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Polarized photoluminescence and time-resolved photoluminescence from single CdS nanosheets

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We have utilized polarized low temperature photoluminescence (PL) to probe the electronic states and structural symmetries of individual CdS nanosheets. High resolution transmission electron microscopy measurements indicate highly crystalline material with different nanosheets exhibiting significant variations of the direction of the c axis, which are consistent with polarization measurements of PL from single CdS nanosheets. The quality of the nanosheets is reflected in measurements of exciton lifetimes of ~ 200 ps, a value significantly longer than observed for CdS nanowires whose diameter is the same as the thickness of these nanosheets, but shorter than that observed in bulk crystals. © 2008 American Institute of Physics. [DOI: 10.1063/1.2907507]

The spatial confinement of carriers in many nanoscale semiconductor structures makes them highly attractive because of their unusual optical and electrical properties. Semiconductor nanosheets (NSs) are particularly appealing because while they have one dimension in the nanoscale range, their other two dimensions are in the micrometer range making them easier to incorporate into existing or new optoelectronic device structures.^{1–9} NSs now form the basis for a number of optoelectronic devices including field effect transistors and light emitting diodes.^{1,5,6,9} The rapid development of applications for NSs, including CdS NSs, indicates that even more striking uses for these novel nanostructures might be possible if growth conditions were optimized and their electronic states and structural symmetries understood.

In this letter, we demonstrate that low temperature polarized micro-photoluminescence (micro-PL) is a powerful method that can be used to determine the c axis of CdS single NSs. In addition, time-resolved PL measurements provide a characterization of both the quality and the low surface recombination velocity of these single NSs, measures that are important for potential applications. As we will show, high resolution transmission electron microscope (HR-TEM) images provide evidence that the NSs are single crystalline with hexagonal wurtzite structure. Time-resolved PL measurements give exciton recombination lifetimes of ~ 200 ps which are significantly longer than that of the near band edge emission recently observed in single CdS nanowires (< 50 ps),^{10,11} but shorter than the lifetimes observed in bulk CdS crystals.

The catalyst-assisted vapor phase transport growth method was used to grow the CdS NSs.¹² The size and shape of the NSs are quite uniform with individual NSs ~ 5 μm in width, ~ 40 – 50 nm in thickness, and up to several tens of micrometers in length, all dimensions much larger than the

CdS Bohr radius (3 nm) and thus no quantum confinement effects are expected.

To measure single structures, the NSs were dispersed from the growth substrate into an ethanol solution and then deposited onto either a silicon substrate or a TEM microgrid, resulting in a dilute array of NSs with an average separation of hundreds of micrometers. The crystallinity and structure of individual CdS NSs were investigated by HR-TEM. Figure 1(a) shows the end of a CdS NS, with an enlarged image of the region noted by the square box. The prominent wrinkling of the NS surface in the large-field image may be indicative of strain resulting from the Van der Waal's forces which hold the NS flat to the substrate. The HR-TEM image in the lower inset of Fig. 1(a) shows a highly crystalline wurtzite structure with the c axis approximately perpendicular to the long axis of the CdS NS. Figure 1(b) shows a different CdS NS of similarly highly crystalline wurtzite structure, however, with the c axis not perpendicular to the long axis of the NS.

Low temperature PL measurements were taken either with a cw argon ion laser or with a 200 fs, 432 nm frequency-doubled Ti-sapphire mode-locked laser. The NSs dispersed on a Si substrate are placed onto the cold finger of a continuous-flow helium cryostat. A $50\times/0.5\text{NA}$ (numerical aperture) long working length microscope objective was utilized for both illumination and collection of the PL from a single NS. The polarization of the excitation could be controlled and the emitted PL analyzed using a matched set of Glan-Thomson linear polarizers and Babinet-Soleil compensators. The PL was dispersed by a triple spectrometer working in subtractive mode, and detected either by a 2000×800 pixel liquid nitrogen-cooled charge-coupled device detector for cw measurements or a fast microchannel plate phototube for pulsed measurements. Time resolution was obtained using time-correlated single photon counting techniques.¹³ The temporal system response was measured to be < 80 ps, and the optical resolution and laser focal spots were 1.5 μm . All measurements were conducted at 15 K.

