Enhanced surface-excitonic emission in ZnO/Al$_2$O$_3$ core–shell nanowires

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Abstract
We report the influence of an Al$_2$O$_3$ shell on the photoluminescence emission of ZnO
nanowires. At room temperature, the spectrum of the core–shell nanowires shows a strong
reduction of the relative intensity of the green defect emission with respect to the
near-band-edge emission. At 5 K an increase of the relative intensity of the surface exciton band
with respect to the donor-bound exciton emission is observed. Annealing the core–shell
nanowires at 500 °C does not increase the green defect luminescence at 5 K. We propose a
model explaining the spectral changes.

In recent years, high-quality ZnO nanowires have been synthesized using various fabrication methods, and nanowire batches grown with different methods, under different conditions and post-processing procedures, have been extensively studied and compared [1–4]. With the growing interest in ZnO nanowire-based devices, the focus of research is now shifting towards more complex nanowire assemblies like ZnO/polymer compound structures and nanowire-based core–shell structures [5–7]. For many applications thin coatings with amorphous or crystalline inorganic materials might even offer an improved stability compared to ZnO/polymer compounds. In order to optimize nanowire-based devices, the influence of the nanowire surface on the device properties such as conductivity, light emission, absorption and gain, have to be understood. The surface-to-volume ratio of ZnO nanowires is large enough for surface effects to play a crucial role in optical as well as electronic properties [8]. In this work, the results of photoluminescence investigations of ZnO/Al$_2$O$_3$ core–shell nanowires are presented and discussed. A model will be developed to explain the observed spectral features, in particular the dramatic increase of the surface-excitonic emission and the significant reduction of the deep-level emission in the core–shell nanowires.

ZnO nanowires were grown by using physical vapor deposition with Au as the catalyst on a Si substrate. Typical growth temperatures and times were 850–920 °C and 30–60 min, respectively. The length of the nanowires is about 5 μm, with a diameter of about 50–100 nm. Due to the relatively high growth temperature, they exhibit an overall good crystalline quality. The grown sample was cut in half; one part was used as a reference sample, and the other was used to fabricate ZnO/Al$_2$O$_3$ core–shell nanowires by depositing thin Al$_2$O$_3$ films on the as-grown ZnO nanowires using atomic layer deposition (ALD). Trimethylaluminum (Al(CH$_3$)$_3$) and water were selected as the aluminum precursor and oxygen reactant sources, respectively. The deposition was started at a substrate temperature of 70 °C and a background pressure of 0.15 Torr. The Al$_2$O$_3$ shell thickness was controlled by the number of precursor/purge cycles. We used 60 cycles to obtain an amorphous alumina layer with a thickness of 10 nm. Transmission electron microscopy (TEM) investigations confirmed a smooth layer encapsulating the whole nanowire (figure 1). For some of the photoluminescence (PL) measurements, the core–shell nanowires were annealed at 500 °C for 2 h in air.

PL investigations were carried out in a liquid helium bath cryostat in a temperature range from 300 to 5 K. A HeCd laser excited 10^6 to 10^8 nanowires simultaneously with a wavelength of 325 nm and an excitation density of about 100 mW cm^{-2} (measured at the sample surface). An Ocean Optics HR2000 spectrometer was used to measure spectra from 200 to 1100 nm, and a Spex 1404 monochromator with an attached CCD camera for high-resolution spectra of the near-UV region.

