

Effects of post-growth annealing treatment on the photoluminescence of ZnO nanorods

D. Wang, N. Sathitsuksanoh¹, H.Y. Yang¹, H. W. Seo, Y. H. Tzeng², C. C. Tin, M. J. Bozack, J. R. Williams, and M. Park³

Department of Physics, Auburn University, Auburn, AL 36849

¹Department of Chemical Engineering, Auburn University, Auburn, AL 36849

²Department of Electrical and Computer Engineering, Auburn University, Auburn, AL

³Corresponding Author: email (park@physics.auburn.edu)

The luminescence of ZnO exhibits a band edge UV emission peak and a broad visible emission band related to the deep level defects. The mechanism of the defect related electron-hole recombination process in ZnO has been under intensively studied, and yet it remains as a controversial subject. In this work, post-growth annealing treatment was carried out to investigate the mechanism governing the visible luminescence in ZnO nanorods synthesized using a thermal chemical vapor deposition (CVD) method.

Among the different mechanisms proposed to explain the visible luminescence, oxygen vacancy (V_O) is widely accepted as the most probable candidate, although no consensus could be reached regarding the charge state of the oxygen vacancy: singly ionized¹ or doubly ionized oxygen vacancy². Oxidation annealing was usually employed to modify the level of oxygen deficiency in ZnO, however contradictory results regarding the effect of annealing on the luminescence property of ZnO have been reported. In some experiments³⁴, the visible luminescence was found to be greatly enhanced after the oxidation annealing while the band edge UV luminescence reduced; the exact opposite

was observed in some other experiments^{5 6}. It was also found that the intensities of the visible and UV luminescence depend on the annealing temperature^{7 8}.

The ZnO nanorods studied in this work were grown on Si(100) substrates by thermal CVD method using Zn as the precursor.⁹ The wurtzite lattice structure was confirmed by XRD pattern. Raman spectrum (Fig. 2 inset) indicates that the nanorods are of good crystal quality. SEM image (Fig. 1) shows that most of the nanorods have diameters between 100 nm and 200 nm and a length of several micrometers. Room-temperature PL spectrum (Fig. 2) shows a near-band-edge (NBE) peak is located at about 3.2 eV and the green luminescence (GL) band is at about 2.5 eV.

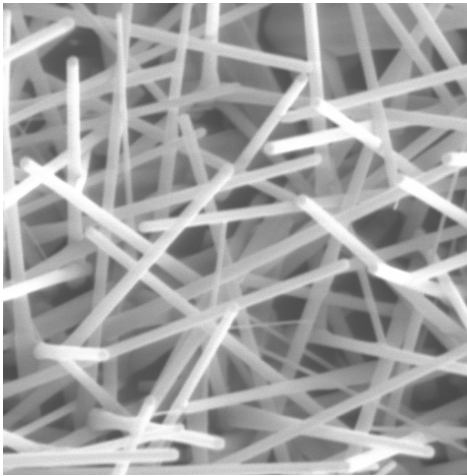


Figure 1. SEM image of the as-grown ZnO nanorods. Image size: $6 \times 6 \mu m$.

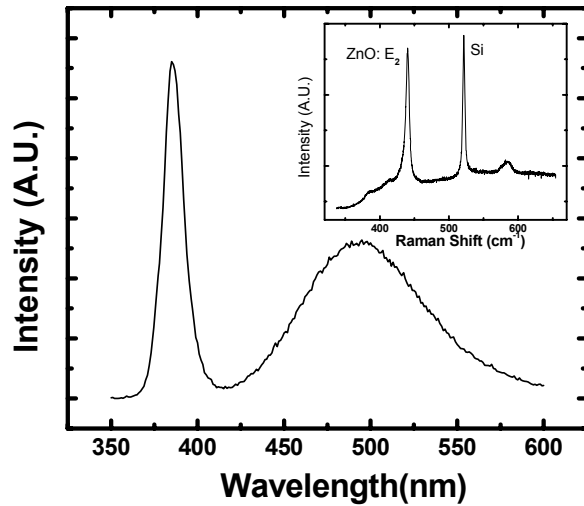


Figure 2. PL spectrum and Raman spectrum (inlet) of the as-grown ZnO nanorods (sample A, B and C).

The as-grown sample was then cut into three pieces to undergo different annealing processes (hereafter to be called as sample A, B and C). Sample A was annealed in oxygen atmosphere at 400°C for 1hr. The PL spectrum (not shown) of the annealed sample does not exhibit any changes.

Sample B was first annealed in pure oxygen flow at 800°C for the 1hr. Then it was annealed again in vacuum at 800°C for 1 hr. PL spectrum (Fig. 3) was collected after the oxygen annealing and subsequent vacuum annealing. It was found that the oxygen annealing greatly enhance GL while reduce NBE, but after the vacuum annealing the original PL spectrum of the as-grown sample was recovered.

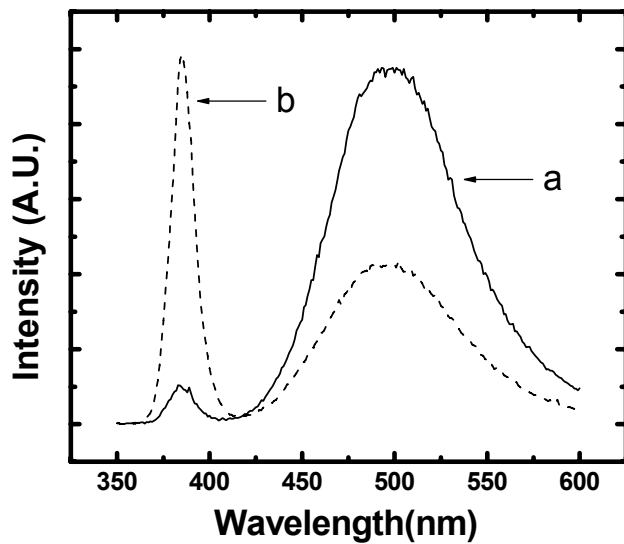


Figure 3. PL spectrum of ZnO nanorods (sample B) collected after two consecutive annealing processes: after oxygen annealing (a), and after subsequent vacuum annealing (b).

