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Effect of precursor solutions stirring on deep level defects concentration and spatial distribution in low temperature aqueous chemical synthesis of zinc oxide nanorods

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Hexagonal c-axis oriented zinc oxide (ZnO) nanorods (NRs) with 120-300 nm diameters are synthesized via the low temperature aqueous chemical route at 80 °C on silver-coated glass substrates. The influence of varying the precursor solutions stirring durations on the concentration and spatial distributions of deep level defects in ZnO NRs is investigated. Room temperature micro-photoluminescence (µ-PL) spectra were collected for all samples. Cathodoluminescence (CL) spectra of the as-synthesized NRs reveal a significant change in the intensity ratio of the near band edge emission (NBE) to the deep-level emission (DLE) peaks with increasing stirring durations. This is attributed to the variation in the concentration of the oxygen-deficiency with increasing stirring durations as suggested from the X-ray photoelectron spectroscopy analysis. Spatially resolved CL spectra taken along individual NRs revealed that stirring the precursor solutions for relatively short duration (1-3 h), which likely induced high super saturation under thermodynamic equilibrium during the synthesis process, is observed to favor the formation of point defects moving towards the tip of the NRs. In contrary, stirring for longer duration (5-15 h) will induce low super saturation favoring the formation of point defects located at the bottom of the NRs. These findings demonstrate that it is possible to control the concentration and spatial distribution of deep level defects in ZnO NRs by varying the stirring durations of the precursor solutions. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4929981]

I. INTRODUCTION

Having a diversity of one-dimensional (1D) nanostructure morphologies with relatively high exciton binding energy (60 meV), direct wide band gap (3.37 eV at room temperature), and radiative deep level intrinsic point defects covering the whole visible region, zinc oxide (ZnO) has been considered as one of the potential candidates for many optoelectronic devices.1–4 The room temperature luminescence of ZnO nanostructures is commonly characterized by two main bands, a sharp UV near-band-edge emission (NBE) centered at around 380 nm and the above mentioned broad deep-level emission (DLE) which literally covers the region between 400 nm and up to 750 nm.5–15 According to the peak position, the broad emission band is likely to be composed of different sub-bands since it is known that there is a green emission band (500–550 nm), which is often attributed to oxygen and zinc vacancies (V_o, V_Zn).11,14–16,17 in addition to the yellow and orange-red bands. The yellow emission band (550–600 nm) and red emission band (620–750 nm) are commonly attributed the presence of OH groups and to the oxygen interstitials (O_i) present

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on the surface of the ZnO NRs. Due to the position of the green emission at the middle of the board wide visible spectra, these bands are often called the “green emission band”. However, the control over synthesis conditions to obtain ZnO nanostructures with specific concentration and specific spatial distribution of intrinsic point defects is a key factor for realizing the above mentioned-applications. Among the different synthesis methods used for ZnO nanostructures, the low temperature solution based methods are promising due to many advantageous. Also, in particular, a low temperature solution based synthesis method results in ZnO nanostructures possessing relatively large intrinsic point defect concentrations. Moreover, optical properties of ZnO nanostructures synthesized by the low temperature solution approach are sensitive to synthesis parameters and conditions, i.e. pH, precursor concentration, temperature, and reaction time. Therefore, despite that the origin of the DLE in ZnO is highly controversial, much attention has been paid to control concentration of these defects using the above-mentioned synthesis parameters. Previously, it has been reported that the relative intensity ratio of the NBE to the DLE in ZnO NRs increases after annealing, which was contributed to the decrease of the deep level defects. On the other hand, a significant change in this ratio has been observed upon doping ZnO NRs with selective elements, and the concentration of the V_0 was considered as the origin of the observed modified ratio. Thus, understanding the synthesis mechanism of solution synthesized ZnO nanostructures, especially the preparation conditions of the precursor solutions, is a critical aspect of determining the optical properties of the final product. The driving force for chemical reactions leading to nucleation and crystal synthesis from solutions is the need to minimize the free energy of the whole system, and the direction of the crystal synthesis is determined by the surface activities of the growing facets under specific synthesis conditions. Further, the thorough mixing of individual synthesis precursor solutions is critical for obtaining aliovalent proper substitutions in solid solutions and, thus, solution-based methods commonly require low temperature and are very effective in producing high quality nanocrystalline samples. Thus, stirring of precursor solutions in preparation steps is required for the enhancing the chemical homogeneity of the ionic species and hence increase the synthesis rate by lowering the influence of the activation energy during the synthesis process. However, to the best of our knowledge, no particular study was performed to investigate the stirring durations of precursor solutions as a way to control the specific concentration and specific spatial distribution of radiative point defects in ZnO nanostructures. The synthesis of ZnO nanostructures in the aqueous solutions, when zinc nitrate hexahydrate and hexamethylenetetramine are used as precursor solutions proceeds via certain key parameters as mentioned above. The main effect of these parameters in the synthesis of ZnO NRs is control of the rate of hydrolysis of the hexamethylenetetramine (OH\(^-\) concentration), which further react with Zn\(^{4+}\) and decompose to Zn(OH)_2 and later form the targeted ZnO nanostructures. Thus, in this work we demonstrate a possibility to control the OH\(^-\) concentration in the preparation step by varying the stirring durations of the precursor solutions. The as-synthesized ZnO NRs have been characterized by electron microscopy, micro-photoluminescence (\(\mu\)-PL) and cathodoluminescence (CL). The effect of the stirring durations on the concentration and spatial distributions of the radiative deep level defects in as-synthesized ZnO NRs is investigated.

