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Growth-induced Stacking Faults of ZnO Nanorods Probed by Spatial Resolved Cathodoluminescence *

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Low density ZnO nanorods are grown by modified chemical vapor deposition on silicon substrates using gold as a catalyst. We use high resolution photoluminescence spectroscopy to gain the optical properties of these nanorods in large scale. The as-grown samples show sharp near-band-gap luminescence with a full width at half maximum of bound exciton peaks at about 300 μeV, and the ratio of ultraviolet/yellow luminescence larger than 100. Highly spatial and spectral resolved scanning electron microscope-cathodoluminescence is performed to excite the ZnO nanorods in single rods or different positions of single rods with the vapour-solid growth mechanism. The bottom of the nanorod has a 3.31-eV luminescence, which indicates that basal plane stacking faults are related to the defects that are created at the first stage of growth due to the misfit between ZnO and Si.

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Extended defects (i.e., stacking faults, dislocations, etc.) play important roles in crystal growth and device performance.[1] However, it challenging to characterize the defects at nanoscale. To probe the localized defects at nanoscale, transmission electron microscope (TEM),[2−4] scanning capacitance measurements,[5] photocurrent,[6] scanning photocurrent microscopy, etc.[7] have been adopted. Typically, TEM is often utilized by scratching nanorods from substrates, then dispersing them in a solution. After drying the solvent on the TEM grid, nanorods will be characterized to be perfect single crystals.[2−4] However, with this scratch-dispersion method, the information of the interface between the substrate and the initial growth of the nanorod is lost, which could be vital in some specific applications such as ultraviolet (UV) sensors, and defects also could be induced by the sample preparation procedure.[8] In comparison, scanning electron microscope-cathodoluminescence (SEM-CL) is a nondestructive and spatial resolved technique that enables local defects to map in semiconductors.[9−11] By adjusting the acceleration voltage of the scanning electron microscope (SEM), the penetration depth and diffusion of the electrons can be tuned from 50 nm to several micrometers,[12] which means that SEM-CL has better resolution than micro-photoluminescence (PL).[13,14] Therefore, it is convenient to use SEM-CL to probe the defects in nanostructures.[11]

ZnO is a promising semiconductor with wide band gap of 3.37 eV at room temperature, large exciton binding energy (60 meV), pizoelectricity, and good bio-compatible properties.[15] Due to their high surface-to-volume ratio, low cost, and perfect and flexible single crystals that grow on nearly all substrates, ZnO nanostructures become excellent candidates in nanophotonic, sensing and energy harvesting applications.[16−18]

In this work, we grew high-quality ZnO nanorods and then used high spatial and spectral resolved cathodoluminescence spectroscopy to probe the optical properties of ZnO nanorods in detail. A low acceleration voltage (2 kV) was adopted to achieve high spatial and spectral resolution of the cathodoluminescence, thereafter we can gain more information from the nanorods/substrate interface along the growth direction of the ZnO nanorods in detail.

The ZnO nanorods were grown on (100) silicon via a modified chemical vapor deposition (CVD) process using gold as a catalyst. Details of the growth were reported Ref. [19]. The morphology of the ZnO nanorods was examined by scanning electron microscopy (SEM, LEO DSM 982). High-resolution photoluminescence (HR-PL) was performed inside a liquid-He-flow cryostat excited by a He-Cd laser, where a circular spot of some 100 μm diameter is excited. The emitted light was dispersed by a 1-meter monochromator with a 1200 groves/mm grating and recorded by a liquid-nitrogen cooled charge-coupled-device (CCD) camera. The spectral resolution was

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better than 100 μeV. Spatial resolved SEM-CL spectroscopy was utilized to characterize the optical properties of the ZnO nanorods. We utilized 2 kV of the acceleration voltage to excite the single nanorod with a spatial resolution about 50 nm. A monochromator with a focal length of 900 mm and optical grating of 1200 groves/mm was used, the detection was performed by an LN2-cooled CCD camera with 1024×256 pixels. The resolution of the SEM-CL setup is better than 400 μeV.[10]

