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Photoluminescence transient study of surface defects in ZnO nanorods grown by chemical bath deposition

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Two deep level defects (2.25 and 2.03 eV) associated with oxygen vacancies ($V_o$) were identified in ZnO nanorods (NRs) grown by low cost chemical bath deposition. A transient behaviour in the photoluminescence (PL) intensity of the two $V_o$ states was found to be sensitive to the ambient environment and to NR post-growth treatment. The largest transient was found in samples dried on a hot plate with a PL intensity decay time, in air only, of 23 and 80 s for the 2.25 and 2.03 eV peaks, respectively. Resistance measurements under UV exposure exhibited a transient behaviour in full agreement with the PL transient, indicating a clear role of atmospheric O$_2$ on the surface defect states. A model for surface defect transient behaviour due to band bending with respect to the Fermi level is proposed. The results have implications for a variety of sensing and photovoltaic applications of ZnO NRs. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4914067]
An SEM image of the ZnO NRs is given in Fig. 1. Lower resolution SEM images (not shown) demonstrate uniform coverage of the NRs over a large sample area. Our CBD ZnO NRs have a diameter and height \( \sim 150 \) nm and 1 \( \mu \)m, respectively. The NRs are oriented along the ZnO c-axis,\(^{12}\) and perpendicular to the substrate surface. The NR structure remains in the annealed sample, though a few nano-pits formed on the tips of the NRs.

The effect of drying and O\(_2\) annealing on the PL spectra is demonstrated in Fig. 2. The spectra consists of two peaks, one in the UV (shown in the inset of Fig. 2) and one at \( \approx 550\) nm related to defects. The defect peak, in all samples, can be fitted with two DLS peaks at 555 nm (2.25 eV) and 610 nm (2.03 eV). The annealed sample exhibits a large red shift of the defect peak to \( \approx 650\) nm, which can be fitted with two DLS peaks at 610 and 651 nm, and has the largest PL intensity in vacuum indicating that we may have increased the Zn-related defect concentration.\(^{16}\) Therefore, due to the reduction of the 555 and 610 nm peaks after annealing, we associate these peaks with \( V_o^- \).\(^{5,16}\) Furthermore, Fig. 2 demonstrates a decrease of the DLS peak intensity from the ND to the 2 week aged and the dried sample. This feature is understood as a result of organic species,\(^{14}\) defect complexes\(^{17}\) due to water,\(^{15}\) or OH groups\(^{13}\) loosely bound to the NR surface introduced during CBD. These defect species can act as shallow donors, are easily removed after UV exposure,\(^{14}\) and create a \( \pm 10\) nm shift in the DLS PL spectrum. Therefore, we conclude that drying the sample removes these defect species from the surface lowering, but stabilizing the PL intensity. The inset in Fig. 2 shows the UV peak centred at 382 nm for all samples. The intensity of the ND sample is almost 1.5 times the dried sample, and 7.8 times the annealed sample. This result is likely due to the observation that transitions do not occur from band to band, but with shallow defect states near the conduction band minimum (CBM) or valence band maximum (VBM), which are reduced during the O\(_2\) anneal.\(^{18}\) Many authors state that a reduction in the UV peak indicates a reduction in the optical quality of the sample, and thus a reduction of the UV sensing capability.\(^{4,5}\) We believe that this assessment is premature as it does not segregate the role of different defects types in UV sensing.

Fig. 3 shows the PL spectra for the dried sample taken both in air and vacuum. The DLS PL intensity is higher when measured in air, which is consistent with the ND sample (see Fig. 2). This result indicates that atmospheric O\(_2\) promotes defect radiative transitions, which we discuss further below. The 555 and 610 nm fits are shown, with a relative intensity of \( I_{555} \approx 1.2 \ I_{610} \) and \( I_{555} \approx 2.6 \ I_{610} \) in air and vacuum, respectively. We ascribe the 555 nm and 610 nm peaks to surface related \( V_o^- \), and \( V_o^+ \) respectively. Though our assignment of the \( V_o \) states is indirect, it is in agreement with the literature,\(^{13,16,19}\) and supported by our model below.

