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Cathodoluminescence variation of a single tapered CdS nanowire

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ABSTRACT

Cathodoluminescence (CL) spectra are taken from the spots with different diameters on a single tapered CdS nanowire to investigate the size-dependent surface effects. Strong deep level (DL) emission is detected at the spots with small diameter, and the intensity ratio of deep level (DL) to the near band gap emission (NBE) emission is gradually enhanced with shrinking diameter. The experimental results demonstrate that surface effects strongly modulate the luminescence of the tapered nanowire and dominate the DL emission in the tapered nanowire. The CL spectra of a single straight nanowire with uniform diameter are also studied. The straight nanowire only exhibits perfect luminescence properties with NBE emission centered at 511 nm, revealing that surface effects do not affect the straight nanowire with relatively large and uniform diameter.

1. Introduction

As a classic I–IV group semiconductor, one-dimensional (1D) CdS nanowires have been excellent candidates for nano-based electronic and optoelectronic applications for nanogenerators, waveguides, photoconductors, logic gates, field emitters, solar cells and thermoelectronics because of the direct band gap of 2.4 eV, the quantum confined electron energy state and high surface-to-volume ratio [1–11]. CdS nanowires usually exhibit both near band edge (NBE) emission and deep level (DL) emission. Up to now, most works have been focused on the synthesis of CdS nanowire and investigated origin of NBE and DL emission in CdS nanowire bulks [12–17]. Nevertheless, considering the nanowire bulks are of different diameter, morphology and/or chemical composition, this will arouse confusion to the studies of true origin of the luminescence properties. So, investigating luminescence properties on an individual nanowire can effectively eliminate the variance and average effect in CdS nanowire bulks, and illuminate origin of NBE and DL recombination indeed. Some literatures investigate luminescence properties of a single CdS nanowire and suggest some probable mechanism for the luminescence in the single CdS nanowire [18–20]. However, as far as we know, how the luminescence properties are affected by shrinking diameter is still quite limited. Here, we present cathodoluminescence (CL) studies on a single tapered CdS nanowire with shrinking diameters from bottom to top. CL spectra are taken from the spots with different diameters on a single tapered nanowire. The experimental results demonstrate that surface effects strongly modulate the luminescence of the tapered nanowire and dominate the DL emission in the nanowire. Moreover, CL spectra of a single straight CdS nanowire with uniform diameter are still studied, which indicates that the surface effects cannot arouse the DL emission in the straight nanowire.

2. Experimental

The tapered and straight CdS nanowires were synthesized by well-known thermal evaporation method using high-purity CdS powders as source materials. Details of the preparation were described elsewhere [21,22]. For the CL studies, as-synthesized CdS nanowires are scratched off the Si substrates and transferred onto cleaned silicon wafer. The dispersion quality and morphologies are observed by scanning electron microscopy (SEM), and CL measurements of a single nanowire are performed on an Oxford Instruments MonoCL2 spectrometer attached in the SEM. The resolution of the CL instrument is 0.5 nm. The focused electron beam was scanned over the surface, and the emitted light was collected with a parabolic aluminum mirror and guided to the slit of a grating monochromator with a focal length of 20 cm. The measurement was conducted at an accelerating voltage of 10 kV and probe current of 200 pA.

3. Results and discussion

Fig. 1a and b shows the SEM and CL images of a single tapered CdS nanowire, respectively. The length exceeds ca. 5 μm and the diameter gradually shrinks from ca. 250 nm to 100 nm, which facilitates to investigate surface effects on a single nanowire. The CL image (Fig. 1b) indicates that CL emission of the single tapered nanowire is gradually weak from bottom to top. To study the surface effects, CL spectra are collected at spots with different diameters on the single nanowire. As seen from Fig. 1a, four spots are marked with black arrows and numbered with 1–4 in descending diameter order. Fig. 2a shows the CL spectra taken from these

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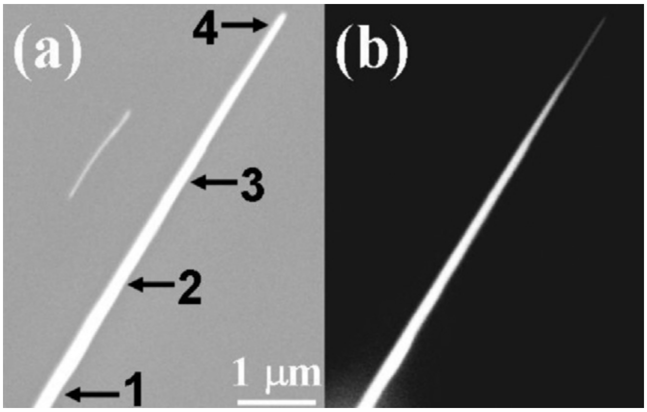