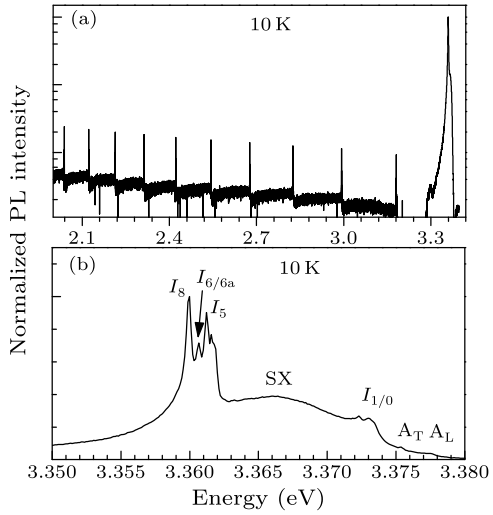

Fig. 1. Low temperature (T = 10 K) PL spectra of the high quality ZnO nanorods (a) in a broad spectral range. (b) In the near-band-gap region showing details of bound and free exciton recombinations.

To probe the optical properties of the ZnO nanorods, PL was performed to gain the basic optical properties of the as-grown ZnO nanorods. Figure 1(a) shows an overview from 2.0 eV to 3.4 eV of the PL spectrum of the ZnO nanorods. We can see that it can be divided into two parts, the near-band-gap range with sharp peaks linked with free and bond excitons, specifically, the ratio between UV luminescence and green (centered at 2.45 eV)/orange (centered at 2.1 eV) luminescence is larger than two orders of magnitude, which demonstrates less copper impurity, zinc vacancies or oxygen vacancies.[22,20] Please notice that the sparks in the spectrum are artifacts created inevitably during the rotation of the grating of the monochromator. Figure 1(b) shows the near-band-edge region of the PL-spectrum, A_L (free A excitons polariton-longitudinal), A_T (free A excitons polariton-transverse), $I_{1/0}$ (excitons bound to ionized donors), SX (surface defects),[21] I_4 (hydrogen donor bound exciton), I_5, $I_{6/6a}$ (Al donor bound exciton), I_8 (Ga donor bound exciton) lines were clearly resolved as compared with the review article by Meyer *et al.*[22] and results from our group.[23] The full width at half maximum (FWHM) of the HR-PL peaks can reach as small as 300 μeV, which indicates the high quality of the ZnO nanorods in large scale.

Figure 2(a) shows the SEM image of the ZnO nanorods after growth. The ZnO nanorods have a length of 5 μm and diameter of about 200 nm with length/diameter ratio larger than 50. Hexagonal facets were observed of the as-grown sample, which illustrates that the growth of the nanorods follows a vapor-liquid-solid (VLS) initiated vapor-solid (VS) growth mechanism.[19] In addition, the hexagonal tips firmly demonstrate the c-direction growth of the nanorods, and the ZnO nanorods have uniform diameters during growth, except for at the very beginning.

