Excitons and surface luminescence of CdS nanoribbons

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The morphology and optical properties of CdS nanoribbons were studied by transmission electron microscopy and photoluminescence spectroscopy. The wurtzite-structured nanoribbons have a uniform rectangular cross section and grow along the [120] crystallographic direction. They are enclosed by small indice surfaces and have a highly perfect crystalline interior, free of extended defects. Luminescence peaks assigned to free and bound excitons were observed from these nanoribbons at low temperatures. In addition, a surface related luminescence band was also identified, showing that the proximity of unpassivated surfaces does not lead to dissociation of excitons in CdS nanoribbons of high purity and structural quality, even when their thickness is around 20 nm. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1644625]

The richness of fundamental phenomena as well as the potential applications in nano-technologies has raised rapidly growing interests in nano-dimensional materials. Quasi-one-dimensional (1D) nano-semiconductors in the form of nanowires and nanoribbons have recently been successfully fabricated in many laboratories and by many methods.[1] Among these, CdS is of considerable importance in optoelectronic applications because of its band gap energy, which happens to be in the visible. Photoluminescence (PL) of bulk CdS crystals was studied in detail a long time ago.[2] At room temperature, a single broad green emission peak was observed. The richness of its emission spectrum is only revealed at low temperatures. Through these studies the origins of a variety of exciton complexes and impurity centers had been identified.[3–5] As the dimensions of the structures shrink, the effects of surface states on their electronic properties become progressively significant. This is particularly so for free standing quasi-1D structures as their interior is inevitably close to the enclosing surfaces in the other two dimensions. Furthermore, these surfaces are often oxidized, if not during growth, by exposure to ambient afterwards. For quasi-two-dimensional structures like quantum wells and quasi-zero-dimensional quantum dots, surface roughness and charges are known to affect the luminescence spectra in many ways.[6,7] We show in this letter that the unpassivated surface of highly crystalline CdS nanoribbons does not prohibit the formation of excitons, even when their thickness is reduced down to as little as 20 nm.

The CdS nanoribbons were grown by simple thermal evaporation process using CdS powder. The experimental setting was described elsewhere.[8] The products show a belt-like morphology with an average width of hundreds of nanometers, and length in the range of several tens of micrometers. The general morphology and crystallinity of the products were examined by scanning electron microscopy (LEO 1450VP) and x-ray diffraction (Rigakau RU-300 with Cu $K\alpha$ radiation). Detailed microstructure analysis of the

products was investigated by transmission electron microscopy (TEM) using a Tecnai 20 microscope operating at 200 kV. The cross-sectional TEM sample was prepared using Microtome. Temperature dependent PL spectra were measured from the CdS nanoribbons mounted on a cold finger in a continuous cycle cryostat using the 325 nm line of a HeCd laser. The excitation power density amounts to about 500 W/cm^2 and the emitted light was collected by lenses and dispersed by a 0.75 m Spex 1702 spectrometer equipped with a 1200 l/mm grating. The spectral resolution of the spectrometer was set at 250 μeV in all measurements. To more accurately extract the peak positions the obtained spectra were fitted with Gaussian peaks.

Figure 1(a) shows a typical CdS nanoribbon lying on a carbon grid. The high-resolution image of the same nanoribbon was taken with the electron beam along the CdS [100] zone axis, as shown in Fig. 1(b), revealing the hexagonal structure of the nanoribbon. The Fourier transform of the high-resolution image is shown in Fig. 1(c), demonstrating the [120] crystalline direction as the growth direction of the nanoribbons. TEM study of tens of nanoribbons suggests a universal growth direction for them. The nanoribbons' morphology is confirmed by the cross-sectional TEM image shown in Fig. 1(d), which reveals the rectangular cross section of the ribbon. Although most of the nanoribbons have a thickness of ~20 nm, a small portion of them have widths less than 10 nm [Fig. 1(d), inset]. Figure 1(e) is the high-resolution image of a part of the cross-section area. The Fourier transform [Fig. 1(f)] of the high-resolution image reveals a two-dimensional symmetry similar to those projected from the CdS [120] zone, further confirming [120] as its growth direction. The exact shape of the nanoribbon can be deduced from the above results, i.e., nanoribbon with rectangular cross section, the termination surfaces [Fig. 1(g)] of the nanoribbons are the (002), (010) and ($2\bar{1}0$) crystalline planes, respectively. There is a thin amorphous layer, most likely an oxide, less than 1 nm thick, that covers these surfaces.

