

Cathodoluminescence Inhomogeneity in ZnO Nanorods

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Abstract

Luminescence properties of vertically aligned, crystalline ZnO nanorods are studied by cathodoluminescence (CL) spectroscopy and microscopy. Results show that luminescence characteristics vary dramatically with location on the nanorod as well as CL excitation depth. Cathodoluminescence inhomogeneity is observed between the nanorod tip and sidewalls, accompanied by a variation in the chemical environment of surface oxygen ions as probed by photoemission spectroscopy. Our findings demonstrate that CL can provide useful information on the local optical properties of nanostructured materials, which is simply beyond the capability of other methods.

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Text

ZnO has attractive properties for possible applications in ultraviolet (UV) light emitting devices [1], photocatalysis [2] and solar cells [3]. Understanding the role of defects and their spatial distribution in ZnO is extremely important in many of these applications, particularly those utilising nanostructured ZnO. Surface defects have been found to affect the performance for such applications. For example, surface impurities such as hydroxyl are known to quench the UV emission in ZnO [4], while other surface defects can hinder charge transfer between ZnO and adsorbed molecules at the interface [5].

In this Letter, we report cathodoluminescence (CL) inhomogeneities in ZnO nanorods with diameters > 100 nm. No quantum confinement effect is expected for the nanorods (the Bohr exciton radius of ZnO is 2.34 nm [6]), however the impact of the surface is immense due to the large surface-to-volume ratio. The luminescence of ZnO nanostructures at room temperature is commonly characterised by two bands: an UV near-band-edge (NBE) emission centred at 380 nm and a defect-related green emission at ~ 520 nm. Although photoluminescence (PL) measurements on individual sub-micron structures are possible [7], the spatial resolution and the accuracy of the technique are limited by the diffraction limit and poor signal-to-noise ratio. In most studies, PL spectroscopy is taken from ensembles of ZnO nanostructures and has thus far produced very large discrepancies in the luminescence results [8-10]. In this work, the local luminescence properties of ZnO nanorods were characterised by high spatial resolution CL and angle-resolved X-ray photoelectron spectroscopy (XPS). The results demonstrate that a luminescence spectrum typically obtained with conventional PL may not represent the optical properties of all parts of the nanorods.

Highly oriented ZnO nanorods were grown onto an *a*-plane sapphire via the chemical vapour transport method with the use of Au as catalyst, as described in detail elsewhere [11].

The morphology and structure of the grown sample were characterised using a FEI Quanta 200 scanning electron microscope (SEM), which is equipped with a Gatan MonoCL3 CL spectroscopy/imaging system. The CL signal was detected using a Hamamatsu R943-02 Peltier cooled photomultiplier tube. Low-voltage CL was employed to improve the spatial resolution and surface sensitivity. The typical beam energy used in this work was 1 – 5 keV, corresponding to a primary electron penetration range $R_e = 15 - 200$ nm. All CL spectra were corrected for the overall detection response of the CL spectroscopy system. The crystallography of the ZnO nanorods was characterised by X-ray diffraction (XRD) on a Siemens D5000 X-ray diffractometer. Additionally, the electronic structure of the nanorods was investigated by XPS, which was conducted on the wide-range SGM (BL-24A1) beamline at the National Synchrotron Radiation Research Centre (Taiwan). XPS survey spectra of the sample revealed only zinc and oxygen signals and no other impurities were detected.

Fig. 1a shows a top view micrograph of the aligned ZnO nanorod array. The image reveals the hexagonal symmetry of the nanorods and shows that most of the ZnO nanorods grow perpendicular to the substrate. The ZnO nanorods all have a height of approximately 5 μm and their diameters range between 100 and 800 nm. Conventional (θ - 2θ) XRD on the sample verifies the SEM result showing that the vertically aligned nanorods are oriented in the [0001] ZnO direction parallel to the $[11\bar{2}0]$ sapphire substrate (Fig. 1b). The diffractogram displays only two peaks with strong intensity, (0002) and (0004), which are both multiples of the [0001] ZnO growth direction, indicating that the nanorods are highly crystalline and were grown with the c-axis orientation. This epitaxial growth is consistent with the in-plane orientation relationship between ZnO and a -plane sapphire, which has recently been explored by Campos *et al* [12], while the nanorod body is enclosed by six crystallographic equivalent $\{10\bar{1}0\}$ facets. The alignment of nanorods is further confirmed by the θ -rocking curve of the ZnO (0002) plane, which has a full width at half maximum

(FWHM) of 1.3° (inset of Fig 1b). The narrow FWHM implies that the c-axes of the nanorods are well aligned to the substrate normal.

CL spectra obtained from individual nanorods display a NBE emission at 3.3 eV (380 nm) and a broad green band centred at 2.3 eV (520 nm). CL exhibits similar luminescence properties among vertically aligned nanorods; however, the intensity ratio of NBE/green varies strongly with probe location on the nanorod (Fig. 2). At the same acceleration voltage (5 kV), the green intensity of the nanorod tip is considerably weaker than that of the sidewalls. Weak green emission from the tip is indicative of better crystalline structure. Decreasing the acceleration voltage to 1 kV reduces the intensities of both NBE and green emissions as expected. However, the green peak is now completely dominant over the NBE emission. The relatively strong green band at ultralow voltage operation (the effective CL excitation depth < 10 nm) supports previous findings that the green luminescence originates from the ZnO surface [13, 14].