Fig. 1. (a) SEM and (b) panchromatic CL image of a single tapered nanowire.

spots, indicating sharp and strong NBE emission in these four spots. Moreover, the intensity of NBE emission decreases with shrinking diameter and obvious DL emission at 765 and 766 nm collected from spot 3 and 4 are observed, respectively. To more easily compare integral intensity ratio of DL(I_{DL})/NBE(I_{NBE}) and NBE emission peak position, normalized CL spectra to the NBE emission peaks are presented, as shown in Fig. 2b. I_{DL}/I_{NBE} increases from 0 to 0.59 with shrinking diameter and I_{DL} increases notably faster, indicating that DL emission becomes more dominant at spots with small diameter. Generally, the origin of DL emission is related to the bulk defects, intrinsic point defects and/or surface defects. Nevertheless, well crystalline wurtzite lattice is clearly seen in the HRTEM image of tip of the nanowire, as shown in Fig. 2c. No obvious bulk defects such as dislocations, stacking faults and twinning defects are observed, indicating the well crystalline quality of the tip of the tapered nanowire. The corresponding fast Fourier transform (FFT) pattern (inset of Fig. 2c) indicates the nanowire is grown along polar [0 0 0 1]. These results indicate that the effects of bulk defects on the DL emission are negligible.

The local chemical compositions significantly affect the physical and chemical properties of nanostructures. Here, we investigate the chemical compositions of different spots at the single tapered nanowires by EDS. Though EDS measurement just present a semi-quantitative analysis results and these values do not reflect the actual composition of the nanowire, it can offer comparable data on different spots in the same nanowire. The ratio of Cd to S is close to 1:0.8911 and 1:0.8926 at the bottom and top of the nanowire, respectively, which indicates that the chemical composition of the two spots is almost same and intrinsic point defects distribute uniformly along the nanowires or do not exist in the nanowire. The CL spectrum collected from bottom spot 1 only exhibits perfect NBE emission, while that from top spot 4 exhibits strong DL emission. These results demonstrate that intrinsic point defects are not the main reason for the DL emission. So, we deduce that surface effects instead of intrinsic point defects dominate the variation of DL emission with diameter here.

Because the tapered nanowire with a smaller diameter holds a larger surface-aspect ratio, the surface modulation is enlarged and thus the surface effects are enhanced. As for the metastable nanostructures, their surface has high surface energy and holds surplus charges [23,24]. These surplus charges must be eliminated by relaxation, reconstruction or absorption to form stable surfaces, which results in that some surface defects are introduced during surface stabilization process. Because a nanowire with a smaller diameter holds a larger surface-aspect ratio, the more dense defects e.g. surface S vacancies (V_S) are introduced onto the surfaces, which results in the enhancement of the DL emission with shrinking diameter [24,25]. Moreover, tense stress can induce the surface effects. The tense stress is increased with decrease of size of the nanowires. The tense stress-induced surface effects are often encountered in the other tapered nanowires such as ZnO. We further observe that there are blue shifts of the NBE emission peaks recorded at the

