Size-dependent recombination dynamics in ZnO nanowires

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A deep understanding of the recombination dynamics of ZnO nanowires (NWs) is a natural step for a precise design of on-demand nanostructures based on this material system. In this work we investigate the influence of finite-size on the recombination dynamics of the neutral bound exciton around 3.365 eV for ZnO NWs with different diameters. We demonstrate that the lifetime of this excitonic transition decreases with increasing the surface-to-volume ratio due to a surface induced recombination process. Furthermore, we have observed two broad transitions around 3.341 and 3.314 eV, which were identified as surface states by studying the dependence of their life time and intensitiy with the NWs dimensions. © *2010 American Institute of Physics.*
[doi:10.1063/1.3294327]

Over the last five decades the fundamental properties of ZnO have been widely studied by many authors.[1] Its large band gap of 3.3 eV, large exciton binding energy of about 60 meV, and its structural compatibility with GaN are some the many advantages that make ZnO interesting concerning device applications. A renewed interest in this material system has emerged in the last years due to great improvements on its growth techniques. Its applications into piezotronics have been recently discussed since they represent the ultimate step for an efficient integration into novel devices. In addition, much effort has been put in fabricating low dimensional structures[2] such as nanodots, nanocrystals, tetrapods, nanorods, and nanowires (NWs) due to the advantages offered by quantum confinement. Nevertheless, despite the great variety of nanostructures produced up to date, scaling ZnO or any material into the nanoscale present some complications as some of its physical properties depend on the dimensionality and, thus, need to be revisited. Recently, the mechanical properties of ZnO were found to be different to those of bulk material.[3] The importance of surface states as possible recombination channels in NWs was also discussed.[4] A complete revision of the optical, electrical, and mechanical properties is mandatory when the surface-to-volume ratio is not negligible. The recombination dynamics in ZnO NWs have been recently studied by many authors.[4–8] Different recombination times with single and biexponential decays have been reported for different nanostructured systems. This situation is somehow dissapointing since it might lead to different interpretations of the possible recombination channels in these nanostructures. Although direct comparison between all these data is not possible since the lifetime depends on many different scattering processes (which might differ for different growth techniques), the knowledge of its dependence with the NWs size is desirable. In a recent letter,[8] the lifetime of the free exciton was investigated for NWs with different length but equal diameter. The authors have observed that the lifetime increases as the length of the NWs increases. Nevertheless, the influence of the surface on the NWs recombination processes might be stronger for the smaller NW diameter due to the increasing surface-to-volume ratio. It is our main purpose to investigate the influence of the diameter on the surface states of the NWs, as well as on its excitonic recombination processes.

In this letter, we present a systematic study of recombination dynamics in ZnO NWs with different sizes. We demonstrate that the lifetime of the main excitonic transition around 3.365 eV decreases for the smaller NW diameters due to surface induced recombination. This result was also confirmed within each sample by the observation of fluctuations in the lifetime of the 3.365 eV exciton. In addition, we have observed two broad transitions around 3.341 (S_1) and 3.314 eV (S_2) whose intensity increases for the smaller NWs diameters. Comparing their intensities and recombination times to those of the main excitonic recombination around 3.365 eV we conclude that S_1 and S_2 might originate from surface states.

ZnO NWs were grown by a Au catalyzed vapor-liquid-solid process on SiO_2/Si substrates.[9] Three samples with different mean wire diameter of d=70, 110, 170 nm (named as A, B, and C, respectively) were grown from different Au catalyst. For samples A and B sputtered Au was used as catalyst with nominal thicknesses of 10 and 20 nm, respectively. In the case of sample C, Au colloids were used as catalyst. The NWs were grown from a ZnO powder mixed with graphite powder and the synthesis was carried out in a horizontal quartz tube. The furnace was heated at 900 °C and Ar was used as carrier gas. Structural characterization was performed by field emission scanning electron microscope (FESEM) with a Hitachi H-4100FE. The high structural quality of the NWs was studied in a previous work[10] using high resolution transmission electron microscopy. The structural analysis shows the high crystal quality of the ZnO
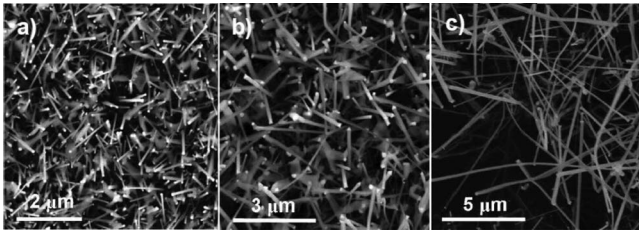
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FIG. 1. FESEM images of three samples with ZnO NWs of different diameters of (a) 70 nm, (b) 110 nm, and (c) 170 nm. Samples A and B were grown with sputtered Au as catalyst while sample C was grown using an colloidal Au nanoparticles as catalyst.
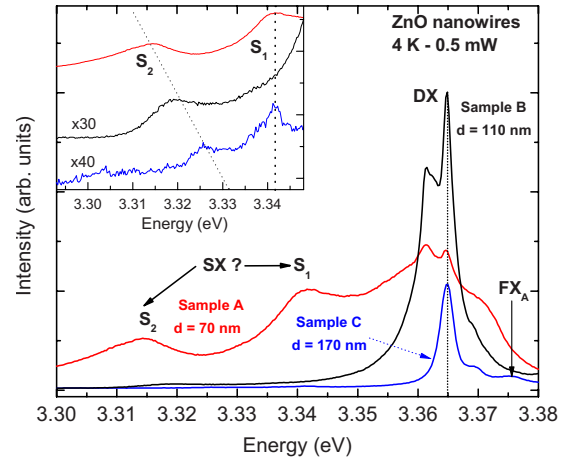