The luminescence behaviour is illustrated more clearly in Fig. 3, which show an SEM image of ZnO nanorods and monochromatic CL images recorded from the same area. Panels b) and c) of Fig. 3 clearly show that the NBE emission distributes uniformly over the nanorod; however, the CL image of defect distributions displays a remarkable inhomogeneity between the nanorod tip and sidewalls. The monochromatic CL images demonstrate that low-level luminescence signals from nanostructures can be obtained and that CL can provide a direct comparison of local optical properties by minimizing any possible external perturbations, such as effects of a non-uniform excitation density throughout the electron-solid interaction volume [15]. All nanorods can be clearly resolved as individual emitters and this represents a significant advantage over the conventional PL method. The observed luminescence inhomogeneity could not have been distinguished without the high spatial resolution afforded by CL. Furthermore, the CL intensity variation with location demonstrates

that a luminescence spectrum typically obtained with conventional PL may not represent the optical characteristics of all the faces of ZnO nanorods.

In CL measurements, the greatest number of electron-hole pairs is generated at a depth of $\sim R_c/3$ [15]. However, one has to take into account the diffusion length, i.e. the distance within which carriers can diffuse to the surface where they recombine. This diffusion length in ZnO was estimated to be ~ 60 nm [16], thus a large proportion of injected carriers can reach the surface at low acceleration voltages (< 5 kV). Based on this discussion and with a view that surface oxygen vacancies can potentially be the recombination centre for the green emission [14, 17], XPS studies were carried out to investigate the chemical structure of the tip and sidewalls of the nanorods. Angle-resolved XPS spectra were acquired at different detection angles, θ_d , measured with respect to the c -axes of the vertically aligned nanorods. It is expected that any spectra obtained at normal incidence ($\theta_d = 0$) is dominated by the surface of the nanorod tip, while contributions of the sidewalls become increasingly more important as θ_d increases. Figure 4 compares the O 1s XPS spectra of the nanorods acquired at three θ_d angles. The binding energy scale was referenced to the Au $4f_{7/2}$ at 84.0 eV. It can be seen in Fig. 4a that, with increasing angle θ_d , the O 1s line shape becomes broader on the high-binding-energy side. The change in the line width is small but significant. The O 1s line shape is similar to those of oxygen-deficient ZnO surfaces [18] and can be resolved by a Voigt fitting distribution into two peaks at 529.9 and 531.3 eV, which have been attributed to O^{2-} ions surrounded by fully coordinated Zn atoms and O^{2-} ions in oxygen-deficient ZnO, respectively [18, 19]. It can be seen in panels (b) and (c) of Fig. 4 that the intensity of the non-stoichiometric component increases with θ_d , indicating a higher level of oxygen deficiency on the sidewalls of the nanorods.

The increase in the oxygen defect density on the sidewalls is consistent with the enhanced green emission as revealed by CL. These experimental observations justify an

assignment of green emission to oxygen defect states present on the surface of the ZnO nanocrystals. A comparison with literature [17, 20] suggests that the green luminescence is likely caused by the radiative recombination of a hole with a singly ionised oxygen vacancy (V_o^\bullet) defect. This assignment remains controversial although there is general agreement that oxygen vacancies are involved in some way in the green luminescence in ZnO.

In summary, we have shown that CL can provide useful information on local optical properties and defect distributions in semiconductor nanostructures. Inhomogeneities in optical and chemical properties of the ZnO nanorods are observed. Our results indicate that interpretations of luminescence data from PL measurements on ensembles of ZnO nanostructures can be misleading and should be taken with caution because of possible inhomogeneities within a nanostructure.

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Figure Captions

Fig. 1. (a) SEM image of vertically aligned ZnO nanorods grown on an *a*-plane sapphire, showing nanorods with regular hexagonal shape and good crystallinity. (b) Semi-logarithmic XRD θ - 2θ plot of the ZnO nanorods. Inset shows the rocking curve of the ZnO (0002) plane.

Fig. 2. CL spectra obtained from the tip and the sidewalls of the ZnO nanorods with a focused electron beam at 5 kV, 2 nA and 300 K (normalised to the intensities of the NBE emission peak), with the analogous spectrum of the tip at 1 kV for comparison.

Fig. 3. Secondary electron (SE) and monochromatic CL images acquired at 3.3 eV (NBE emission) and 2.3 eV (green). The images were obtained from the same area. The contrast in the green emission between the tip and sidewalls is clear.

Fig 4. (a) Comparison of the O 1s XPS spectra of the nanorods acquired at different detection angles of photoelectrons, θ_d . The spectrum is broadened to the high-binding-energy side as θ_d is increased from 0° to 60° . (b and c) The O 1s spectra can be resolved into two peaks corresponding to two chemically different environments.