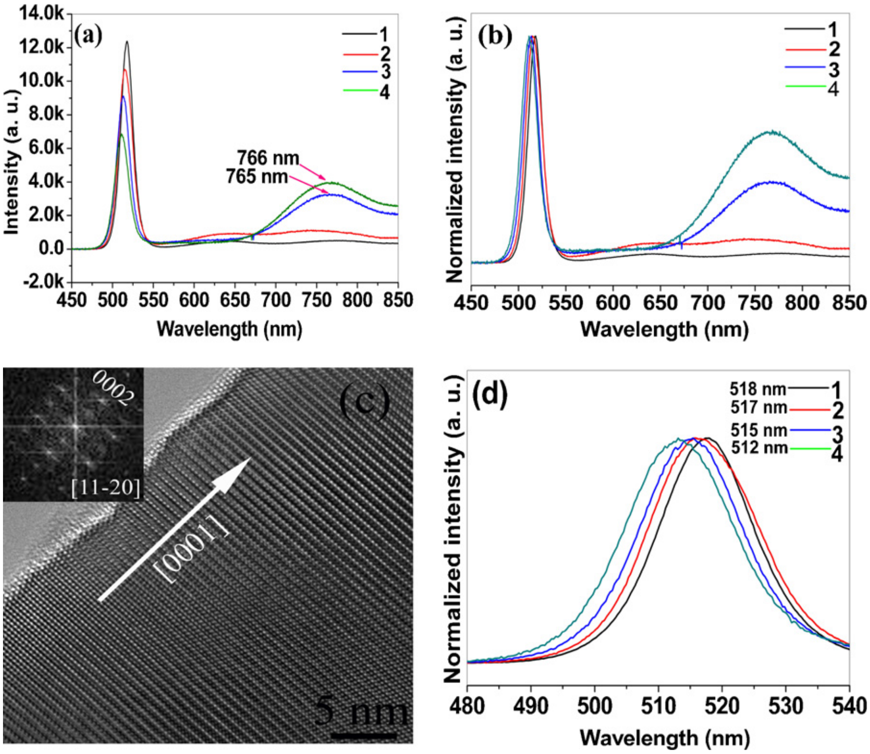

Fig. 2. (a) CL spectra taken from the four spots using arbitrary intensity and (b) intensity normalized to NBE emission peaks. (c) HRTEM image of the tip of the taper nanowire. (d) Normalized CL spectra of enlarged NBE emission taken from the four spots.

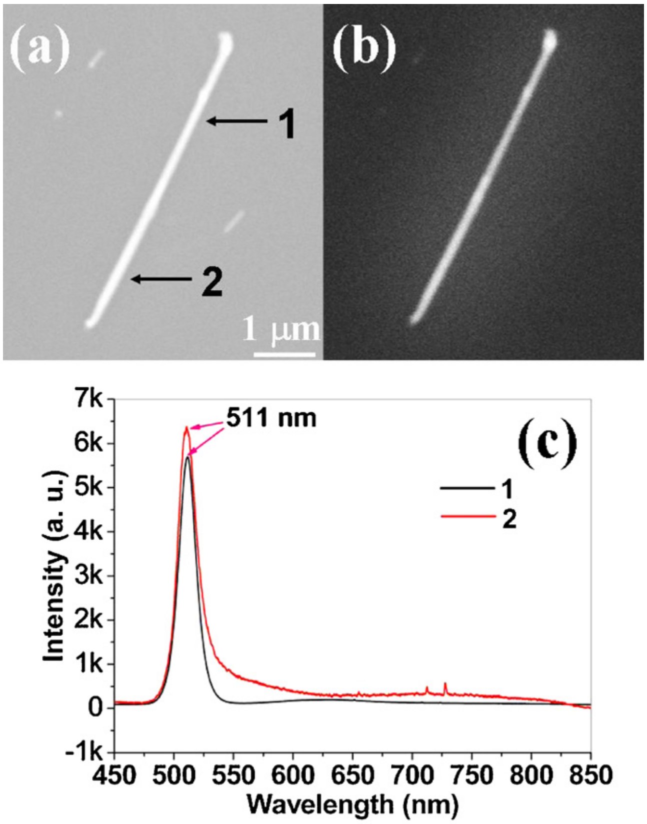

Fig. 3. (a) SEM and (b) panchromatic CL image of a single straight nanowire. (c) CL spectra taken from two spots numbered 1 and 2 in (a).

spots 1–4 where the diameter is descending. The center of the NBE emission is ca. 518, 517, 515 and 512 nm observed at the spots 1–4, respectively. Such size-dependent blue shift of NBE emission is often encountered in ZnO nanowires. This has been attributed to the reduction of the band gap caused by the nano-size confinement and domination of surface excitons [26]. We deduce that the explanation can be applicable for the size-dependent blue shift of NBE emission in the tapered CdS nanowire here.

The CL property of straight nanowire is also investigated, which presents different feature from that of the tapered nanowire. Fig. 3a and b shows the SEM and CL images of the straight nanowire, respectively. The diameter is ca. 100 nm and is uniform along the growth direction. The CL image of the nanowire indicates the intensity of the emission is almost unchanged along the nanowire. Fig. 3c shows the CL spectra taken from the spots 1 and 2 marked in Fig. 3a. Obviously, only strong NBE emission centered at 511 nm appears and no DL emission is detected at both spots 1 and 2. Moreover, size-dependent blue shift of the NBE emission is not observed. These results indicate that surface effects on the straight nanowire do not worked, and the blue shift of the NBE emission is dependent on the variation of the diameter.

4. Conclusions

In summary, luminescence properties of a single tapered CdS nanowire are investigated by CL spectra collected at spots with different diameter. Strong size-dependent surface effects are observed. It is found that perfect luminescence property is detected at spot with relatively large diameter, while DL emission is observed at the spots with small diameter. Integral intensity ratio of I_{DL}/I_{NBE} increases with shrinking diameter and I_{DL} increases notably faster, indicating that DL emission becomes more dominant at spots with small diameter. It is suggested that surface effects strongly modulate the luminescence of the tapered nanowire and dominate the DL emission in the nanowire. The CL spectra of a single straight nanowire with uniform diameter exhibits perfect CL properties with NBE emission centered at 511 nm. No DL emission is detected, revealing that surface effects do not affect the CL properties of the straight nanowire with relatively large and uniform diameter.

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