

Intersubband absorption in CdSe/Zn_xCd_yMg_{1-x-y}Se self-assembled quantum dot multilayers

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The authors report the observation of intersubband absorption in multilayers of CdSe/Zn_xCd_yMg_{1-x-y}Se self-assembled quantum dots. The samples were grown by molecular beam epitaxy on InP substrates. For samples with the CdSe dot layers doped with Cl and with the deposited CdSe equivalent layer thickness between 5.2 and 6.9 ML, peak absorption between 2.5 and 3.5 μm was observed. These materials are promising for intersubband devices operating in the mid- and near-infrared ranges. © 2007 American Institute of Physics. [DOI: 10.1063/1.2679783]

The study of self-assembled semiconductor quantum dots (QDs) has attracted much attention due largely to the anticipation that devices (lasers and detectors) made from these materials may yield improved performance.¹ Recently, there has been a great deal of interest to study intersubband (ISB) absorption in QDs and to fabricate ISB devices, such as infrared photodetectors (IPs) with QDs. Compared to IPs made of quantum wells (QWs), QD IPs promise two major advantages. The first is that due to the three-dimensional confinement of carriers in a QD, QD IPs in principle may respond to normal incident light, although experimentally the results are not always consistent, with reports that in many QD systems the absorption is strongly polarization dependent. The second is that the existence of the phonon bottleneck effect² in QDs greatly reduces the electron-phonon interaction. Photoexcited carriers would therefore be more efficiently swept away as photocurrent before relaxing to the ground state. Most of the work reported so far has been performed on In(Ga)As QDs.³⁻⁸ Very recently, ISB absorption in GaN/AlN QDs has been studied for fabricating QD IPs in the fiber-optics communication wavelength region.⁹

In this letter, we report ISB absorption in CdSe/Zn_xCd_yMg_{1-x-y}Se self-assembled QDs. Zn_xCd_yMg_{1-x-y}Se is a wide band gap II-VI semiconductor that can be grown lattice-matched on InP substrates. By simply changing the CdSe deposition time the size of the QDs can be continuously tuned so as to have the band-to-band emission covering the whole visible spectral range.¹⁰ The size of the CdSe QDs can also be modified by changing the Mg concentration in the Zn_xCd_yMg_{1-x-y}Se barrier layer.¹¹ The large conduction band offset in the material system may

allow us to fabricate ISB devices, such as QD IPs, in the mid- and near-infrared ranges. Although CdSe QDs have been previously grown with various barrier layers, such as ZnSe,¹²⁻¹⁴ Zn_xMn_{1-x}Se,¹⁵ and Zn_xBe_{1-x}Se,¹⁴ to date there has been no report on the experimental observation of ISB absorption in CdSe QDs self-assembled on any kind of barrier material, including Zn_xCd_yMg_{1-x-y}Se.

The samples were grown by molecular beam epitaxy (MBE) on (001) semi-insulating InP substrates in a dual-chamber Riber 2300P MBE system. After the removal of the oxide layer under an As flux and the growth of a 0.15 μm InGaAs buffer layer in the III-V growth chamber, the samples were transferred through the vacuum modules to the II-VI growth chamber. There, the InGaAs surface was exposed to a Zn flux for 20 s followed by the growth of a 10 nm low-temperature Zn_xCd_{1-x}Se buffer layer at 200 °C. After these steps, which are needed for adjusting the III-V and II-VI interfaces to improve the material quality of the epitaxial layers, the substrate temperature was raised to 300 °C to grow the subsequent layers. A 60 nm Zn_xCd_{1-x}Se buffer layer was grown before the growth of the multilayer stacks of CdSe/Zn_xCd_yMg_{1-x-y}Se QDs. Three samples with 50 repeats were grown for this study. In all three samples, the Zn_xCd_yMg_{1-x-y}Se barrier layer thickness is 18 nm. The band gap of the Zn_xCd_yMg_{1-x-y}Se barrier is about 3.0 eV at 77 K as determined from separate calibration layers. Samples A and B have identical structures except that sample A is undoped while in sample B the CdSe QD layers were doped with Cl (using ZnCl₂ as dopant). The nominal CdSe thickness deposited for samples A and B is 1.56 nm, corresponding to 5.2 ML. For sample C, CdSe QD layers with a nominal deposited thickness of 6.9 ML were also doped with Cl. The actual dot sizes are unknown. From atomic force microscopy (AFM) measurement results on uncapped QDs, the

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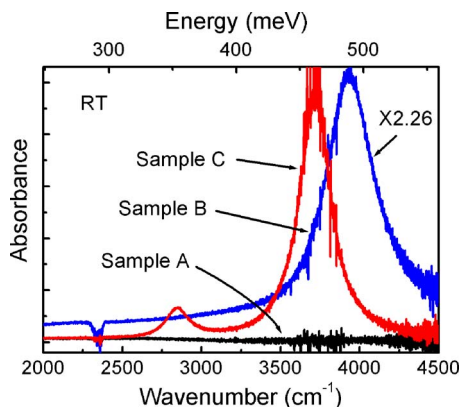


FIG. 1. (Color online) Absorbance of CdSe/ZnCdMgSe QD multilayer stacks measured by FTIR at RT.

height of the dots can be inferred to be in the range between 2.5 and 4.5 nm while the lateral size is between 30 and 60 nm.