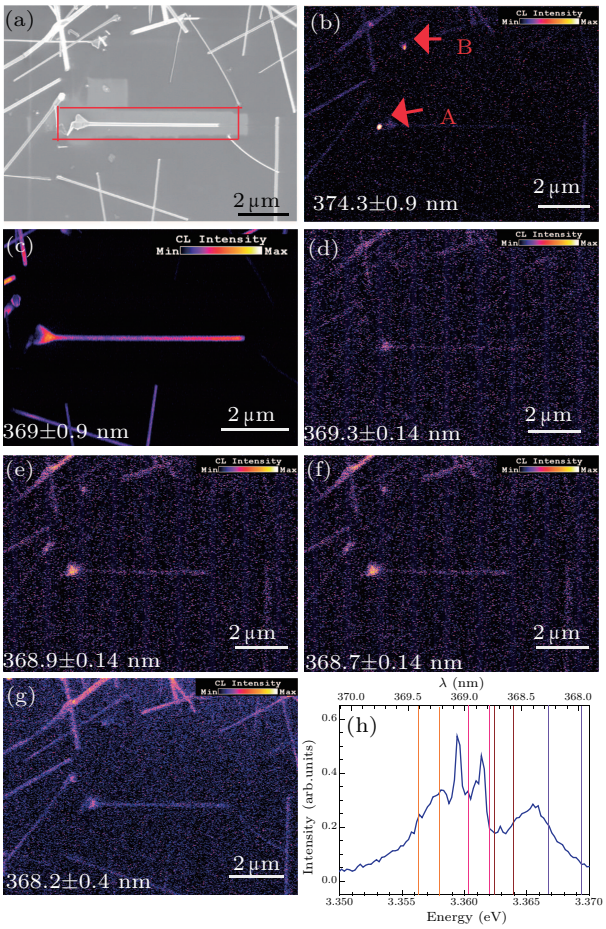

Fig. 2. Monochromatic CL mapping images of single ZnO nanorods in the near-band-edge range at 12 K. (a) The corresponding SEM micrograph, and monochromatic spectral imaging at (b) 374.3±0.9 nm, (c) 369±0.9 nm, (d) 369.3±0.14 nm, (e) 368.9±0.14 nm, (f) 368.7±0.14 nm, (g) 368.2±0.4 nm, (h) the high resolution spectrum in comparison for the selective spectrum in the CL mapping.

SEM-CL was performed to reveal details of the optical properties of the ZnO nanorods. Firstly, the whole ZnO nanorod (as marked in Fig. 2(a)) was chosen to be excited, the spectrum of the near-band-edge region was shown in Fig. 3. The distributions of the 2 keV electron injection in ZnO surface was simulated by a Monte Carlo simulation[24] (Fig. 3), which confirms that the setup has a spatial resolution of 50 nm. We can purposefully divide the spectrum into two regions: the excitonic region and the 3.31 eV region.[25]

From the bound exciton region, we can see the excitonic peaks which can be marked as I_5, I_8, I_9 (In donor bound exciton).[22] The surface band region is also visible.[21] The similarity of the PL and SEM-CL is due to the similarity of the recombination process of the photo/electron excited quasi-equilibrium carriers. The electronic nature of the 3.31 eV is unambiguously identified as a free-to-bound (e, A_0) transition, which is related to the recombination of electrons from the conduction band with holes localized at relatively shallow acceptor states. The binding energy of the acceptors is 130 meV.[25] These basal plane stacking faults can be misinterpreted in some of the p-type doping experiments and especially during the heterostructure device fabrication.

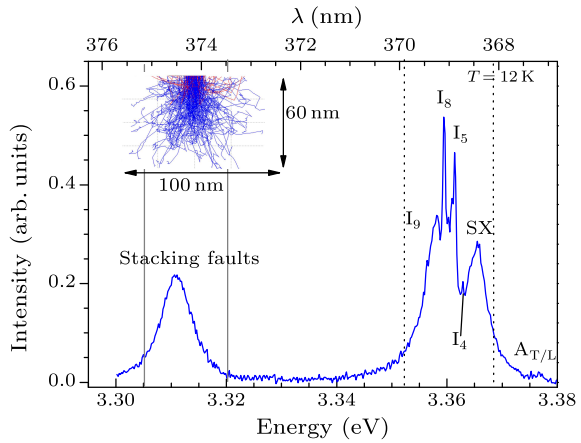

Fig. 3. CL spectrum of the ZnO nanorod. The inset shows several 2 keV electron trajectories in a 100-nm-thick ZnO and the radical distribution of the trajectories at a depth of approximately 50 nm. The dotted and solid lines mark the spectrum region chosen for monochromated CL images in Figs. 2(b) and (c), respectively.

