phys. stat. sol. (b) **241**, No. 3, 546–549 (2004) / **DOI** 10.1002/pssb.200304278

Contactless electroreflectance studies of II–VI nanostructures grown by molecular beam epitaxy

Martín Muñoz[*, 1], **Hong Lu**[1], **Shiping Guo**[1], **Xuecong Zhou**[1], **Maria C. Tamargo**[1], **Fred H. Pollak**[2], **Y. S. Huang**[3], **C. Trallero-Giner**[4], and **A. H. Rodríguez**[4]

[1] Chemistry Department, City College of the City University of New York, Convent Ave. at 138th Street, New York, 10031, USA
[2] Physics Department, Brooklyn College of the City University of New York, 11210, USA
[3] Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan, Republic of China
[4] Department of Theoretical Physics, School of Physics, University of Havana, San Lazaro y L, 10400 La Habana, Cuba

Received 23 September 2003, revised 26 September 2003, accepted 22 November 2003
Published online 12 February 2004

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

The interband transitions of a single quantum well structure of $Zn_{0.53}Cd_{0.47}Se/Zn_{0.27}Cd_{0.23}Mg_{0.50}Se$, lattice matched to InP, and of a capped CdSe quantum dot structure have been investigated using contactless electroreflectance. From a comparison of the quantum well optical transitions with those calculated using the envelope function approximation we determined the band offsets for this system. The electroreflectance spectrum of the quantum dot structure shows transitions originating from all the portions of the sample including the quantum dots and the wetting layer. Assuming a lens shape geometry and that the effective height-to-radius ratio observed in uncapped quantum dots is preserved, the size of the capped quantum dots was determined using the observed electroreflectance transitions, and the effective mass approximation.

1 Introduction In recent years there have been increasing efforts in the development of semiconductor nanostructures such as quantum wells (QWs), and quantum dots (QDs). Technological applications such as the development of quantum cascade lasers (QCLs) and the stimulated emission of QD-structures motivate this trend. Considerable advances have been achieved in the development of the QCLs, however, there are still many limitations of these lasers, such as the unavailability of QCLs operating in continuous wave (CW) mode at room temperature (RT) and the absence of QCLs operating at short wavelengths. Both of these limitations can be overcome if materials with larger conduction band offset (CBO) are used for these devices. The optical properties of self-assembled QDs have been widely studied using photoluminescence (PL), photoluminescence excitation spectroscopy, and time resolved photoluminescence, however the information obtained is restricted to lower energy states and does not allow to study the shape of the QD potential or the coupling effects in stacked structures. In this work we present contactless electroreflectance (CER) studies of QW structures to investigate the band offsets of $Zn_{0.53}Cd_{0.47}Se/Zn_{0.27}Cd_{0.23}Mg_{0.50}Se$ and of CdSe QDs with ZnSe barriers to establish their optical and structural properties. The advantages that CER offers for the spectroscopy of nanostructures are the observation of signals coming from the different parts of the structure and the observation of both ground state and higher order transitions.

[*] Corresponding author: e-mail: mmunoz@sci.ccny.cuny.edu, Phone: +1 212 6508376, Fax: +1 212 6506848

2 Experimental details The MBE system used in this work and the detailed steps to grow these materials are described in Ref. [1]. The QW structure used in this work was grown on a semi-insulating InP (100) substrate and consisted of a lattice matched InGaAs buffer layer, a ZnCdSe interfacial layer (~70 Å), ZnCdMgSe (E_0 = 2.8 eV at RT) barriers and a QW of $Zn_{0.53}Cd_{0.47}Se$. The nominal thickness of the QW, and the bottom and top barriers are 50Å, 0.5 and 0.1 μm, respectively. Finally, the structure was capped by a 70Å thick ZnCdSe cap layer to protect ZnCdMgSe from oxidation. Details of the procedure used to grow the QD structures are given in Ref. [2]. The QD structures consist of a GaAs buffer layer followed by a GaAs/AlAs short-period superlattice (SL) and a GaAs layer then a ZnSe buffer layer. The CdSe QDs were formed by depositing 2.5 MLs of CdSe on ZnSe at 320 °C, in the case of the sample used for PL and CER measurements, a ZnSe top barrier or cap layer of 100 nm was grown at 270 °C to confine the QDs. No cap layer was grown on the sample used for atomic force microscopy (AFM) measurements. The interband transitions in these structures were determined using CER [3], which 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. We placed the samples between these two capacitor plates and achieved electromodulation by applying an ac voltage of 1.2 kV, 200 Hz across the electrodes.

