# Comparison of the spectral and temporal emission characteristics of homoepitaxial and heteroepitaxial ZnO nanowires

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Using metalorganic chemical vapor deposition, we have grown ZnO nanowires (NWs) on ZnO(0001) as well as on $Al_2O_3$(0001) and Si(111) substrates. The optical properties of these NWs are studied by continuous-wave and time-resolved photoluminescence spectroscopy. Both the spectral and the temporal characteristics of the NWs are found to be virtually identical despite the different substrates and the different morphology of the NWs. This study thus provides strong experimental evidence for the hypothesis that NWs remove the constraints introduced by the substrate. © *2011 American Institute of Physics*. [doi:10.1063/1.3567548]

Semiconductor films grown on foreign substrates often suffer from a high dislocation density and residual strain due to a mismatch of the lattice constants and thermal expansion coefficients. The optical and electrical characteristics of the epitaxial material may be severely affected by these structural imperfections. Consequently, semiconductor devices relying on a high material quality are either restricted to homoepitaxy or require a sophisticated buffer layer on top of a foreign substrate in order to release the strain and reduce the dislocation density.

During the last decade, semiconductor nanowires (NWs) have attracted a lot of interest as they seem to offer a number of advantages over bulk semiconductors. Particularly, their dimensions and shape should allow for an efficient elastic relief of strain[1,2] and, more importantly, the escape of threading dislocations intersecting the NW to the nearby NW sidewalls.[3] This mechanism is expected to result in virtually dislocation-free material regardless of the substrate and thus to facilitate the integration of III–V and II–VI semiconductors on Si. In other words, NWs of sufficiently small diameters are believed to remove any constraints regarding the substrate.

These expectations have, however, never been subjected to an actual experimental examination. Indeed, such an examination is complicated by the fact that the synthesis of NWs on different substrates often demands different conditions. For instance, GaN NWs do form spontaneously under appropriate conditions on Si,[4] but their formation on bare $Al_2O_3$ requires the presence of metal particles inducing vapor- solid-solid growth.[5] GaN NWs prepared on these substrates exhibit significant differences in structural as well as optical quality. These differences, however, are likely to be caused by the presence of the metal particle at the growth front and not by the different substrates.[6]

Here, we study ZnO NWs grown by metalorganic chemical vapor deposition (MOCVD) on Si(111) denoted as sample A, $Al_2O_3$(0001) denoted as sample B and ZnO(0001) denoted as sample C. ZnO NWs form spontaneously on all of these substrates, including ZnO itself, without the need for any external agent. Structurally, the NWs of all three samples are of single-crystalline wurtzite structure. To detect more subtle deviations from crystalline perfection such as strain and the presence of defects, we employ low-temperature continuous-wave and time-resolved photoluminescence (TRPL) spectroscopy.

The growth of the ZnO NWs was carried out in a Thomas Swan close-coupled showerhead MOCVD reactor used for the synthesis of ZnO as well as GaN-based structures. Diethylzinc and pure $O_2$ were utilized as precursors, and $N_2$ was used as carrier gas. All samples were grown directly on either Si(111), $Al_2O_3$(0001) or ZnO(0001) wafers. The growth temperature $T_G$ was varied between 550 and 615 °C for the NWs, while a homoepitaxial ZnO layer serving as a reference was grown at 1000 °C. Table I summarizes the parameters for the samples presented in this study.

Low-temperature (10 K) PL experiments have been performed by exciting the samples with the 325 nm line of a HeCd laser. The excitation density was limited by neutral density filters to about 2 $W/cm^2$. The laser was focused to a spot with a diameter of about 3 $\mu$m by a 15× ultraviolet (UV) microscope objective with a numerical aperture of 0.32. The same objective collected the PL signal and focused it onto the entrance slit of an 80 cm spectrometer. A grating with either 600 lines/mm or 2400 lines/mm dispersed the signal spectrally onto a cooled charge-coupled device (CCD) array, resulting in a spectral resolution of either 1 or

TABLE I. Summary of growth-related and structural parameters for the samples presented in this work.

| Sample | A | B | C | Layer |
|---|---|---|---|---|
| Substrate | Si(111) | $Al_2O_3$(0001) | ZnO(0001) | ZnO(0001) |
| $T_G$ (°C) | 615 | 550 | 550 | 1000 |
| Length (nm) | 650 | 280 | 700 | 300 |
| Diameter (nm) | 40 | 60 | 80 | — |
| Density ($cm^{-2}$) | $5\times10^{-9}$ | $5\times10^{-9}$ | $10^{-9}$ | — |