Sample C was first annealed in vacuum at 800°C for 1 hr, and then left in the oxidation furnace under pure oxygen flow at room temperature for 2 days. PL spectrum (Fig. 4) was collected after the vacuum annealing and subsequent 2-day's oxygen exposure. No significant change could be found in the PL spectrum collected immediate after the vacuum annealing, but the PL spectrum collected after the 2-day's oxygen exposure bear similar features to the PL collected after oxidation.

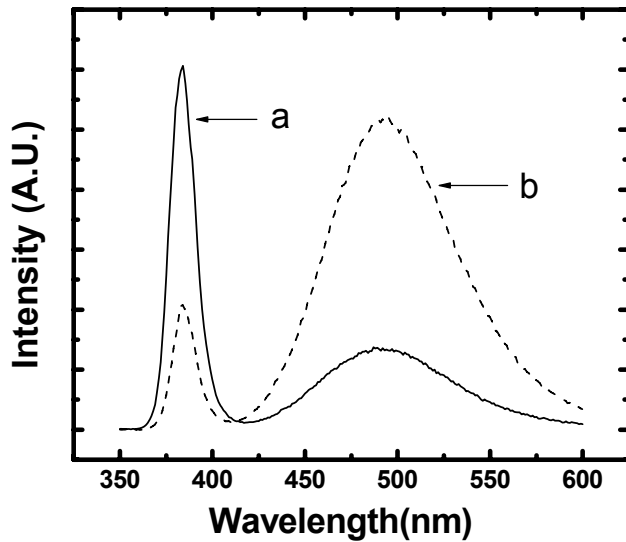


Figure 4. PL spectrum of ZnO nanorods (sample C) collected after vacuum annealing (a), and after subsequent exposure in oxygen ambient for 2 days (b).

We found that there is a close correlation between the observed PL behaviors and the band bending at the surface. Both the comparative study of nanowires with different surface to volume ratio¹⁰ and direct imaging using cathodoluminescence microscopy¹¹ have shown that GL is localized at the surface of the nanowires. The upward band bending caused by the chemisorption of oxygen at ZnO surface¹² drives the photo-generated electron-hole pairs in the depletion region to opposite directions, thus the photo-holes are collected near the surface and the NBE is reduced. The enhanced oxygen adsorption caused by oxygen annealing can partially explain the increasing GL intensity in sample B, the same analysis applies to the vacuum annealing.

However, a recombination center other than V_O is needed in order to fully understand the experimental result. Cu impurity is the other recombination center

that can lead to GL. Garces *et al.*¹³ concluded that the broad structureless GL at 500nm is due to DAP recombination between an electron bound to a shallow donor and a hole loosely bound to the Cu^+ . Korsunskaya *et al.*¹⁴ reported the increase of GL intensity near the cathode and decrease near the anode at 600-700°C when an external electric field was applied across a ZnO single crystal, and the change in GL was attributed to the electro-diffusion of Zn interstitial (Zn_i). The same group also reported that Cu impurity in CdS drifted from anode to cathode in the form of Cu_i^+ under the influence of electric field.¹⁵

We found that the observed change in PL after each annealing process can be explained by considering both the band bending and the migration of impurities. We believe that two major processes happened during the oxygen annealing: (1) the increasing number of chemisorption of oxygen at the surface and the consequently enhanced band bending as mentioned before. (2) the migration of positively charged impurity ions to the surface under the influence of the electric field in the depletion region. Since a substantial amount of photo-holes are swept to the surface, the segregation of impurity ions in the surface region increase the chance of photo-holes being trapped by them. Photo-electrons diffused or tunneled into the surface region can then recombine with the trapped holes.

The same processes happen during vacuum annealing: (1) desorption of surface oxygen and less band bending. (2) migration of impurity ions, similar to what happened in oxygen annealing but to a lesser extent.. Shortly after the vacuum annealing the depletion layer was greatly reduced and the band was still

flat, thus the PL shows strong NBE and weak GL (Fig. 4). After exposure in oxygen ambient for 2 days, the surface was recovered with oxygen and the band was bent again. This re-adsorption of oxygen decreased NBE and increased GL as shown in Fig 4. It is interesting to note that the PL of sample C could not be recovered to the original PL of the as-grown sample due to the redistribution of the impurities inside of nanorods causing more recombination centers near the surface.

At an annealing temperature of 400°C, adsorption and desorption of oxygen can still occur at much lower rate, but significant Zn_i diffusion requires a temperature more than 600°C, other impurities may need even higher temperature to migrate. This explains the insignificant change in the PL of sample A caused by the annealing processes.

As for the identity of this impurity, Cu⁺ seems like a good candidate, but the source of Cu contamination in the growth process can not be determined. Zn_i related complex was also suggested¹⁶, but it was shown¹⁶ that the interstitial Zn⁺ diffuse to the surface to form [Zn²⁺-O²⁻] surface pair which emits UV light. More information is needed to identify this impurity.

In conclusion, we have carried out oxygen and vacuum annealing experiment to study the mechanism of GL of ZnO nanorods synthesized by thermal CVD. Our experiment results reveal that V_O is not the dominant recombination center for GL observed in the present sample. A model based on the interplay between the band bending at the surface and the migration of

positively charged impurity ions was proposed, which satisfactorily explains the observed change in PL after each annealing process.

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