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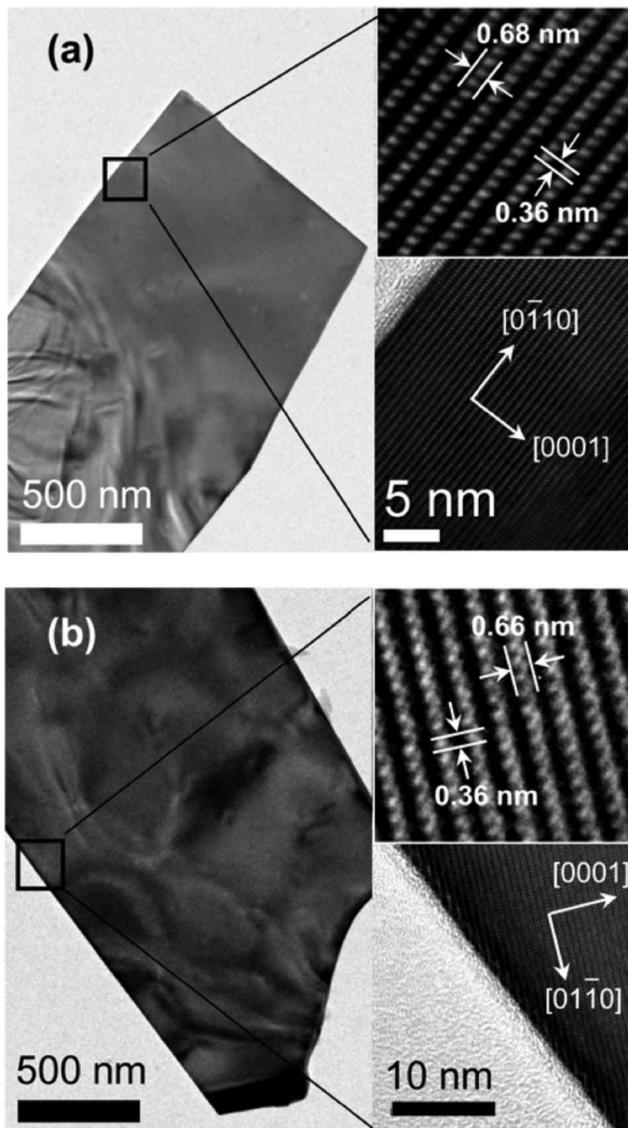


FIG. 1. Low and high magnification TEM images of two different CdS NSs. Insets to figures on right side show the HR-TEM image of the NS with fast Fourier transformation images. Note that the crystallographic c axis is not always perpendicular to the long axis of the NS.

In Figs. 2(a) and 2(b), we show typical low temperature cw PL spectra of two different single CdS NSs. Spectra were measured with the excitation laser circularly polarized, while the emission passed through a linear polarization analyzer at different angles measured from 0° (0° is alignment parallel to the long axis of the NS). The spectra are characterized by a relatively narrow peak at 2.547 eV [full width at half maximum (FWHM) ~ 4 meV] and a much broader emission near 2.563 eV (FWHM ~ 11 meV). This broader emission peak varies in energy in different NSs and often displays internal structure due to contributions from different exciton states. The known exciton lines for CdS include an A free exciton at 2.553 eV and a B free exciton at 2.569 eV. Two bound exciton states have been recorded in CdS. The narrow peak at 2.547 eV is consistent with the I_{2A} recombination line from an A exciton bound to a neutral donor. The I_{2B} line would result from the B exciton-neutral donor recombination.^{14,15} The energies for these four known states are marked by vertical lines on each of the spectra in Figs. 2(a) and 2(b).

Both free and bound excitons associated with the A - and B -hole bands of wurtzite CdS recombine and emit strongly

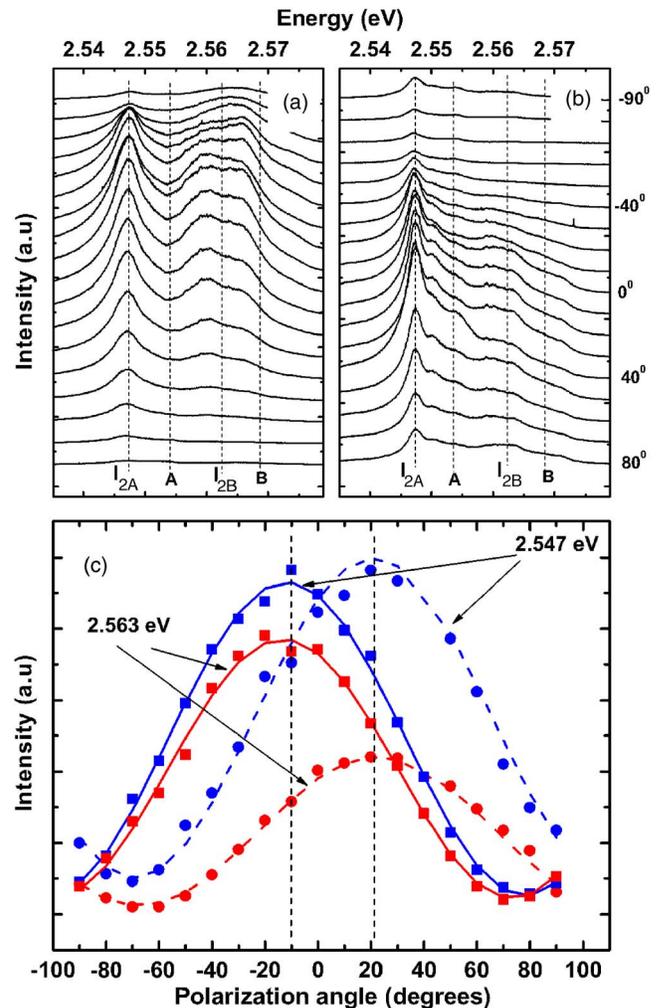


FIG. 2. (Color online) [(a) and (b)] PL spectra of two different CdS NSs. (c) PL intensity as a function of detection angle of the PL emission at 2.547 and 2.563 eV from these two NSs (squares and circles, respectively).