Since the deep-level luminescence is rather weak compared to the PL spectrum, only near-band-edge monochromated CL mapping was recorded. CL mapping centered at 3.31 eV (374.3 nm, stacking faults), 3.3600 eV (369 nm, bound excitons), 3.3573 eV (369.3 nm, I_9), 3.3609 eV (368.9 nm, I_5), 3.3627 eV (368.7 nm, I_4), 3.3673 eV (368.2 nm, free exciton/SX) are shown in Figs. 2(b)–2(g). Except for the homogeneous luminescence, the 3.31 eV emission is highly localized (marked by arrows in Fig. 2(b)). Due to the fact that the emission of the CL mapping is only from the positions where nanorods exist, we can safely exclude of the existence of the wetting layer as usually observed by others.[26] To further elucidate the stacking faults, 10 spots were chosen from bottom to top of the nanorods to be excited of the ZnO nanorod in Fig. 4 (the same nanorod as shown in Fig. 2(a)). Because of the large volume of the ZnO nanorods at the bottom of the ZnO nanorods as seen in Fig. 2(a), the PL intensity of the first two spots is three times higher than the rest of the spots. Only the first spot of the chosen nanorods has the stacking-fault-related luminescence centered at 3.31 eV. This phenomenon is not difficult to understand, since the crystal structures of silicon and ZnO are cubic and hexagonal, respectively, and lattice constant of silicon is 0.54301 nm while the lattice constant of ZnO is 0.32498 nm in the a direction and 0.52066 nm in the c direction. The lattice mismatch $f = \Delta a/a = (a_{\rm Si} - a_{\rm ZnO})/a_{\rm Si} = 40.2\%$. Thus, there exists strain in the interface between ZnO nanorods and the silicon substrate at the first stage of the growth. This strain can create many defects, such as dislocations or stacking faults. From the CL spectrum, we can see that the peak positions of the luminescence are the same as the peaks free of strain,[22] which means that the whole nanorods are strain-released. Thus at the initiated growth period, the gold, zinc, and oxygen form an alloy, also due to the incorporation of gold at this period,[27] combined with the low formation energy of the stacking faults,[28] basal stacking faults can form. One more thing to stress is that the stacking faults are not created all the time, which means that this effect is also influenced by local growth conditions.

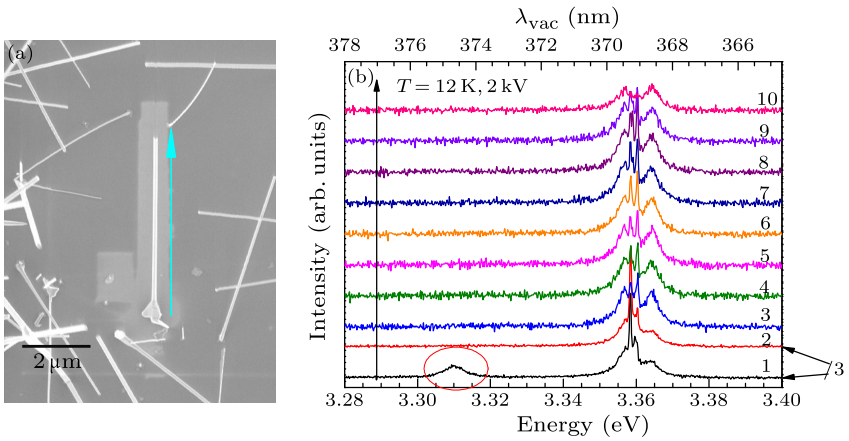

Fig. 4. SEM-CL spectrum of a ZnO nanorod with line scan. (a) SEM micrograph with scan direction. (b) The corresponding CL spectrum at different locations.

In conclusion, high-quality ZnO nanorods have been grown on (100) silicon in relatively low density by a modified CVD process. The SEM micrograph indicates that the ZnO nanorods possess a VLS initiated VS growth mechanism and have a length of 5 μm and diameter about 200 nm. The HR-PL measurement shows that the ZnO nanorods have suppressed yellow or green luminescence and sharp near-band-edge luminescence with an FWHM below 300 μeV. Spatially resolved SEM-CL was used to excite the whole ZnO nanorod, which has stacking-fault luminescence and sharp near-band-gap luminescence. A full scan over the whole ZnO nanorods reveals that at the first stage of the ZnO growth, basal plane stacking faults are created. More attention should be paid to the interface of hetero-growth, which has a dramatic influence on the performance of devices.

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