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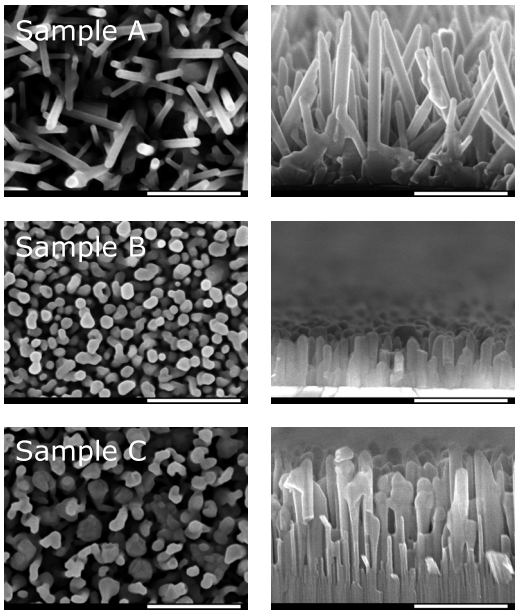


FIG. 1. Topviews (left) and sideviews (right) of as-grown ZnO NWs on Si (top), $Al_2O_3$ (middle), and ZnO (bottom) as obtained by a scanning electron microscope. The scale bars correspond to 500 nm.

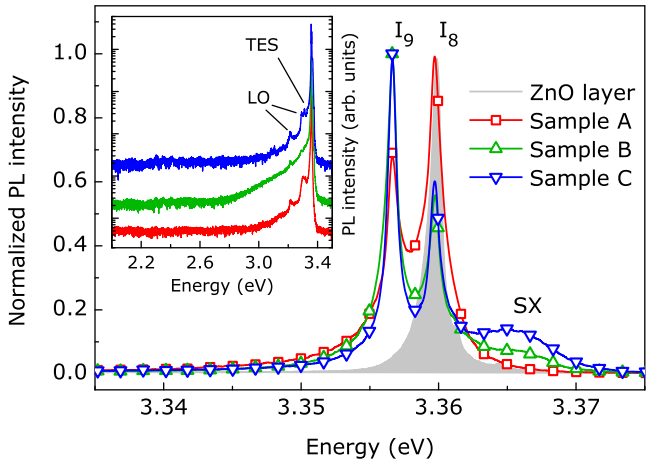


FIG. 2. (Color online) Normalized high resolution PL spectra recorded at 10 K of the samples under investigation. The gray-shaded area depicts the PL of a ZnO layer grown homoepitaxially in the same MOCVD system. The inset shows the PL of the NW samples on a logarithmic scale for a larger energy range. The PL spectra are vertically shifted for clarity.

0.25 meV. The absolute spectral position was calibrated with the HeCd laser line at 325.02(2) nm [3.814 66(23) eV]. The transition energies are thus accurate to within 30 $\mu$eV. TRPL transients were measured using the second harmonic of an optical parametric oscillator pumped by a tunable femtosecond Ti:sapphire laser. Again, the excitation wavelength was 325 nm. The excitation pulses had a duration of 200 fs at a repetition rate of 76 MHz. A 22 cm spectrometer dispersed the signal spectrally, which was then detected by a streak camera. The spectral and temporal resolution of the system was 2 nm and less than 5 ps, respectively.

Scanning electron micrographs of the three NW samples are shown in Fig. 1. Their morphology differs drastically. While the NWs of samples B and C grow perpendicular, the NWs of sample A are strongly inclined without any preferred direction or angle similar to the report of Nayak *et al.*[7] Coalesced NWs can be found in all three samples with sample C showing strongly coalesced NWs and even wall-like structures. The average NW diameter ranges from 40 nm in sample A to 80 nm in sample C with strong variations in NW diameter in samples B and C. The NW length varies from 280 to 700 nm. These numbers are summarized in Table I.

The pronounced differences in morphology, however, do not manifest themselves in the PL spectra of the samples as seen in Fig. 2. In fact, the PL spectra of the three NW samples are virtually identical regarding the energy, width, and intensity of the transitions observed. All the samples exhibit two distinct, sharp transitions labeled according to Ref. 8 as $I_9$ at 3.3566 and $I_8$ at 3.3597 eV, which originate from excitons bound to neutral In and Ga donors [$(D^0,X)$], respectively. The presence of these impurities can be attributed to the parallel use of the reactor for (In,Ga)N growth. The gray-shaded curve depicts the PL spectrum of a homoepitaxial ZnO layer grown in the same reactor. It is dominated by the $I_8$ transition, but additionally exhibits weak transitions at 3.3612 and 3.364 eV, most likely being due to the $I_5$ and the $I_3$ lines.[8] The linewidth [full width at half maximum (FWHM)] of the $I_8$ and the $I_9$ transitions in the NWs ranges from 0.7 to 1.1 meV. These values belong to the narrowest linewidths reported for NW ensemble luminescence.[9–12] An additional, comparatively broad transition due to the radiative recombination of surface excitons (SX) can be found at 3.365 eV (Refs. 9, 13, and 14) in the PL of samples B and C. All of the above values are compiled in Table II for an easy comparison.