FIG. 2. (Color online) PL spectra at 4 K for samples A, B, and C. The vertical dashed line shows the position of the DX=3.365 eV neutral-bound exciton recombination. The inset shows the detail of the low energy region where two surface related transitions labeled as S_1 and S_2 are observed.

NWs, and reveals the [0001] as principal growth direction. In addition, the NWs surface roughness is estimated to be of the order of one atomic layer. The optical properties of these nanostructures were investigated using a micro-photoluminescence (PL) setup. A frequency-doubled Ti:sapphire laser set at 3.496 eV (355 nm) was focused onto the samples using a $50\times$ microscope objective specially designed for UV operation. The emitted PL was collected by the same microscope objective and recorded spectrally resolved by a liquid nitrogen cooled charge-coupled device camera. The objective was mounted on a XY piezoelectric stage which allows steps of 100 nm. Nevertheless, the resolution was limited by the numerical aperture NA=0.75 of the objective, and can be estimated from the radius of the first Airy disk as $d=1.22\lambda/2\text{NA}\approx 290$ nm, where $\lambda=355$ nm is the wavelength of the incident laser light. For the time-resolved measurements we have used the time correlated single-photon counting technique with a time resolution of about 20 ps.

In Fig. 1 we show FESEM images for the samples A, B, and C. The NWs do not grow vertically aligned due to the lattice mismatch between the ZnO and the amorphous SiO_2/Si substrate. We have chosen this random orientation of the NWs to obtain a lower effective wire density, which in combination with a high spatial resolution micro-PL setup allows to reduce the inhomogeneous broadening due to size distribution. This configuration is extremely convenient in order to study the size-dependence of the recombination dynamics since depending on the sample's NWs density, from one to a few wires are present within laser spot. We point out that this represents an important advantage of our experimental conditions compared to previous ones,[2,4,5] since the horizontal spatial orientation of the NWs (which is originated in the lattice mismatch with the SiO_2 layer) reduces the NWs density that is probed within the laser spot. This cannot be achieved in the case of vertically aligned NWs, which are generally grown over ZnO substrates, producing a higher effective NWs density.

The low temperature PL spectra for samples A, B, and C is shown in Fig. 2. The free exciton line is observed for sample C around 3.375 eV, while for samples A and B it is hardly observed since it might be obscured by the stronger bound excitons. The transitions observed around 3.365 eV are assigned to their corresponding bound excitons in bulk ZnO.[11] For the three samples a common line is observed around 3.365 eV. The origin of this transition is somehow controversial with two following possible candidates: (i) a donor bound exciton recombination[11] (DX), (ii) a surface localized exciton.[12] It is not our purpose to discuss in detail

the origin of this transition but instead to use it as a probe to investigate size-dependent effects taking into advantage the fact that it is observed in the three samples. Nevertheless, we have some reasons to believe that this transition originates from a bound exciton recombination as we will show from the time-resolved PL (TRPL) spectra and temperature dependence. Finally, we show in the inset to Fig. 2 two broad bands around 3.341 and 3.314 eV labeled as S_1 and S_2, respectively. The position of S_1 does not depend on the wire diameter while its intensity increases with increasing the surface-to-volume ratio. On the contrary, S_2 shifts to lower energies with decreasing the wire diameter while its intensity increases. The fact that the intensity ratios I_{S_1}/I_{DX} and I_{S_2}/I_{DX} increase with decreasing the NW diameter is an indicator that these bands might originate from surface states in the NWs. In fact, the S_2 band was recently assigned to a free-to-bound transition (e,A^0) related to the intersection of basal plane stacking faults with the surface of the material.[13]

In Fig. 3 we show the TRPL spectra of the DX at 3.365 eV and 4 K for the three samples. In order to ensure comparable lifetimes all the experimental conditions were un-
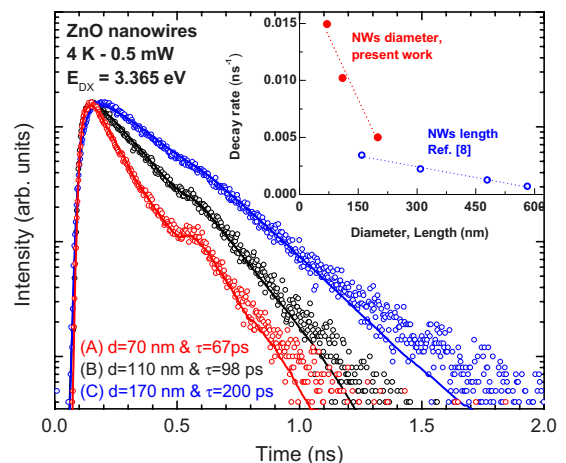