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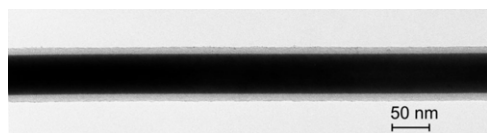
Figure 1. TEM bright-field image of an Al_2O_3 core–shell nanowire. The ZnO core appears black, and the amorphous Al_2O_3 shell gray.
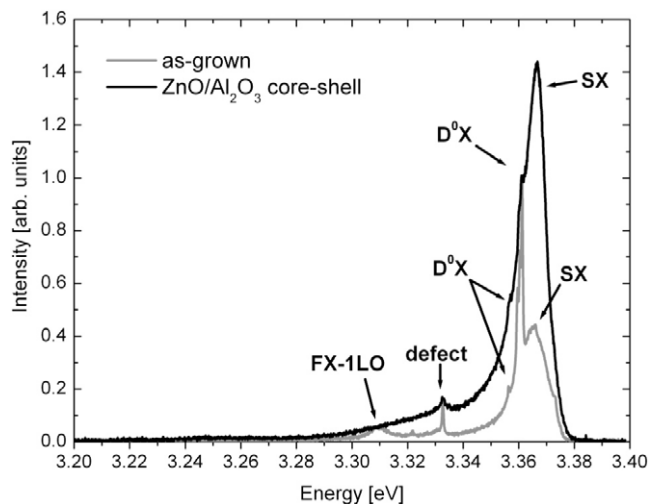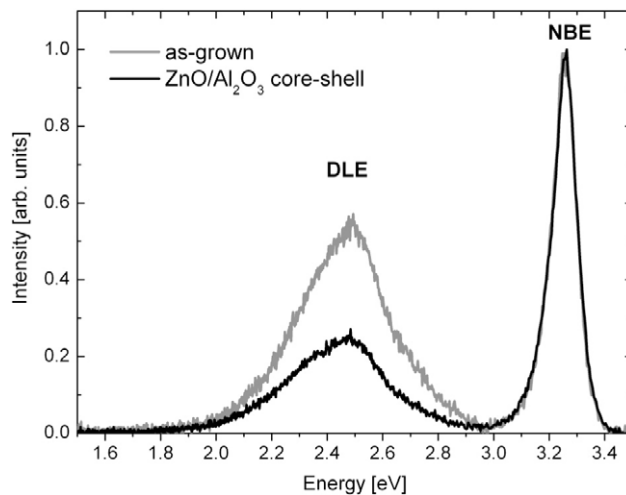

Figure 2. Photoluminescence spectra of the core–shell sample and the as-grown reference sample. The sample temperature is $T = 5$ K. The spectra are normalized to the maximum of the D^0X line at 3.361 eV.
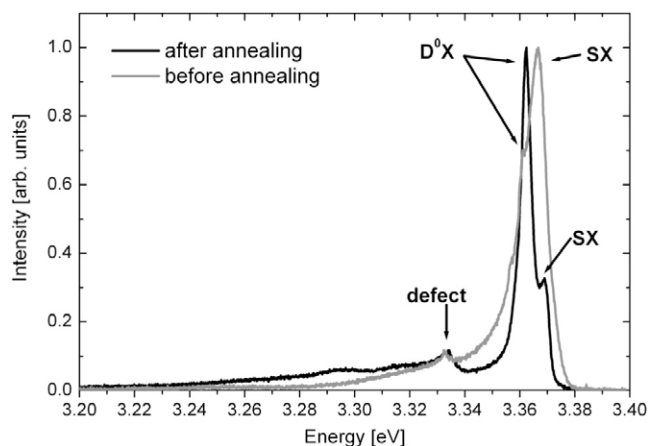

Figure 3. Photoluminescence spectrum of the core–shell sample and the as-grown reference sample at room temperature. The spectra are normalized to the near-band-edge emission.


Figure 4. Normalized photoluminescence spectrum of the core–shell sample before and after annealing at 500 °C for 2 h. The sample temperature was $T = 5$ K.