The inset of Fig. 2 depicts the PL spectra of our samples over a large energy range. Close to the main $(D^0,X)$ transitions, their first and second longitudinal optical phonon replicas are visible at about 3.29 and 3.21 eV.[15] Furthermore, the two-electron satellites of the $(D^0,X)$ transitions are observed at around 3.315 eV.[16] No traces of green luminescence, which is frequently observed for ZnO and attributed to native defects,[17] are detected. This absence of green luminescence and the sharp and intense exciton transitions comparable to a homoepitaxial ZnO layer illustrate the high optical quality of the NWs regardless of the substrate.

The high intensity observed in the PL spectra of the NWs suggests a high internal quantum efficiency. To substantiate this presumption and for obtaining quantitative data, we perform TRPL spectroscopy. Figure 3 shows the PL transients for the three NW samples at a temperature of 15 K. These transients are integrated over all excitonic transitions observed in Fig. 2 and are thus a measure of a combined PL decay time. The similarities between the samples are once again striking. All transients are nonexponential, but exhibit

TABLE II. Energies and linewidths of the excitonic transitions observed in the PL spectra of the ZnO NW samples. Also given is their combined ($\Sigma$) decay time.

| Sample | | A | B | C |
|---|---|---|---|---|
| Substrate | | Si(111) | $Al_2O_3$(0001) | ZnO(0001) |
| $I_9$ | Energy (eV) | 3.3566 | 3.3566 | 3.3566 |
| | FWHM (meV) | 0.7 | 0.9 | 0.8 |
| $I_8$ | Energy (eV) | 3.3597 | 3.3597 | 3.3597 |
| | FWHM (meV) | 1.1 | 0.8 | 0.8 |
| SX | Energy (eV) | — | 3.365 | 3.365 |
| $\Sigma$ | Decay time (ps) | 310 | 240 | 240 |

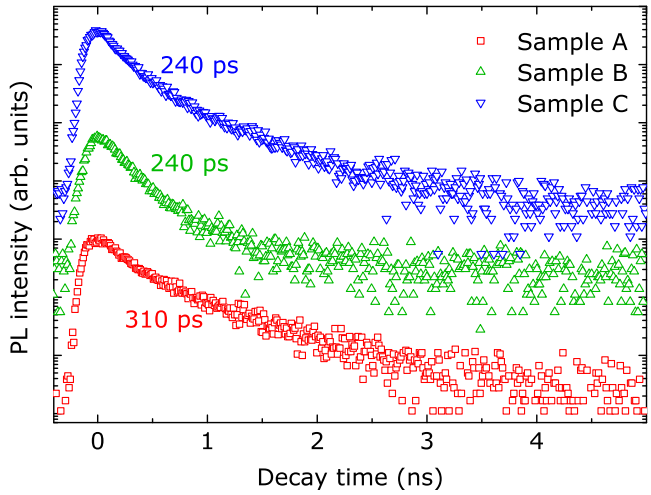


FIG. 3. (Color online) PL transients of the near-band-edge transitions of the three NW samples measured at 15 K. The 1/e-decay times are given in the graph. The curves are vertically shifted for clarity.

comparable 1/e-decay times of 240 (samples B and C) to 310 ps (sample A). These values are longer than values reported in the literature.[13,18–20] Still, the decay is governed by nonradiative recombination as indicated by lifetimes on the order of 1 ns for donor-bound exciton emission in bulk ZnO.[15] An obvious candidate for such nonradiative processes in NWs is recombination via surface states as also discussed in the literature.[19,20] For surface recombination, the decay times are expected to be proportional to the NW diameter. However, our data do not support such a correlation.

To summarize, our data show conclusively that the properties of NWs are, in contrast to layers, indeed largely independent of the substrate used for growth. Instead of selecting substrates with regard to the closest structural, chemical and thermal match with the intended epitaxial layer, the choice may now be made freely, focusing only on economic issues.

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