3 Results and discussion The solid line in Fig. 1(a) is the measured RT CER spectrum. The energies corresponding to the transitions observed were obtained using a fit, shown by the dashed line, based on the first derivative of a Gaussian lineshape[3]. The values obtained from this fit are indicated by arrows in the figure and presented in Table 1. The notation E*n*H(L)*m* in Fig. 1 indicates that the transitions are from the n^{th} conduction subband to the m^{th} valence subband of heavy (H) or light (L) hole character, respectively.

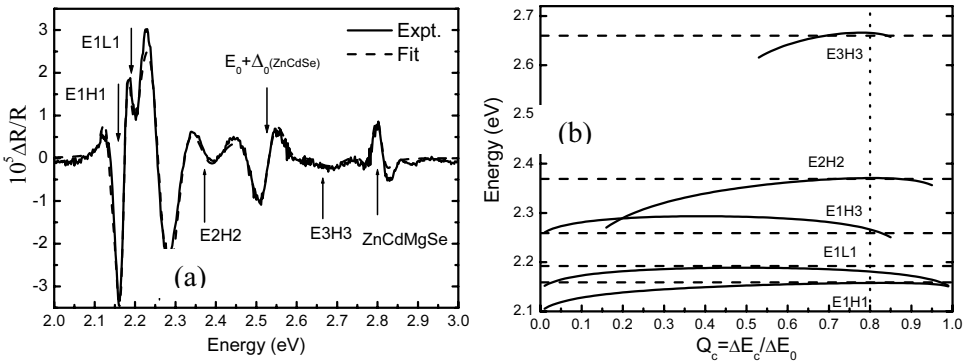

Fig. 1 (a) The solid line represents the experimental $\Delta R/R$ spectra. The dashed line is a fit yielding the energies indicated by the arrows. (b) The energy of the transitions determined by the envelope function approximation vs. Q_c.

Assignment of the transitions was done according to following considerations. The identification of the signal from the barrier at 2.8 eV was straightforward considering the 77 K PL signal and its thermal energy shift. The intensities of the transitions at 2.159 eV and 2.192 eV exhibit a ratio close to three suggesting that they are associated with the heavy and light hole transitions, respectively [3].

In order to calculate the energies corresponding to the observed transitions we have followed the envelope approximation [4]. Figure 1(b) shows the results of the calculated energies of the different transitions as a function of the parameter $Q_c = \Delta E_c/\Delta E_0$ in solid lines for the transitions that fit better the experimental values of the transitions, represented by the horizontal dashed lines. These transitions correspond to the symmetry allowed and symmetry forbidden but parity allowed transitions. As indicated in this figure by the dotted vertical line, the best agreement between the calculated and the experimental values for all the transitions was found for $Q_c = 0.82$ (ΔE_c = 590 meV) and a QW thickness of 51.9 Å. As

shown from Fig. 1 and Table 1, there is very good overall agreement. There is only a small discrepancy in the E1L1 transition attributed to the small compressive strain present in the QW, which blue-shifts the E1L1 transition by 5 meV [5], improving the agreement with the experimental results. The identification of other near lattice-matched systems with large conduction band offsets, such as the one presented here, may yield practical alternatives for the design of QCLs with better performance.

Table 1 Experimental, reported, and calculated interband energies and parameters of the QW structure.