polarized perpendicular to the c axis.^{14,15} Figure 2(c) displays the peak PL emission intensities of the two respective NSs (squares and circles, respectively) at 2.547 and 2.563 eV as a function of the angle of the linear polarization analyzer relative to the long axis of the NS. The red and blue curves are fits to $\cos^2 \theta$. We see that the emission of both peaks is strongly polarized. In the first NS [Figs. 2(a) and 2(c)], the maximum intensity occurs in the direction nearly parallel (-10°) to the NS long axis. For a wurtzite structure, this indicates that the c axis of this particular NS is almost perpendicular to the long axis of the NS. The second NS [Figs. 2(b) and 2(c)], displays a very different polarization response with a peak intensity at about $+20^\circ$ suggesting the c axis in this second NS is 110° from the NS long axis. This result is consistent with the variability shown by the TEM results. This also directly demonstrates that polarized PL measurements provide a convenient nondestructive way in which to determine a NS's crystal orientation.

To gain more insight into the quality of these NSs, we display time-resolved PL at one position centered on a single NS. The NS is excited by 200 fs laser pulses at 432 nm every 13 ns. In Fig. 3(a), the time-resolved PL spectrum of a NS is shown as a two-dimensional (2D) image, plotted in false color on a logarithmic scale with the most intense emission indicated in red. The vertical axis of the map represents

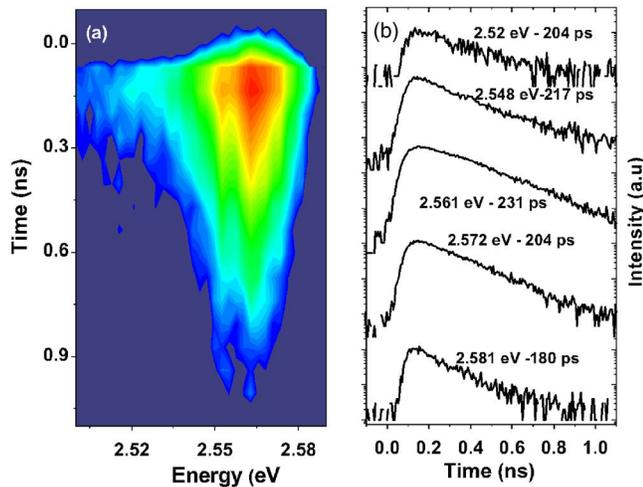


FIG. 3. (Color online) Time-resolved PL obtained from a single NS. (a) A 2D image of time vs energy and (b) time decays of PL taken at different emission energies from (a).

the time after the laser pulse, while the horizontal axis represents the emission energy. In this image, PL emission at energies 2.547 and 2.563 eV (I_{2A} and I_{2B}) are the most intense spectral features.

In Fig. 3(b) time decays are extracted from the time-resolved spectra at several different energies. The I_{2A} and I_{2B} lines exhibit time decays which are single exponential with lifetimes of approximately 200 ps. This lifetime is somewhat shorter than that measured in bulk CdS (500 ps–1 ns),^{16,17} but significantly longer than the near band edge emission observed in single CdS nanowires (<50 ps).¹⁰ These long lifetimes are a reflection of the quality of these CdS NSs.

In conclusion, we have shown that catalyst-assisted vapor phase growth of CdS NSs with large width-to-thickness aspect ratios results in high quality hexagonal wurtzite single crystals, as is reflected in the HR-TEM measurements. These NSs display intense near band edge emission A- and B-related exciton emission. Time-resolved measurements reveal 200 ps lifetimes, which are much longer than CdS nanowires whose diameters are the thickness of these NSs, but somewhat shorter than those observed in bulk crystals (up to

1 ns). This suggests that future passivation of the NS surfaces may result in even higher quantum efficiencies. Polarization-resolved PL measurements show strongly polarized emission which reflect recombination selection rules for the wurtzite band symmetries. In particular, we find that analysis of the polarized emission axis can rapidly reveal the orientation of the c axis within single NSs. We have demonstrated that the use of polarized spatially resolved spectroscopy can be important in efforts to optimize growth of these NSs to obtain highly reproducible materials which is essential for future application development.

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