Enhancement of UV emission and optical bandgap of ZnO nanowires via doping and post-growth annealing

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Keywords: nanowires, zinc oxide, hydrothermal growth, optical bandgap, near band edge emission

Abstract
Zinc oxide (ZnO) nanowires (NWs) are gaining importance in optoelectronics because of their excellent electrical and optical properties. However, defects in the NW structure leads to suppression of the near-band-edge (NBE) ultraviolet (UV) emission, limiting their full potential for applications in optoelectronic devices. In this work, we present enhancement in NBE emission and bandgap modulation in ZnO NWs hydrothermally grown on sputtered Al-ZnO (AZO) films. Al dopant incorporation and post-synthesis thermal annealing are found to increase the NBE emission. Compared to Al-doping, the post-growth annealing produces a more significant enhancement in the NBE emission and a substantial increase of 34.5 meV in the optical bandgap, along with suppression of defect-related deep level emissions caused by oxygen vacancies and interstitials. This further improves the applicability of the ZnO NWs in stable, room temperature emission devices.

1. Introduction
In recent years, one-dimensional nanostructures have been extensively researched on due to their wide scale potential applications [1, 2]. Compared to their bulk or thin film counterparts, nanostructures have a higher surface area to volume ratio, can exhibit quantum effects, and are capable of greater modulation of their band structure [3]. Zinc oxide (ZnO), an n-type semiconductor material with a direct wide bandgap of ~3.4 eV and a high exciton binding energy of 60 meV, has excellent optical and electrical properties [4–6]. One-dimensional (1D) ZnO nanostructures have found diverse applications in optoelectronic devices, photovoltaic cells, photoelectrodes, piezoelectric transducers, light-emission devices, lasers and sensors [7–12]. Doping is one of the important approaches to enhance the performance of 1D nanostructure-based optoelectronic and photovoltaic devices [13]. The incorporated dopant can change or cause a shift in the band gap, thus essentially tuning the optical properties [14]. The structure and crystallinity also determine its optical behaviour [15]. In the present work, we have grown ZnO NWs on Al-ZnO (AZO) seed layer film by a facile one pot hydrothermal method. AZO film was chosen as the seed layer because it can also act as a transparent conducting oxide (TCO) layer, thus enabling better carrier extraction in device implementation. We have studied Al-doping of the NWs as well as post-growth thermal annealing and report how UV emission can be enhanced and how optical band gap of the NWs can be engineered. Both the Al dopant incorporation and thermal annealing help widen the bandgap with the latter method being more efficient in improving NBE emission and suppressing oxygen vacancies and interstitials related emissions, thus enhancing the optical properties of these NWs.

2. Experimental methods
2.1. Sputter deposition of the AZO seed layer
AZO seed layers were deposited by RF magnetron sputtering on Corning glass and silicon (Si) substrates. We used our previously obtained sputter deposition conditions [16] of RF power 150 W, substrate temperature 250 °C, and pressure 4.7mTorr, resulting in AZO film thickness of about 100 nm after 19 min of deposition.
2.2. Growth of doped and undoped ZnO NWs on AZO and post-growth annealing

The undoped ZnO NWs were grown by our previously reported \[17\] hydrothermal method, with 25 mM zinc nitrate hexahydrate \([\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}]\) and 25 mM hexamethylenetetramine (HMTA) in the ratio of 1:1 by volume as precursor solutions. For growing Al doped ZnO NWs, measured quantities of aluminum nitrate nonahydrate \([\text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}]\) was added to the precursor solution in order to obtain different Al/Zn atomic percentages. The NWs were grown with the growth surface facing down in an autoclave. After the growth, the samples were rinsed with DI water and dried. Some as-grown NW samples were annealed in forming gas (90% \(\text{N}_2\)/10% \(\text{H}_2\)) at 475 °C for 1 hour in a quartz furnace.

2.3. Structural and optical characterization

Scanning electron microscopy (SEM, Zeiss ULTRA Plus) and transmission electron microscopy (TEM, JEOL 2010F STEM) were used to study the morphology of the ZnO NWs grown on the AZO films. X-ray photoemission spectroscopy (XPS, Thermo-VG ESCALab 250) was used to analyze the chemical composition of the NWs. Photoluminescence of the NWs was measured at room temperature using a fluorescence spectrometer (Edinburg) with 320 nm excitation (Xe lamp).