Transition	E1H1 (eV)	E1L1 (eV)	E1H3 (eV)	E2H2 (eV)	E3H3 (eV)	$E_0+\Delta_0$ (eV)	E_0 (Barrier) (eV)
Experiment	2.159	2.192	2.259	2.369	2.660	2.525	2.800
Calculated	2.158	2.180	2.261	2.371	2.664	2.52*	

*Reported in Ref. [6].

We also investigated the QD structures using CER. The AFM studies on the uncapped QD structure, shown in Fig. 2(a), showed that the dots have a lens shape with average radius of $r = 52.5$ nm, an average height of $h = 18$ nm, an effective ratio h/r=0.34, and a dot density of 4.6×10^8 cm^{-2}. The solid line in Fig. 2(b) is the measured RT CER spectrum. The transitions originating in the SL/buffer region (<2.2 eV) present a series of Franz-Keldysh oscillations, and were fit using Lorentzian broadened electro-optical functions [3]. The transitions originating from the QDs, wetting layer (WL), and barrier (>2.2 eV) were fit using the first derivative of a Gaussian lineshape [3] due to their bound origin. The values obtained from this fit, shown by the dashed line, are indicated by arrows in Figure 2 and presented in Table 2. The identification of the signals from the buffer layer at E_0(GaAs), $E_0+\Delta_0$(GaAs) and ZnSe barriers at E_0(ZnSe), respectively were straightforward when compared with the established values in the literature, as shown in Table 2. The assignment of the other transitions was done according to the following considerations. Using an envelope model calculation [4] we obtained that the lowest transition, 1C–1H, for this short period SL is 1.876 eV, which agrees well with the signal at 1.873 eV.

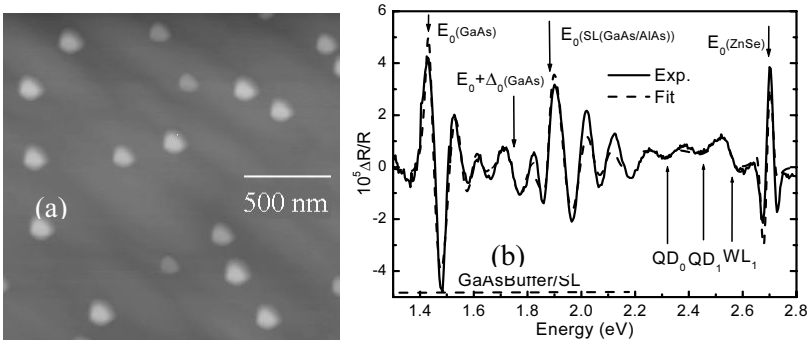

Fig. 2 AFM image (2×2 μm) of uncapped CdSe quantum dots deposited on ZnSe and CER spectrum of capped CdSe quantum dot structure. Solid and dashed lines represent the experimental data and the fit, respectively.

The notation mC–nH(L) refers to the transition between the m^{th} conduction and the n^{th} valence state of heavy or light hole character, respectively. In order to identify the transition coming from the WL we performed an envelope calculation [4]. Taking into consideration that the biaxial strain changes the CdSe band gaps and assuming that there is no intermixing between the wetting layer and the ZnSe barriers the WL lowest heavy hole transition, 1C–1H, and thickness are 2.560 eV and 4.7 Å ≈ 1.5 ML, respectively. In order to identify the transitions originating from the QDs, the shape of the quantum lens has been modeled by a spherical cap of height h and circular cross section with radius r. It is possible to show that for a quantum dot with lens-shape geometry the energy of the transitions depend on the ratio h/r, the energy levels, N_e and N_h, and the angular momentum numbers, M_e and M_h, for the electron and hole,