If we assume that the Cl doping efficiency in CdSe is approximately the same as that in ZnCdSe, the two-dimensional (2D) carrier densities in samples B and C are estimated to be about 3×10^{11} and $4 \times 10^{11} \text{ cm}^{-2}$, respectively. (Doping calibrations were done with ZnCdSe layers which can be grown lattice matched on InP.) The 2D doping density mentioned here is the sheet density that would be spread evenly in the material if the CdSe were grown two dimensionally. However, AFM measurement results on uncapped QDs show that the QDs only cover a few percent of the surface area. Therefore, the actual carrier density in the QDs is expected to be much higher, more than one order of magnitude higher than the values mentioned above.

The samples are capped with 25 nm $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ layers. We note that for In(Ga)As QDs grown on GaAs substrate, only a limited number of the multilayer stacks can be grown due to the buildup of strain in the layers. In our material system, we can grow a much larger number of repeats by using the strain-compensation technique.

Intersubband absorption measurements were performed using a Nicolet Nexus-870 Fourier transform infrared (FTIR) spectrometer equipped with a liquid nitrogen cooled HgCdTe detector. Samples were fabricated to the waveguide geometry with parallel 45° facets. Figure 1 shows the absorbance of the three samples at room temperature. The spectra were obtained by taking the ratio of *p*-polarized spectra over *s*-polarized spectra. For sample A, which is undoped, no absorption features were observed. An absorption with a peak at $2.54 \mu\text{m}$ (0.49 eV) was observed for sample B. Lorentzian line fitting of the absorbance spectrum yields a full width at half maximum (FWHM) of 46 meV. The narrow linewidth ($\Delta\lambda/\lambda_p \sim 9.4\%$) is an indication of a relatively uniform distribution of dot sizes. For sample C, two absorption peaks were observed: at $2.69 \mu\text{m}$ (0.46 eV) with a FWHM of 29 meV ($\Delta\lambda/\lambda_p \sim 6.3\%$) and at $3.51 \mu\text{m}$ (0.35 eV) with a FWHM of 20 meV ($\Delta\lambda/\lambda_p \sim 5.7\%$). There are several possible explanations for the origin of the two peaks observed in sample C, including (1) the presence of a bimodal size distribution of the QDs and (2) the existence of transitions involving more than two energy levels in the QDs. If we assume that the two peaks originate from a bimodal size distribution, we would expect to see two emission peaks in the photoluminescence (PL) spectra. Therefore PL measure-

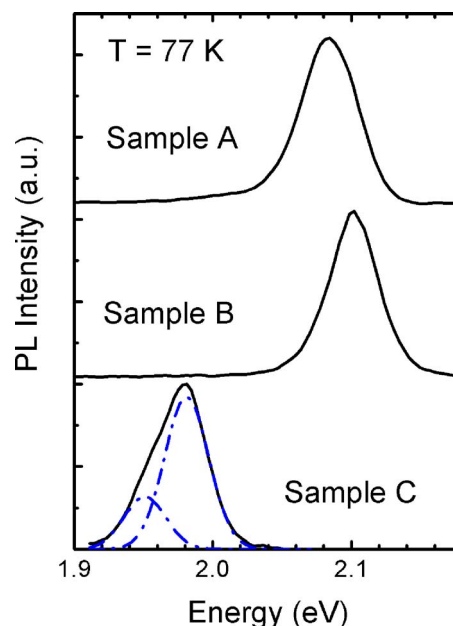


FIG. 2. (Color online) PL spectra of three CdSe/ZnCdMgSe QD multilayer stacks measured at 77 K.

ments were made to help clarify the possible origin of the two absorption peaks.

Figure 2 shows the PL spectra for the three samples measured at 77 K. Comparing the PL spectra of samples A and B to that of sample C, the emission energy of C shifts to lower energy as a result of increased dot size, which is consistent with our previous observations.¹⁰ Although samples A and B were grown under the same growth condition with the same structure, except for the doping of the QDs, the emission energy of sample B is slightly higher than that of sample A. This may be due to a slight effect of the presence of Cl on the CdSe dot size. Besides being shifted to lower energy, the PL spectrum of sample C is asymmetric and can be deconvoluted into two Gaussian peaks (shown by the dash-dotted lines) with 30 meV separation. Although the origin of the second PL peak is not clear at present, it cannot be related to the two absorption peaks in sample C, which are separated by 110 meV. In fact, if the two absorption peaks of sample C were due to two different QD sizes, the smaller size QDs of sample C (with ISB absorption at 0.46 eV) would be similar in size to the QDs of sample B (with ISB absorption at 0.49 eV). Thus, we would expect to see a PL peak for sample C at approximately the same energy as the peak in sample B. The absence of a PL peak for sample C at a position close to the PL emission energy of sample B argues against the possibility that the two absorption peaks originate from a bimodal size distribution. On the basis of this argument, we attribute the presence of the two absorption peaks in sample C to the existence of transitions involving more than two levels within the dots.