3. Results and discussion

3.1. Morphology of the ZnO NWs Grown on AZO films

Figure 1(a) shows the TEM image of the tip of the grown ZnO NW. The high resolution (HR) TEM image in figure 1(b) reveals a crystalline structure with observable atomic rows. The selected area electron diffraction (SAED) pattern shown in the inset further confirms the single crystalline nature of the structure. The NWs have hexagonal wurtzite structure and the lattice plane spacing was 0.52 nm along the axis of the NW which confirms growth in the (001) direction. Finally, the cross-section and top view SEM images in figures 2(a) and (b) show the dense and upright nature of the NW arrays.
3.2. XPS analysis of doped and undoped ZnO NWs
For the Al-doped NWs that were synthesized by adding calculated amounts of Al(NO$_3$)$_3$·9H$_2$O to the precursors, XPS was used to study the chemical states of Zn, O and Al. Figure 3(a) shows the full XPS spectra of the undoped and doped (with 1%, 2.5% and 5% Al) NWs. In figure 3(a), the Zn2p$_{3/2}$ peak at 1022.4 eV is greater than the Zn2p$_{1/2}$ peak at 1045.5 eV, and the peak of metallic Zn with binding energy of 1021.5 eV is absent. This indicates that most of the Zn atoms are in a positive divalent oxidation state. The peak around 530 eV is due to the electron binding energy of O1s in the Zn-O bond. For both undoped and doped ZnO NWs, the Zn and O peaks are similar and the only difference in their XPS spectra occurs due to Al peaks. In order to analyze Al related peaks, figure 3(b) shows peaks in the 68–80 eV range in greater details. In figure 3(b), the Al2p$_{3/2}$ is located at around 74.8 eV which can be attributed to Al-O bonding. Also the metallic Al peak (72.7 eV) is unnoticeable, meaning that Al is successfully incorporated in the ZnO lattice and is present in an oxidized state. However, for 5% doped NWs, the Al2p$_{3/2}$ peak has shifted to around 77 eV. This shift might be due to a higher oxidation state of Al when the doping level is increased. The curve for the undoped NWs also suggests that there was no/minimal Al contribution from the AZO seed layer.

3.3. Photoluminescence (PL) Analysis of ZnO NWs
The normalized PL spectra of the undoped ZnO NWs are shown in figure 4(a). The UV emission peak at around 380 nm (3.26 eV) is attributed to NBE emission originating from exciton transition. The broader peak around 570 nm (in the 1.91–2.61 eV range) is due to a combination of transitions involving deep level defects. In figure 4(b), we show Gaussian fitting for these possible deep level emissions (DLE). The three fitting emission peaks located at 503 nm (2.47 eV), 553 nm (2.24 eV) and 611 nm (2.03 eV) can be attributed to ionized oxygen vacancies (V$_{O}^+$), oxygen interstitials (Oi) and neutral oxygen vacancies (V$_{O}$) respectively [18]. These three defect levels and transitions obtained from the Gaussian fitting are schematically shown in figure 4(c). In the measured PL, the small secondary peak around 680 nm is actually a relic of the PL detector in our fluorescence lifetime spectrometer, so the fourth fitting peak at 670 nm is ignored.

3.3.1. Effect of doping on PL
The normalized PL spectra of the ZnO NWs with different levels of Al doping are plotted in figure 5. It can be observed that in doped samples the intensity of the NBE emission steadily increases with increasing doping level. We also note that the oxygen vacancies and interstitials related DL emission intensity is slightly decreased with high Al doping due to compensation of Al ions in the ZnO lattice. With 5% Al doping, the ratio of NBE to DL emission intensity is 11 times higher than that with no doping. The peak at 760 nm in the doped samples is actually second-order UV peaks caused by the high-intensity primary UV emission (380 nm). This second order peak becomes prominent when the intensity of UV peak becomes higher than that of the visible peak.