II. EXPERIMENTAL

The ZnO NRs were obtained by the low temperature aqueous chemical synthesis. A seed layer consisting of ZnO nanoparticles (NPs) was deposited on a glass substrate coated with a thin film of Ag/Cr (120 nm/20 nm) and then annealed in conventional oven at 120 °C for 10 minutes. For the precursor solutions, a 0.05M of Zn(NO_3)_2 \cdot 6H_2O and 0.075M of C_6H_{12}N_4 (HMT) were dissolved in a deionized (DI) water and stirred continuously for 10 minutes in separate beakers. The precursor solutions were then carefully mixed and stirred at room temperature for 1, 3, 5 and 15 hours, respectively, with a speed of 600 rpm. The ZnO NRs, were then synthesized by submerging the seeded substrates inside the precursors solution and keeping them in a preheated oven at 80 °C for 6 hours. Afterwards, the samples were rinsed with DI-water to remove any residuals, and finally dried using blowing nitrogen.
The morphology and crystal structure of the as-synthesized ZnO NRs were characterized using field-emission scanning electron microscopy (FE-SEM) Gemini LEO 1550 and powder X-ray diffraction (XRD) Philips PW1729 diffractometer equipped with Cu-Kα radiation (λ = 1.5418 Å) operated at 40 kV and 40 mA, respectively. The electronic structure was analyzed by X-ray photoelectron spectroscopy (XPS) measurements recorded by Scienta ESCA-200 spectrometer using monochromatic Al Kα x-ray source (1486.6 eV). The defect emission were investigated by room temperature micro-photoluminescence (µ-PL) spectroscopy using a 266 nm continuous wave laser as excitation source. In addition, more defect ananlysis was investigated with Cathodoluminescence (CL) using Gatan MonoCL4 system combined with Gemini LEO 1550 FE-SEM. Both the PL and CL spectra were collected at room temperature.

III. RESULTS AND DISCUSSION

Figure 1(a)–1(d) shows top view FE-SEM images of the as-synthesized ZnO NRs prepared from the solution stirred for 1, 3, 5 and 15 h, respectively. As can be clearly seen, all images show vertically aligned hexagonal-shaped ZnO NRs. However, as the stirring durations is increased the diameters of the NRs was observed to increase from 120 nm for the 1 h stirring durations to 180 nm and 300 nm for the 3 and 5 h stirring durations, respectively. Upon increasing the stirring durations further, the NRs diameter decreases (200 nm for 15 h stirring durations). The increase in the diameters can be attributed to an enhanced OH⁻ concentration with increasing stirring durations, which (OH⁻ concentration) should be controlled during the whole synthesis process of the ZnO NRs to maintain a favored synthesis. The increase and decrease of the diameter of the NRs upon increasing the stirring durations is believed to be related to the super saturations state of the OH⁻ and Zn²⁺ species. There are two super saturations states, high and low. The high super saturations state favors the synthesis nucleation, while the low super saturations state favors the synthesis process.

Structural quality of the ZnO NRs has been confirmed by XRD diffraction illustrated in Figure 2(a). The XRD patterns of all the as-synthesized ZnO NRs prepared under different stirring durations show peaks, which can be indexed to the hexagonal wurtzite structure of ZnO (JCPDS Card No.36-1451). The as-synthesized ZnO NRs prepared under stirring durations of 1, 5, and 15 h exhibited a strong (002) peak, and a relatively weak (001) peak, demonstrating preferred growth orientation along the c-axis. While for the as-synthesized ZnO NRs prepared under stirring
durations of 3 h, exhibited relatively high (101) peak intensity compared to the (002) peak, suggesting different preferential growth orientation. The different nanorods growth orientation of the 3 h sample is also seen from the SEM figure (Fig. 1(b)).