FIG. 3. (Color online) Low-temperature TRPL spectra at 3.365 eV for samples A, B, and C. A monoexponential lifetime is observed for the samples. The inset shows the scattering rates in full symbols and also the results from Ref. 8 for comparison.
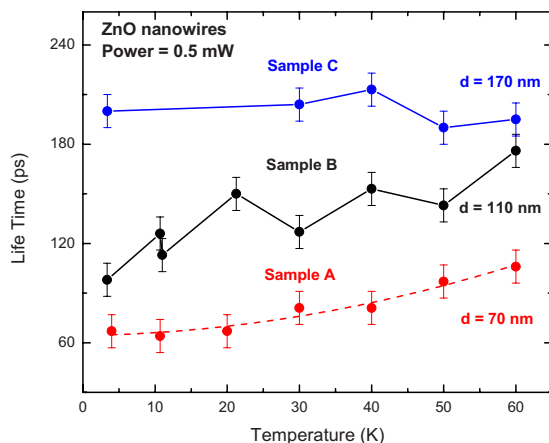
FIG. 4. (Color online) Temperature dependence of the lifetime of DX for samples A, B, and C. The curve in dashed line is a quadratic fit to data points for sample A. The lifetime decreases as increasing the surface-to-volume ratio of the NWs.

changed. A monoexponential decay is observed for all the samples with lifetimes of $\tau = 67$, 98, and 200 ps for samples A, B, and C, respectively. We believe that this systematic increase in the lifetime with increasing the wire diameter is related to a surface assisted recombination process, i.e., the lifetime of the DX exciton is influenced by the surface proximity. Consequently, for the smaller NW diameters (d=70 nm) the shorter recombination times are achieved ($\tau = 67$ ps). In addition, we show in the inset to Fig. 3 the scattering rates as function of the NWs diameter together with the results from Ref. 8 which relates the scattering rates of the free exciton at ambient temperature to the length of the NWs. Although direct comparison between the absolute values would not be correct since they correspond to different excitonic transitions, it is still possible to compare their slopes. A difference of a factor of 10 between them shows that the scattering rate varies faster with reducing the diameter of the NWs compared to their length. This result indicates the predominant influence of the surface in the recombination mechanisms of the excitons. The lifetime of S_1 and S_2 was also studied for samples A and B. For S_1 we have obtained a monoexponential dependence with time constants of $\tau_A = 76$ ps and $\tau_B = 109$ ps at 4 K. On the contrary, a biexponential decay was observed for S_2 with $\tau_A^{1,2} = 179$ and 702 ps and $\tau_B^{1,2} = 116$ and 551 ps also at 4 K. The lifetimes of S_2 (in the NWs) are compatible with those observed in ZnO nanocrystals[13] with the long component being a signature of a free-to-bound transition as discussed in Ref. 14.

The temperature dependence of the decay time of DX is shown in Fig. 4. For sample A, a quadratic dependence of the lifetime with temperature is observed from the fit in dashed line. This increase in the lifetime is understood in terms of thermally induced exciton redistribution in reciprocal space.[15] For sample B, this quadratic dependence is obscured by fluctuations which are beyond the experimental error. This is explained taking into account that with varying the temperature, the position in the sample is slightly changed so that contributions from wires with different diameters are possible. From the fluctuations observed in Fig. 4 we can estimate a diameter distribution of 70 ± 5 nm, and 110 ± 30 nm for samples A and B, respectively. In addition, the fact that we observe these fluctuations within each sample is another indicator of the dependence of the lifetime

with size of the NWs. For sample C, almost no variation is observed over the whole temperature range. Although a larger lifetime is observed for this sample, which is in accordance with its larger wire diameter, a strict comparison is difficult due to the different Au catalyst used in the growth mechanism. This may lead to a different bound excitonic structure due to the inclusion of different impurities in the growth process, which could also contribute to different exciton scattering rates. Nevertheless, this is not the case for samples A and B since they were grown in the same conditions. The only difference between these samples is the thickness of the sputtered Au catalyst. Consequently, direct comparison between their optical properties is fair since a similar impurity distribution is expected.

In summary, comparing ZnO NWs of different sizes we were able to show that the recombination time of the DX =3.365 eV donor bound exciton decreases for the smaller NW diameters. A similar effect was also observed within each sample studying the thermal fluctuations of the recombination time of the DX, which was originated by contribution of different NWs due slight variations in the position of the laser spot with temperature. In addition, two transitions labeled as $S_1 = 3.341$ eV and $S_2 = 3.314$ eV were observed for all the samples. Studying their intensities and recombination times we were able to show that these may arise from surface localized states. These results are of great interest for a precise design of ZnO-based nanostructures, since they represent a step toward a deep understanding of size-dependent recombination dynamics in this system.

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