3.3.2. Effect of annealing on PL
Figure 6(a) compares the PL spectra of undoped NWs before and after thermal annealing in forming gas. Annealing significantly enhances the NBE emission while almost completely suppressing the visible DL emission. Comparing the DL emission peaks of the unannealed and annealed NWs in figure 6(a), we observe that the DL emission peak has reduced by over 90% after annealing. Gaussian fitting has been performed for the DLE after annealing and the fit peaks have been plotted in figure 6(b). From figure 6(b), the intensities of the
three fit peaks corresponding to $\text{Vo}^+$, $\text{O}_i$ and $\text{Vo}$ after annealing have been denoted as $\text{Vo}_{\text{annealed}}^+$, $\text{O}_{\text{annealed}}$ and $\text{Vo}_{\text{annealed}}$ respectively. Similarly, from figure 4(b), the intensities of the three fit peaks corresponding to $\text{Vo}^+$, $\text{O}_i$ and $\text{Vo}$ before annealing have been denoted as $\text{Vo}_{\text{unannealed}}^+$, $\text{O}_{\text{unannealed}}$ and $\text{Vo}_{\text{unannealed}}$ respectively. To further investigate to what extent annealing suppresses defects, the ratio of the fit peak intensities after annealing to that before annealing is given in table I in the inset of figure 6(b). From the table it is evident that after annealing oxygen interstitials are almost completely eliminated and oxygen vacancies are significantly suppressed. This indicates that post-growth annealing increases the probability of recombination of free excitons and reduces the concentration of O-related point defects of vacancies and interstitials. While annealing temperature of 475 °C is not high enough for the diffusion of N$_2$ into the ZnO NWs, it is sufficient for oxygen interstitials to progressively

Figure 4. (a) PL spectra obtained for the undoped ZnO NWs, (b) Gaussian fit of the DL emission of the undoped ZnO NWs. (c). Transitions for ZnO NWs obtained from Gaussian fit of PL spectra.

Figure 5. Measured PL spectra of the undoped and doped (1%, 2.5% and 5% Al) NWs.
diffuse into oxygen vacancies in N$_2$ ambient. Consequently, although there is no external interaction, post-growth annealing seems to result in the passivation of O-related defects due to the rearrangement of atoms internally. Similar trend was observed for the doped samples as well. In order to compare the enhancement in the NBE emission relative to defect-related emissions, the peak intensity ratio $ENBE_{\text{DL}}$ is plotted for both annealed and un-annealed NWs as a function of doping (figure 6(c)). While the ratio increases with Al doping as discussed in the previous section, post-growth annealing causes much sharper increase in the $E_{\text{NBE}}/E_{\text{DL}}$ ratio for all doping levels. For the undoped NWs, the ratio increased 150-fold after annealing.

Another interesting observation is the blue shift in NBE emission peaks after annealing. Figure 7 shows the PL spectra of the samples in the UV region. Table II presents the observed blue shift for each doping level. The highest shift (34.5 meV) occurred for the low/un doped samples. The results suggest that for high doped NWs the annealing treatment enhances the free carrier concentration, for example by increased dopant activation, thereby causing a net increase in optical bandgap. In the low/un doped samples improved crystallization due to
annealing could also have contributed to the blue-shift. Overall, the observed increase in NBE emission and suppression of DL emission and the enhancement of the optical bandgap suggest that the post-growth annealing of hydrothermally grown ZnO NWs improves their suitability for stable, room temperature operation in emission devices.

4. Conclusion

In this work, we have synthesized undoped and doped ZnO NWs on sputtered Al:ZnO seed layers. Al-doping of the NWs was achieved by adding controlled amounts of Al(NO$_3$)$_3$.9H$_2$O to the precursor solutions. The NWs were analyzed by SEM, TEM, XPS, and PL. It is found that the optical bandgap in the NWs can be increased not only by increasing the doping level but also by post-growth thermal annealing. The enhancement in UV emission achieved by annealing is far superior to that achieved by doping. The near band-edge UV emission becomes stronger after thermal annealing while the defect-related deep level emission caused by oxygen vacancies and interstitials is almost completely suppressed. The ratio of NBE to DL emission peak intensities increases 150-fold after thermal annealing for the undoped NWs. The annealing also causes a blue-shift in the UV emission peaks, with the highest shift of 34.5 meV obtained for the undoped samples. The enhancement in optical bandgap and UV emission makes the post-growth annealed ZnO NWs attractive for stable emission devices.

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