We measured the 555 nm PL intensity as a function of time to understand the effect of UV excitation on our ZnO NRs, shown in Fig. 4. First, the ND sample exhibits essentially no change in the PL intensity whether in air or vacuum. We assume that the PL transient is suppressed because of the loosely bound surface defect states. In contrast, after 1 week of drying, we measured a PL transient with an exponential decay time of \( \sim 70\) s. Comparing with the dried sample, in vacuum, there is no transient, while in air, there is a marked exponential decay with two components at 23 and 165 s, and a relative intensity of \( I_{23} \approx 1.2 \ I_{165} \). On the other hand, the annealed sample shows no defect transient, because of the reduction in the \( V_o \) concentration. A similar result was found in UV sensors, whereby O\(_2\) annealing reduces the UV sensing performance.\(^{20,21}\) Furthermore, the transient time of the 610 nm peak (not shown) is slower than the 555 nm peak with a single component \( \approx 80\) s.

Finally, in Fig. 5, a comparison between sample resistance and PL intensity as a function of time under UV
Bending in the depletion region forces \( V_0 \) to desorb from the sample surface, which reduces the depletion region and the number of \( V_0^+ \) sites; simultaneously, electron (filled circles) conduction electrons. It is also possible that \( V_2^+ \) (unoccupied) states will form at the surface with sufficient band bending. The result of all these factors is to further increase the depletion region, represented by \( \Delta \) in Fig. 6 ‘air.’ This picture differs from what was reported earlier, because atmospheric \( O_2 \) does not initially attach to conduction electrons. It is also possible that \( V_2^- \) (singly occupied) states will form at the surface with sufficient band bending. At the same time, possible trap-filling at the surface reduces the ionization state of \( V_0^+ \) or \( V_0^- \) (Ref. 9) and stabilizes the band bending; hence, we assume that the surface is mainly comprised of \( V_0^- \) sites. Therefore, in air, we expect more \( V_0^- \) and \( V_0^+ \) PL centers with a greater probability of transition, because of the larger depletion region. This picture explains why, in air, the defect PL intensity is larger and \( I_{555} \approx I_{610} \).

The bottom part of Fig. 6 depicts what happens after UV exposure. The UV excitation creates an occupation of excited electrons and holes, given by the closed and open circles in Fig. 6, respectively. In vacuum, there is a PL spectrum from the \( V_0^+ \) and \( V_0^- \) state at 2.25 and 2.03 eV, respectively, which is constant over time. While in air, the holes are free to migrate to the surface and neutralize \( O_2 \), allowing \( O_2 \) to desorb from the sample surface, which reduces the depletion region and induces two phenomena. First, electrons in the CB are free to conduct, and thus, a decrease in resistance is measured. Second, as the depletion region bends down, the ionization state of \( V_0^- \) (\( \rightarrow V_0^+ \)) reduces, thus reducing the number of radiative centers, which explains why the PL intensity decreases over time and why the 610 nm peak decays slower than the 555 nm peak. Therefore, \( O_2 \) desorption drives both the PL and resistance transient over the time scale of \( \sim 20 \) s in our samples, while the longer PL transient may be associated with the variation in the \( V_0^- \) ionization state and requires further investigation.

This model of surface defects can help to explain some of the conflicting results in the literature. For example, it has been argued that \( O_2 \) desorption is not a significant process in PPC studies, whereby the metastable state model of Ref. 6 is favored. However, these studies consider thin films, which have a lower concentration of surface defects and thus...
a modified O$_2$ desorption rate compared with NRs.\textsuperscript{15,22–24} In our model, since conduction electrons accumulate at the surface V$_{o}^{+}$ state, response time is correlated with V$_{o}^{+}$ due to surface band bending. Therefore, more band bending implies more V$_{o}^{+}$ states and promotes the V$_{o}^{+} \rightarrow$ V$_{o}$ transition, which can explain why better response was observed for gas sensors with reduced NR diameter.\textsuperscript{25} Furthermore, our model implies O$_2$ desorption is only one route to obtain charge separation through the V$_{o}^{+}$ state. Many authors have found enhanced UV sensing by coating ZnO with a metal\textsuperscript{4} or a conducting polymer,\textsuperscript{26} in agreement with our results using a Au interdigitated mask.

In conclusion, our low cost CBD ZnO NRs exhibit two main surface DLS peaks at 555 and 610 nm due to V$_{o}^{+}$ and V$_{o}$, respectively. The 555 nm PL intensity exhibits a transient in air $\sim$20 s, which is well correlated with the change in resistance under UV excitation. This correlation arises because O$_2$ desorption decreases the band bending and thus the concentration of V$_{o}^{+}$ states; simultaneously, charge separation reduces the sample resistance. The PL transient is suppressed in vacuum, because the depletion region is stable since O$_2$ desorption does not occur. We presented a unified model for these results with implications for photovoltaic, gas, pH, and UV sensing applications.

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