Figure 2(b) shows the O 1s core level XPS spectra of the as-synthesized ZnO NRs prepared under different stirring durations. As shown in Figure 2(b), the O 1s peak for all samples exhibits an asymmetric profile, which can be decomposed to three Gaussian peaks. The main peak at low binding energy centered at (531.1 eV) is related to the Zn-O (O_I) bond within the ZnO crystal lattice. The peak at medium binding energy centered at (532.4 eV) is related to the oxygen-deficient regions (O_{II}) within the ZnO crystal lattice. Finally, the peak at higher binding energy centered at (533.4 eV) is related to the absorbed oxygen on the ZnO surface (O_{III}), e.g. H_2O, O_2. The intensity ratios of the O/Zn calculated using integrated XPS peak areas and the element sensitivity of the O and Zn are summarized in Table I for all samples. It is clear that intensity ratio of the O_{II}/O_I increases with the stirring duration, suggesting the presence of different oxygen-deficient sites and their concentrations as high as in the ZnO NRs synthesized at stirring duration of 5 h.

Figure 3 shows the room temperature µ-PL spectra of the as-synthesized ZnO NRs prepared under different stirring durations. All the PL spectra exhibited a strong emission peak in the UV region with the peak centered at around 385 nm, which corresponds to the band edge (NBE) emission in ZnO dominated by recombination of free excitons. Two peaks were observed in the visible region, these are: the green emission band centered around 527 nm, and the orange-red band centered at 670 nm. As it is well known all these peaks are due to deep level defects emissions. These defects are likely to be oxygen vacancies and interstitials (V_O, O_I).

**TABLE I.** O/Zn ratios are calculated from the integrated XPS spectral peaks for the different as-synthesized ZnO NRs.

<table>
<thead>
<tr>
<th>Stirring duration</th>
<th>Binding energy (eV)</th>
<th>O_I/Zn</th>
<th>O_{II}/Zn</th>
<th>O_{III}/O_I</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 h</td>
<td>531.08</td>
<td>532.41</td>
<td>533.24</td>
<td>0.70</td>
</tr>
<tr>
<td>3 h</td>
<td>531.07</td>
<td>532.54</td>
<td>533.56</td>
<td>0.68</td>
</tr>
<tr>
<td>5 h</td>
<td>531.06</td>
<td>532.39</td>
<td>533.36</td>
<td>0.65</td>
</tr>
<tr>
<td>15 h</td>
<td>531.05</td>
<td>532.43</td>
<td>533.40</td>
<td>0.66</td>
</tr>
</tbody>
</table>
The PL spectra (Figure 3) clearly show that the relative intensity of the NBE peaks increases as the stirring durations were increased until a stirring duration of 5 h and then it starts to decrease. This demonstrates that the concentration of DLE in the ZnO NRs decreases with increasing the stirring durations. This can be explained by the enhancement of the OH$^-\$ concentration with increasing the stirring durations, which lowers the influence of the activation energy during the synthesis process and hence lower the formation energy of the defect. This observation is consistent with the XPS results shown in Figure 2(b). Also, as shown in Figure 3, the sample prepared under stirring duration of 1 h showed slight blueshift in the NBE peak position, suggesting that the sample have high defect concentrations.

In order to investigate the spatial distribution of the DLE emission in ZnO NRs, CL spectra were collected from both the top- and cross-sectional views. The cross-sectional view represents the emission from non-polar surfaces, while the top view CL represents the emission from the top polar surface. Figure 4(a)-4(d) shows different CL spectra for all the samples synthesized for different stirring durations. For each ZnO NR sample, we compare the CL spectra acquired for the top and the cross-sectional views. Consequently, the CL spectra of ZnO NRs reveal that the intensity of the DLE emission was found to be affected by the stirring durations as shown in Figure 4(a)-4(d).

As the stirring durations is increased, the intensity of the non-polar surface compared to the polar surface starts to increase until a stirring duration of 5 h and then starts to decrease. To analyze this observation, the ratio of the NBE to the DLE peak intensities ($I_{\text{NBE}}/I_{\text{DLE}}$) was calculated and plotted as a function of the stirring durations as shown in Figure 5. A significant change in the $I_{\text{NBE}}/I_{\text{DLE}}$ ratio from the polar surface (black solid square) with increasing the stirring durations was observed. While from the non-polar surface (blue solid circle) the $I_{\text{NBE}}/I_{\text{DLE}}$ ratio is almost linear. This result is in agreement with the previous results reporting emission from the polar and non-polar surfaces of ZnO nanorods or wires. This result indicates that the deep level defect concentration in chemically synthesized ZnO NRs might be controlled using the stirring procedure.

Furthermore, in order to get insight the DLE present in the as-synthesized ZnO NRs, the top view CL spectra were decomposed using Gaussian function and the corresponding data are shown in Figure 6(a)-6(d). The asymmetric DLE band can be decomposed into three sub-band emissions in
FIG. 4. CL spectra obtained in top- and cross-sectional view. For clarity, spectra are normalized to the NBE intensity.

view of the PL spectra shown in Figure 3. Yellow emission centered around at 560–575 nm (2.2 eV) was observed for the stirring duration for 1 and 3 h and was attributed to the presence of OH groups and to the oxygen interstitials (O_i) present on the surface of the ZnO NRs. While for stirring duration of 5 and 15 h green emission centered around 549-551 nm (2.3 eV) was observed. The green emission is usually attributed to oxygen and zinc vacancies (V_{O}, V_{Zn}). Orange-red emission centered at around 627-648 nm (1.9), and red emission centered at around 732-747 nm.