Figure 2 shows the normalized near-band-edge spectra of the as-grown reference sample and the ZnO/Al_2O_3 core–shell nanowires at $T = 5$ K. The spectrum of the as-grown sample is dominated by a sharp donor-bound exciton (D^0X) emission line peaking at 3.361 eV. Another D^0X emission line at 3.358 eV is visible as a shoulder of the dominating peak. With a maximum at about 3.365 eV, a broad surface exciton (SX) band is visible [9]. At the lower-energy side of the spectrum, two additional features are observed: a defect-related peak at 3.332 eV [2] and the broad peak of the phonon replica of the free exciton (FX-1LO) at 3.315 eV. In contrast, for the core–shell nanowires the broad SX band dominates the spectrum. The two D^0X lines at 3.361 eV and at 3.358 eV are visible as shoulders on the lower-energy side of the SX band. The SX emission of the core–shell nanowires showed the same trends with increasing temperature and increasing excitation density as we had reported for bare nanowires before [9].

Figure 3 compares the normalized spectra of the as-grown reference sample and the ZnO/Al_2O_3 core–shell nanowires at room temperature. The strong excitonic emission (composed of free exciton (FX) and phonon replicas (FX-1LO, FX-2LO) [10]) in the near-UV regime is clearly observed for both samples. However, the green defect luminescence (DLE, deep-level emission) is less pronounced for the core–shell nanowires compared to the reference sample. At $T = 5$ K both samples show only weak DLE with comparable intensity.

Figure 4 presents the normalized low-temperature spectra of the ZnO/Al_2O_3 core–shell nanowires before and after

annealing at 500 °C for 2 h. After annealing the intensity of the D^0X line peaking at 3.361 eV is enhanced compared to the intensity of the SX emission. For the DLE at $T = 5$ K no differences were found before and after the annealing process.

From the results presented in figure 2 we can estimate the peak intensity of the SX emission for the core–shell nanowires to be 3.2 times higher than for the reference sample. Note that the already strong SX band emission of the as-grown ZnO nanowires is due to the small diameter (50–100 nm) of the ZnO nanowires [11]. The peak intensity of the DLE of the core–shell nanowires at room temperature is reduced by a factor of 2.5 compared to the reference sample. We additionally checked ZnO/Al_2O_3 core–shell nanowires with a shell layer thickness of 5 nm and found the results to be qualitatively the same as for the 10 nm shell layer thickness.

Referring to figure 5 we explain the results by the following model. For an uncoated ZnO nanowire, surface states located within the band gap can be occupied by the
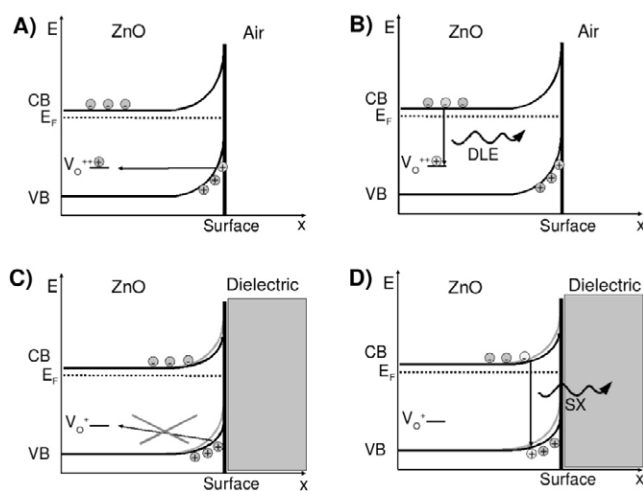
Figure 5. Model of the surface of a ZnO nanowire to explain the spectral changes. (A) Upward band bending at the surface separates electron–hole pairs. The long lifetime of the surface-trapped holes enables a tunneling of the holes into deep levels (V_O^+). (B) By recombination of electrons from the conduction band via the deep levels the DLE is emitted. (C) Coating of the surface with a dielectric layer reduces the band bending and the tunneling rate of holes into deep levels. (D) Increased overlap of electron and hole wavefunctions enhances the relative SX band emission.

majority charge carriers, here electrons for the n-type ZnO. This leads to an upward band bending [12] (figure 5(A)) with an energy separation between the Fermi level and the conduction band minimum at the surface of 1.02 eV for a cleaned ZnO surface according to [12]. The band bending results in a separation of photo-generated electron–hole pairs. A corresponding depletion layer with a thickness of about 20 nm has been confirmed in electrical measurements on single ZnO nanowires [8].

