
</tr>
<tr>
<td>barrier</td>
<td>3.10 (77 K)</td>
<td>3.000</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4 CER spectrum of a MQW sample (ZnCdSe/ZnCdMgSe).
3 Conclusion

In summary, we have grown and investigated the properties of highly doped Zn,Cd$_{1-x}$Se/Zn$_x$Cd$_{y}$Mg$_{1-x-y}$Se MQW structures. The demonstrated doping level of 10$^{18}$/cm$^3$ meets the device requirements. Excellent material quality and growth control of multi-layers by MBE has been demonstrated using several different characterization methods, such as XRD, PL and time-resolved PL. CER was used as the technique to evaluate the intersubband transition energies. The results show that we can design the structures for devices, such as QWIPs, operating in the expected wavelength range. Our results demonstrate that this II–VI material system is a good candidate for fabrication of mid-IR intersubband devices.

Acknowledgements This work was supported by NSF Grant # ECS0217646, and by the NASA URC Center for Optical Sensing and Imaging (COSI) through Grant # NCC-I-03009.

References