FIG. 5. The ration of I_{NBE}/I_{DLE} versus the stirring durations, for both the top- and the cross-sectional views.
(1.7 eV) were observed for all samples, which was attributed to the oxygen interstitials (O\textsubscript{i}) present on the surface of the ZnO NRs\textsuperscript{6,12,15,18}.

Taking advantages of the CL instrument spatial resolution, the spectral evolution of the DLE along an individual nanorod can be investigated. Figure 7 shows a number of specific CL spectra collected for the individual NR in cross-sectional view at different positions between the substrate (NR bottom) and the top of the NR, as indicated in the insert. In such configuration, the electron beam was focused to a spot with a diameter of \(\sim 20 \text{ nm} \). Interestingly, CL spectra taken at point positions at the individual NRs show several rather fine features within the defect emission band, which is different compared to the CL spectra collected for several NRs as shown in Figures 4(a)-4(d). Here we should point out that all the CL measurements were repeatable and the observed features are not related to noise. Consequently, this observation indicates that the broad band has contribution from different defect-related transitions, which will be discussed in separate paper. Results in Fig. 7 indicate an increase in the intensity of the DLE peaks when moving from the NR bottom to the top of the NR for stirring durations of 1 and 3 h (see figure 7(a),7(b)), while for increased stirring durations of 5 and 15 h, the intensity of the DLE peaks shows opposite trend. It decreases while moving toward the tip of the NR (see...
FIG. 7. CL spectra of the individual NRs measured in cross-sectional view. Inset shows cross-sectional SEM images of the ZnO NRs with the indication of the points where CL spectra were taken. For clarity, spectra have been offset in vertical direction.

In zinc-rich environment, the $V_O$ has lower formation energy than interstitial zinc ($Zn_i$), which is most likely the case in our low temperature aqueous solution growth, since the O comes from the super saturation OH$^-$ reactions, while the Zn is produced by zinc nitrate (0.05 M) solution. As mentioned above the control of the super saturation OH$^-$ reactions is critical during the synthesis process. If relatively high amount of OH$^-$ is produced in a short period, the Zn$^{2+}$ ions in the solution will precipitate out quickly due to the high pH environment, and, therefore, Zn$^{2+}$ would contribute little to the ZnO nanorods synthesis and eventually result in the fast consumption of the precursor and prohibit further growth of the ZnO nanorods. Thus, it is highly probable that the stirring of the precursor solutions for 1 and 3 h in the preparation step favors high super saturation under thermodynamic equilibrium during the synthesis process. Therefore, the synthesis solution becomes poor in Zn, favoring the formation of $V_O$, and $O_i$ moving downward tip of the NR (Figure 7(a)). For the 3 h of stirring, the appearance of the emission peaks indicates that the defect distribution starts to change (Figure 7(b)). In contrary, stirring for 5 and 15 h favors low super saturation during the synthesis process, and thus the synthesis solution becomes rich in Zn, favoring the formation of $V_O$ and $O_i$ moving toward the bottom of the NR (Figure 7(c),7(d)).

IV. CONCLUSION

We have investigated the influence of the stirring durations of the precursor solutions on the concentration and spatial distributions of DLE in ZnO NRs. The investigated ZnO NRs were synthesized via the low temperature aqueous solution method. The FE-SEM and XRD data revealed that the as-synthesized ZnO NRs are highly dense, vertically aligned with a hexagonal wurtzite structure and have a preferred growth orientation along the c-axis. According to the XPS analysis a
significant change in the oxygen-deficiency with increasing the stirring durations is observed, probably attributed to the variations of point defects concentration. Room temperature µ-PL spectra were measured for all samples. Two defect related bands, the green, and organge/red bands were observed from the µ-PL investigation. Decomposition of the top view CL spectra were also performed. The results indicated that stirring for relatively short duration led to yellow emission band which then changed to green emission for longer stirring durations. The organge/red and the red emission bands were observed for all stirring durations. Based on the spatially resolved CL spectra taken along individual NRs synthesized by varying the stirring durations, we found that the growth environment changes from high super saturation to low super saturation and thus favoring different deep level defects distribution and type. We also concluded that these defects are likely to be attributed to Vo and O_2 and their presence at the surface varies with the stirring durations. These results suggest that the concentration and spatial distributions of deep level defects of ZnO NRs can be controlled by varying the stirring durations in the precursor solutions.

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