In [13], a model is proposed to explain the origin of the DLE for ZnO nanoparticles which should also apply for ZnO nanowires. According to that model the DLE originates not from the nanowire surface but from within the ZnO nanoparticle 'bulk' material. Since the ZnO structures investigated have diameters well above the exciton Bohr radius of about 1.8 nm, these structures appear as bulk material to the excitons. Singly positively charged oxygen vacancies (V_O^+, one electron at the site of the missing doubly negatively charged oxygen ion, stable in n-type material) are the microscopic origin for a particular DLE band of ZnO nanoparticles [14, 15]. These vacancies need to be activated by trapping of a hole, so an effectively doubly positively charged oxygen vacancy (V_O^{++}) is generated (figure 5(A)). In [13] it is proposed that the holes needed for activation of the oxygen vacancies are provided by the surface of the ZnO nanoparticle. The presence of holes at the surface of photoexcited ZnO crystals was shown before [16]. When electrons from the conduction band recombine into such deep levels, a broad band will be emitted due to phonon interaction of the charged deep centers with the surrounding crystal lattice (figure 5(B)).

The SX emission is generated in a surface layer with a thickness of about 20 nm, as was shown previously [11]. The SX band is emitted from excitons trapped in local potential minima within this surface layer.

The Al_2O_3 shell around the ZnO core surface acts as a dielectric medium and screens the charge carriers located in surface states, thus lowering the effective band bending. A reduced band bending results in a stronger overlap of the wavefunctions of electrons and holes in the surface layer and hence in a higher density of near-surface excitons. An increased probability of forming an exciton will shorten the lifetime of holes at the surface and reduce the probability that a hole trapped at the surface tunnels into an oxygen vacancy (figure 5(C)). At the same time, an increased density of excitons in the surface layer leads to an enhancement of the relative intensity of the SX emission with respect to the D^0X emission emitted from the ZnO nanowire bulk material (figure 5(D)).

Very recently, the coating of ZnO nanowires with a polymer layer was reported to lead to similar changes in the photoluminescence emission of the nanowires [17]. The effect was shown not to be due to a specific chemical bonding of the polymer with the ZnO nanowire surface, but was influenced by the effective dielectric constant of the surrounding material. With respect to the results presented in this work, we conclude that the observed effects in general apply to ZnO nanowires coated with a dielectric material.

The main change in the spectrum after annealing (figure 4) is the rise of the relative intensity of the D^0X line at 3.361 eV. According to [18], this peak can be assigned to excitons bound to aluminum as a shallow donor (I_6). This is due to the diffusion of aluminum from the Al_2O_3 shell into the ZnO core at the given temperature. Note that part of the ZnO diffuses into the Al_2O_3 shell during the annealing process, too [19]. After annealing, the DLE of the sample at $T = 5$ K is unchanged. However, at room temperature an increase of the DLE can be observed, but the near-band-edge emission still remains dominant. This indicates that the ZnO/Al_2O_3 core–shell nanowires exhibit a reasonable temperature stability and effectively shield the ZnO core nanowires. Therefore they can be used to increase the lifetime of ZnO nanowire-based devices.

In summary, we showed that the coating of ZnO nanowires with an amorphous Al_2O_3 layer reduces the relative intensity of the deep-level emission at room temperature as well as at low temperatures. At low temperatures, the near-band-edge region of the core–shell nanowires is dominated by an SX band with a relative intensity being much stronger than the reference sample.

Our results prove that these effects are of a general nature for ZnO nanowires coated with an amorphous dielectric material. Due to the temperature stability of the ZnO/Al_2O_3 core–shell nanowires, they are promising for stable and durable UV-only emitting devices operating at room temperature.

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