For sample C, we tentatively assign the absorption peak at 0.35 eV (Fig. 1) to the transition from the ground state ($n=1$) to the first excited state ($n=2$) and the peak at 0.46 eV to the transition from the first excited state ($n=2$) to the second excited state ($n=3$). As mentioned in the discussion on growth, the base of the QDs is much larger than their height. In fact, we will show later that the polarization behavior of the absorption is QW-like. Due to the QD shape, we may make a rough estimate of the energy levels in the

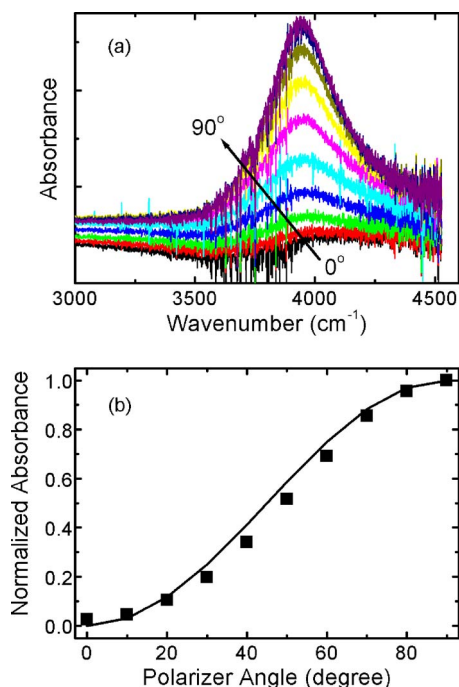


FIG. 3. (Color online) (a) Absorbance of sample B measured at RT at different polarization angles; (b) peak absorbance as a function of polarization angle. Solid line is the plot of the $\sin^2 \theta$ function.

QDs by using the well-established calculation methods for QWs. For sample B with smaller dots (with dot height of about 2.6 nm), only two confined energy levels exist in the well, while for sample C with bigger dots (with dot height of about 3.4 nm), there are three energy levels. The relatively heavy doping in the dots (approximately 500 electrons per dot, corresponding to an equivalent sheet density of about $1 \times 10^{13} \text{ cm}^{-2}$) may make the $n=1$ level fully populated with electrons and the $n=2$ level partially populated. Further experiments, such as temperature-dependent ISB absorption measurements and photoresponse (photocurrent) measurements, may help us better understand the origin of the two absorption peaks observed in sample C.

The absorption peaks observed in both samples B and C are strongly polarization dependent. Figure 3(a) shows the absorbance spectra of sample B measured at different polarization angles, from $\theta=0$ to $\theta=90^\circ$ with an increment of 10° . $\theta=0$ corresponds to s -polarized light, $\theta=90^\circ$ to p -polarized light. The normalized peak absorbance is plotted in Fig. 3(b) as a function of the polarization angle. The absorbance varies with the angle following the $\sin^2 \theta$ relationship (solid line in the figure), which is typical for ISB absorption in QWs.¹⁶ A strong polarization dependence of ISB absorption in QDs has been previously observed in Ge (Ref. 17) as well as GaN/AlN (Ref. 9) QD systems. We explain such polarization dependence as due to the relatively large lateral size (30–60 nm) of our dots: the confinement of electrons is mainly in the growth direction, which makes the ISB absorption QW-like. Because of the large lateral size of the dots, even if there were transitions arising from lateral confinement, the absorption from those transitions would appear at a very long wavelength range due to the close separation of the energy levels. Taking conservatively the lateral size of 30 nm, a simple estimate will predict absorption to

s -polarized light in the 10–20 meV range. This is the range where absorption from free carriers and phonons dominates, which makes the observation of the ISB absorption very difficult. Aslan *et al.*¹⁸ have reported that in InAs/GaAs QDs the ISB absorption is dominated by p polarization in the midinfrared region, while the s -polarized response appears at longer wavelength. The phenomenon that, depending on the base-to-height aspect ratio of a QD, p - and s -polarized responses would appear in different spectral regions has been theoretically addressed by Zhang and Galbraith.¹⁹ In order to observe the absorption of s -polarized light for our QDs, we would need to reduce significantly the lateral size of the dots.

In summary, we have grown stacks of CdSe/Zn_xCd_yMg_(1-x-y)Se QD multilayers with 50 repeats by MBE on InP substrates. We report the observation of ISB absorption in this II-VI QD system. For samples with the QD layers doped with Cl, ISB absorption in the 2.5–3.5 μm spectral range is observed. Two absorption peaks were observed in the sample with larger QDs, which we attribute to transitions involving more than two energy levels in the dots. The ISB absorption is polarization dependent. To obtain ISB absorption with s -polarized light, QDs with smaller lateral size would need to be fabricated. These materials are of interest for fabricating ISB devices operating in the mid- and near-infrared regions.

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