respectively [7]. The allowed optical features observed in the CdSe QD spectral region correspond to the transitions $|N,M>_e \rightarrow |N,M>_h$. As we mentioned, the ratio h/r for our uncapped lens-shaped quantum dots is 0.34. Assuming that this ratio minimizes the energy surface in this system and, therefore, is the most favorable ratio for QDs formation, we determined the that dimensions of the capped CdSe-QDs corresponding to these QD_0 and QD_1 transitions are h = 3.24 nm and r = 9.52 nm. According to this calculation the features QD_0 and QD_1 correspond to the electron → heavy hole transitions $|1,0>_e \rightarrow |1,0>_{hh}$ and $|1,1>_e \rightarrow |1,1>_{hh}$, respectively. This calculation showed that the capped QD sizes are approximately five times smaller than the uncapped ones. The increased size of the uncapped QDs is largely due to ripening phenomena, which occurs due to the absence of the ZnSe cap layer that allows surface migration. As a result some QDs grow at the expense of others, while the ZnSe cap layer will limit this movement. This phenomenon has been observed in CdSe QDs grown on ZnSe [8].

Table 2 Experimental, reported and calculated interband transition energies for the QD structure.

Transition/ Parameter	E_0(GaAs) (eV)	$E_0+\Delta_0$(GaAs) (eV)	SL 1C–1H (eV)	QD_0 $\|1,0>_e \rightarrow \|1,0>_{hh}$ (eV)	QD_1 $\|1,1>_e \rightarrow \|1,1>_{hh}$ (eV)	WL_1 1C–1H (eV)	E_0(ZnSe) (eV)
Experiment	1.428	1.745	1.873	2.320 PL = 2.319	2.455	2.560	2.700
Calculated	1.424*	1.765*	1.876	2.320	2.455	2.560	2.700*

*Reported in Ref. [9].

4 Conclusions In this work we have used the technique of CER to study the optical transitions and establish the dimensions of several microstructures. The presence of ground state and higher order transitions in CER measurements makes it a very useful technique to predict structural, optical and electronic properties of these nanostructures. Using CER and the envelope function approximation we have determined that the conduction band offset of $Zn_{0.53}Cd_{0.47}Se/Zn_{0.27}Cd_{0.23}Mg_{0.50}Se$ lattice-matched to InP is given by Q_c = 0.82, yielding a value of ΔE_c of 590meV. This large band offset suggests that this system may be a good candidate for intrasubband devices, such as QCLs. Further, we determined the interband transition energies of a CdSe-QD structure using CER and identified the transitions corresponding to the WL and QDs. Assuming a lens shape geometry with a height/radius ratio = 0.34 is the most energetically favorable configuration for the QD shape in this system, we found that the capped QDs dimensions in our structure are h = 3.24 nm and r = 9.52 nm.

Acknowledgements This work was supported by the National Science Foundation through grant number ECS0217646. Partial support was also obtained from the Center for Analysis of Structures and Interfaces, and the New York State Center for Advanced Technology on Photonic Materials and Applications.

References

[1] 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).
[2] S. P. Guo, X. Zhou, O. Maksimov, M. C. Tamargo, C. Chi., A. Couzis, C. Maldarelli, I. L. Kuskovsky, and G. F. Newmark, J. Vac. Sci. Technol. B **19**, 1635 (2001).
[3] H. Pollak, in: Group III Nitride Semiconductor Compounds, edited by B. Gil (Clarendon, Oxford, 1998), p. 158.
[4] G. Bastard, Wave Mechanics applied to Semiconductor Heterostructures (Les editions de Physique, France, 1988).
[5] M. Muñoz, H. Lu, X. Zhou, M. C. Tamargo, and F. H. Pollak, Appl. Phys. Lett. **83**, 1995 (2003).
[6] T. Holden, P. Ram, F. H. Pollak, J. L. Freeouf, B. X. Yang, and M. C. Tamargo, Phys. Rev. B **56**, 4037 (1997).
[7] A. H. Rodríguez, C. Trallero-Giner, S. E. Ulloa, and J. Marín-Antuña, Phys. Rev. B **63**, 125319 (2001).
A. H. Rodríguez, C. R. Handy, and C. Trallero-Giner, J. Phys.: Condens. Matter **15**, 8465 (2003).
[8] J. L. Merz, S. Lee, and J. K. Furdyna, J. Cryst. Growth **184/185**, 228 (1998).
[9] O. Madelung (Ed.), Semiconductors–BasicData, 2nd ed. (Springer, Berlin, 1996).