Local luminescence of ZnO nanowire-covered surface: A cathodoluminescence microscopy study

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Vertically aligned ZnO nanowires were synthesized on sapphire through vapor deposition using Au as a catalyst. In addition to the nanowires, the sample surface contained a thin wetting layer of ZnO clusters. Spatially and spectrally resolved cathodoluminescence (CL) microscopy was applied to correlate the luminescent properties and the sample structure. Local CL spectra and monochromatic images revealed that the nanowires are the major source for a strong and sharp emission line, while two weak emissions at lower energies originate exclusively from the wetting layer. Information on stress is also obtained from the relative position of the emission line. © 2005 American Institute of Physics. [DOI: 10.1063/1.1852709]

Quasi-one-dimensional ZnO nanostructures have attracted increasing attention in recent years due to the wide variety of potential applications in nanotechnologies. Self-assembly via the vapor-liquid-solid (VLS) mechanism is a common method for the bottom-up fabrication of vertically aligned ZnO nanowires. Due to the ultraviolet light-emitting characteristics of ZnO nanowires, their luminescence properties are a most attractive subject. A large number of reports deal with the photoluminescence (PL) properties of ZnO nanostructures. It appears that the PL properties vary with the sample morphology, alignment, as well as the preparation method. However, for most of these studies, the spatial resolution for the PL system is well above the micrometer range, which leads to averaging over many nanowires with typical diameters in the range of 100 nm. In addition, the obtained PL spectra averaged over a large area of sample surface, which will, in most circumstances, contain unwanted irregular structures or other luminescing materials. In order to obtain detailed information of the luminescence from individual nanowires, especially to verify the origin of specific emissions, a probe with high spatial and spectral resolutions is needed. From this point of view, cathodoluminescence (CL) microscopy becomes an advantageous investigative tool. Furthermore, CL can potentially give additional information on local stress and impurities in nanostructures, which are usually beyond the capability of other techniques. While CL has been extensively employed for the microscopic characterizations of ZnO thin films, nanoparticles, and other micrometer-sized features, no reports on systematic CL studies of ZnO nanowire samples are available. In this letter, a microscopic characterization of near-band-gap emissions from ZnO nanowires, as well as the simultaneously grown ZnO thin film, using CL microscopy is presented. A correlation between the local optical and structural properties of samples will be discussed in detail.

ZnO nanowires were fabricated via a vapor deposition process inside a horizontal quartz tube (5 cm inner diameter) furnace. An alumina boat loaded with ZnO and graphite powder mixture was heated up to 850 °C and kept at this temperature for 2 h. The substrate, a-plane sapphire sputtered with ~3 nm Au film, was put over the source boat with the Au facing downward. The chamber pressure was maintained at 200 mbar by a constant flow of pure Ar gas. The morphology and structure of the sample surface were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Low-temperature (T = 4 K) CL microscopy was performed in a home-built system based on a JEOL 6400 SEM with a spatial resolution better than 50 nm. The focused electron beam was digitally scanned over the surface and the emitted light was collected by an elliptical mirror and focused onto the entrance slit of a 27 cm focal length grating monochromator. The light is detected by a diode array giving a complete CL spectrum at each pixel. Subsequently, the data are stored and evaluated in a computer resulting in local spot-mode CL spectra, spectrum linescans, as well as pan and monochromatic mappings and emission wavelength images.

The general morphology of the sample surface after our nanowire growth experiments can be seen from the SEM images in Fig. 1. The distribution of the obtained ZnO nanowires is fairly homogeneous over the sample surface [Fig. 1(a)] with a possibility to modify the density from $3 \times 10^3$ to $4 \times 10^4$ cm$^{-2}$ depending on the local Zn vapor concentration and/or the Au film thickness. The ZnO nanowires exhibit an almost uniform shape with a typical height of ~2 µm and a diameter of 80–120 nm [Fig. 1(b)]. The hexagonal shape of the base plane is clearly visible from the inset in Fig. 1, indicating the $c$ orientation of their wurtzite lattices. Most of the nanowires are aligned vertically to the substrate surface because of the epitaxial relationship between the ZnO $c$ plane and the sapphire $a$ plane. TEM investigations (data not shown here) revealed that the nanowires are single crystals without obvious defects. Similar to that reported previously by Wu et al., our ZnO nanowires grow via a VLS epitaxy process, where the Au droplets absorb Zn vapor atoms at the high temperature.
and the Au/Zn liquid alloy serves as a seed for subsequent nanowire growth.