The temperature dependent PL spectra of the nanoribbons are shown in Fig. 2. Many more peaks of higher energies emerge in the low temperature spectra than in the room

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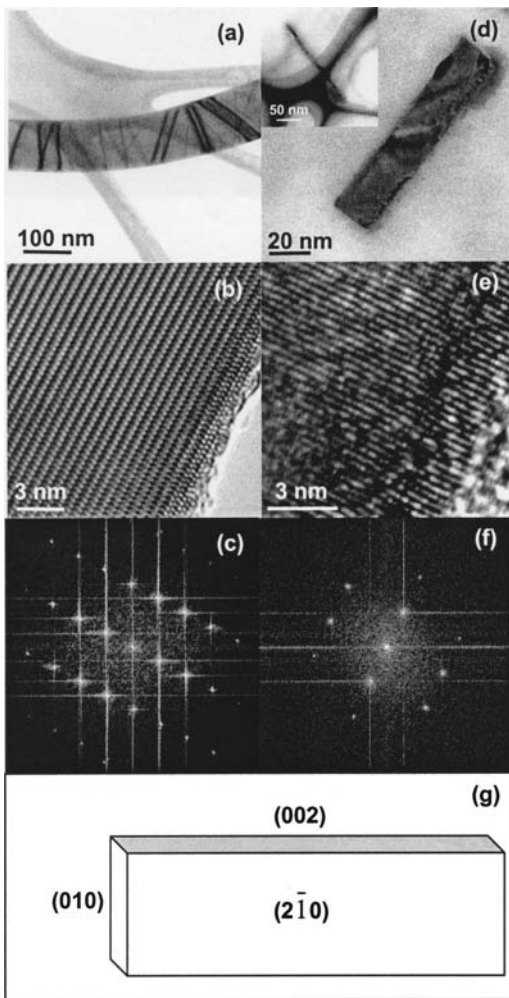
FIG. 1. (a) Low-magnification TEM image of one nanoribbon; (b) the high-resolution image of the same nanoribbon; (c) the Fourier transform of the high-resolution image in (b); (d) The cross-sectional TEM image of the nanoribbon; (e) the high-resolution image of the cross section of CdS nanoribbon; (f) the Fourier transform of the high-resolution image shown in (e); (g) schematic showing the facets of the CdS nanoribbon.

FIG. 2. Temperature dependent PL spectra of CdS nanoribbons (T = 10, 30, 40, 60, 80, 100, 150, 190, 300 K from top to bottom); inset expands the high energy region of a few low temperature spectra.