More careful examination of the sample structure reveals that, besides the vertical nanowires, a mosaic film exists on the sapphire surface. This can be seen clearly from the SEM image in Fig. 2(a) and the cross-sectional TEM image in Fig. 2(b). The latter, together with the high-resolution TEM lattice image in Fig. 2(c), shows that the layer is a wetting film composed of ZnO clusters and faceted Au islands as well as their alloys. In our experiments, a typical thickness of the layer is 30 nm. It is worth mentioning that, from TEM observations at several places of the wetting layer, the ZnO clusters contain some structural defects and are of low crystalline quality compared to the nanowires. The formation process of the wetting layer is similar to VLS: Upon high-temperature annealing, the Au film breaks into liquid nano-droplets. Note that the melting point is lower than the value for bulk Au by the small thickness. The droplets can move on the sapphire surface due to a thermally enhanced surface diffusion. Simultaneously, the Zn vapor atoms dissolve into the droplets and, upon supersaturation, precipitate.

As a yellow-green emission observed from our sample was too weak to be resolved, here we deal only with the near-band-gap emissions. Figure 3(a) shows the CL spectrum integrated from a sample area of $23 \times 18 \mu m^2$. The spectrum is dominated by the neutral donor bound exciton emission $I_8$ (3.3598 eV, assigned from its precise energy position according to Ref. 15) which is associated with Ga donors. The width of the luminescence line full width at half maximum = 3.5 meV, compared to the value for single-crystalline epitaxial ZnO films of about 1.3 meV, indicates a small broadening due to spatial inhomogeneity. Luminescence in the spectral position of the ionized donor bound excitons $I_2/I_3$ and in the range of deeply bound excitons [marked with DBE in Fig. 3(a)] related to structural defects, are also observed. In addition, a weak and broadband at around 3.3245 eV is also visible at the low-energy side of the main peak. It is noted that the whole spectrum is 1.1 meV redshifted with respect to the fully relaxed spectral position, indicating the existence of tensile stress (see the following). Correspondingly, the spatial distribution of luminescence is given by the panchromatic CL image in Fig. 3(b) taken at an inclined
A high CL intensity is detected from the nanowires. The CL properties are indistinguishable from wire to wire. In contrast, only weak and spotlike luminescence is observed from the wetting layer. This indicates that the ZnO nanowires are the main light-emitting source of the \( I_8 \) line. In order to verify the origin of the specific CL lines, local CL spectra and monochromatic images were evaluated in detail. Figure 4(a) gives the spectrum recorded from a single nanowire. The only line observed, sharp and strong, is located at the spectra position of \( I_8 \). The monochromatic image, corresponding to the energy range of 3.3582–3.3618 eV, evidently illustrates that the distribution of the spectrum maximum is confined mainly on the nanowires. Figures 4(e) and 4(c) show the CL spectra recorded from different spots on the sapphire surface. The spectrum intensities are lower than that of the nanowires by one to two orders of magnitude (note that the former were magnified with respect to the latter). In addition to the sharp \( I_8 \) line, broad bands at the lower-energy side, \( \approx 3.2840 \) eV and \( 3.2840 \) eV, are clearly observed. The physical origin of these bands is not clearly understood at this stage. The intensity maps in Figs. 4(b) and 4(c) for the broadbands at 3.3124–3.3311 eV and 3.2774–3.2966 eV, respectively, give spotlike luminescence which originates exclusively from the wetting layer, i.e., from the ZnO clusters. The weakness and broadness of the luminescence from the wetting layer could potentially be explained by two effects: First, the scattering volume is decreased due to the small layer thickness, leading to low spectrum intensity; second, the ZnO clusters in the wetting layer have lower crystalline quality (e.g., defects and local polycrystalline regions) than the nanowires, as evidenced by our high-resolution TEM observations.

Based on the monochromatic images and the variance in spectrum intensities, we conclude that the \( I_8 \)-dominating luminescence in Fig. 3(a) originates mainly from the nanowires, while the weak and broad low-energy bands are from the ZnO cluster-containing wetting layer. Furthermore, it is noteworthy that the \( I_8 \) line from the nanowires is located at the position of the fully relaxed ZnO [Fig. 4(a)], while that from the wetting layer is slightly redshifted by about 2 meV [Figs. 4(b) and 4(c)]. This implies that the nanowires have nearly no stress (and also no quantum confinement effects) while the wetting layer is under tensile stress.\(^7\) It is worth mentioning that measurements from a number of nanowires and different spots on the wetting layer give spectra qualitatively similar to those given in Fig. 4. This confirms a homogenous distribution of the luminescence over the studied area.

In conclusion, a direct correlation of structural and optical properties of the ZnO nanowires has been achieved on a microscopic scale using highly spatially and spectrally resolved CL microscopy. The spatially integrated CL spectra exhibited broad donor bound excitons emission dominated by \( I_8 \). Two weak and broad low-energy bands were also observed. Based on the evaluation of local CL spectra and monochromatic images, the nanowires are the major source of the excitonic \( I_8 \) emission, while the strongly localized low-energy bands originate from the nanosized ZnO clusters in a wetting layer. The CL property indicates the existence of tensile stress in the wetting layer while the nanowires are fully relaxed.


\(^14\) In another experiment, we annealed the Au-coated sapphire in a pure Ar ambient (i.e., in the absence of Zn vapor) at the same temperature. Significant movement of Au was observed.