temperature spectrum. Below 40 K, we see several sharp peaks riding on top of a broad background. Some of them can be readily assigned to known centers by their characteristic energies and line shapes. At 10 K, the two most intense peaks are the I_2 at 2.545 eV and the I_1 at 2.534 eV. They have been assigned to excitons bound to neutral donors and acceptors.[9] There is another peak I_3, assigned to excitons bound to ionized donors, whose presence becomes more obvious in the slightly higher temperature spectra. As temperature rises, donors become increasingly ionized, resulting in a drop of the intensity of I_2 and the emergence of I_3. Since I_3 only appears as a higher shoulder to the broadened I_2, its emission was obtained by fitting to be at 2.550 eV, in agreement with accepted I_3 energy.[2] Unresolved free exciton related peaks are also observed (Fig. 2, inset; labeled as X) at about 15 meV higher than the I_3 peak.[10] The presence of exciton emissions in the nanoribbons, particularly that of the free excitons, shows that they are of high purity and free of extended internal defects. The proximity of oxidized surfaces does not seem to dissociate the excitons, partly because there are few dangling bonds on the small index surfaces and partly because of the rather tight binding energy of excitons
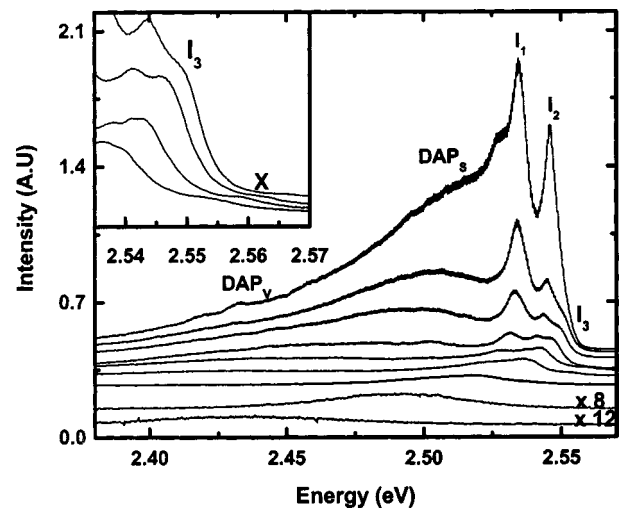
(~ 28–30 meV).[10] In fact, the surface of nanoribbons is barely oxidized compared to that of the nanowire counterparts, because of the regular low-index terminating surfaces. Nanowires usually possess a circular cross section without well-defined terminating surfaces and have a ~ 3 nm oxidized layer. However, we should remark that the widths of the exciton peaks of the nanoribbons are generally wider than those of high quality bulk CdS crystals.[2] In a nanoribbon, the radiative centers are never too far from the influence of the surrounding surface. Fluctuations in the surface charge density and local fields result in the inhomogeneous broadening of exciton peaks.[11] The influence of surface on the PL spectra is also revealed by the broad asymmetric emission background from roughly 2.35 to 2.52 eV. Similar emissions had been observed in the PL of thin CdS platelets and identified as originating from surface donor acceptor pair (DAP) recombinations.[12] The maximum of the DAP emissions is known to shift towards higher energy with increased excitation power density. The confirmation of this in our experiment allowed us to attribute the broad background in our spectra to surface luminescence. Just barely discernable in the figure, there are some small spectral modulations on the
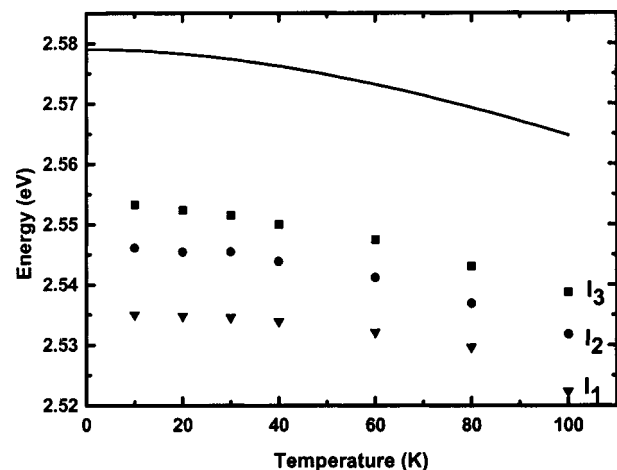

FIG. 3. Temperature dependence of the photon energies of bound exciton peaks in CdS nanoribbons. The solid line is A band gap data from Ref. 10.

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low energy tail of DAP luminescence, two of which around 2.418 and 2.432 eV are readily identifiable, as they are replicated, essentially without any shift, in every spectra obtained below 80 K. They are tentatively attributed to unresolved donor acceptor pair (DAP_V) emissions within the volume of the nanoribbons.[13] The other small modulations are probably caused by the phonon replicas of the various exciton peaks, since they are known to exhibit many phonon sidebands[14] due to the strong exciton-phonon coupling. Assuming the DAP_V emissions are from distant pairs, the binding energy of the acceptor in the pair is estimated from the photon energy, the typical donor binding energy of 33 meV and the accepted band gap of 2.582 eV to be about 117 meV. Therefore, the acceptor is different from the one that is associated with the I_1 emission. Deep acceptors are known to exist in CdS and are responsible for various emission peaks from 2.37 to 2.42 eV in the luminescence spectrum.[15] As temperature rises, the exciton peaks redshift and lose intensity. Above 100 K, they are no longer discernable. Figure 3 shows the temperature dependence of the photon energies of the bound exciton peaks and the energy of the A band gap.[10] It is seen that the exciton peaks essentially track the band gap. We should remark that quantum confinement induced energy shifts of the exciton peaks in our CdS nanoribbons are too small to be detected because the smallest typical dimension (thickness) still far exceeds the exciton radius. At room temperature only a broad peak centered at 2.43 eV is seen. This peak is attributed to the luminescent transitions involving deep levels resulting from vacancy related complexes in CdS crystal by various studies.[16,17] Its position and shape were often found to depend on the method of crystal growth.

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