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

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(Dated: 13 February 2015)

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.

PACS numbers: 68.43.Fg, 68.43.Tj, 73.20.Hb, 73.20.At

Zinc oxide is a wide band gap (≈ 3.2–3.4 eV) n-type semiconductor with a large exciton binding energy (60 meV) and is a promising material for a range of applications. However, studies on low cost ZnO nanostructures (NSs) and thin films are unclear as to the source of n-type conductivity and persistent photoconductivity (PPC), the UV sensing mechanism, and the defect landscape. In particular, the correlation between the defect landscape and sensing (whether gas, pH, or UV) responsivity in low cost ZnO NRs is debated. In one model, the neutral oxygen vacancy (V$_o$) is an n-type donor state, atmospheric O$_2$ absorbs at this site, and a depletion region forms beneath the surface. UV excitation creates electron-hole pairs, holes migrate to the depletion region and O$_2$ desorption occurs, thus reducing the depletion region and increasing the conductivity. Therefore, the kinetics of O$_2$ desorption determine the response time of a UV sensor. In a second model, V$_o$ is reported to be a deep level state (DLS) and so cannot be a donor state. Instead, H occupying V$_o$ sites act as donor states, therefore, the O desorption model does not drive UV sensing. An alternative model suggests that after UV excitation, the DLS forms a metastable state resonant with the conduction band (CB), while the doubly ionized V$_o$ (V$_o^{2+}$) state lies above the CB. This mechanism is reported to explain PPC in UV sensors. Nonetheless, serious critiques over the validity of this model have been presented in the literature.

In either model, the energetic position of the ionized V$_o$ states are central. Experimentally, defect states depend on the carrier concentration and hence the Fermi level (E$_F$). A general consensus finds that V$_o$ lies within the flat band region, while the depletion region is dominated by the singly ionized V$_o$ (V$_o^+$) and/or V$_o^{2+}$ for ZnO NSs. Theoretically, the defect energy depends on the chemical potential and lattice relaxations, which vary between bulk materials, thin films, and NSs. To understand the role of the defect states with respect to O$_2$ desorption, we measured, in air and vacuum conditions, the defect photoluminescence (PL) peak intensity transient over large time scales in ZnO nanorods (NRs). We found a striking correlation between the change in PL intensity and NR resistance under UV excitation. These results indicate a transient in the surface defect structure, whereby, we present a unified model for O$_2$ desorption.

ZnO NRs were grown by chemical bath deposition (CBD). A Si substrate with native oxide was seeded with a ZnO nanoparticle solution (0.1 wt% in ethanol) via spin-coating (200 rpm, 10s and 700 rpm, 20 s). The seeded substrate was then placed in a solution of 25 mM zinc nitrate hexahydrate [Zn(NO$_3$)$_2$·6H$_2$O] and 25 mM hexamethylenetetramine [C$_6$H$_2$(NH$_2$)$_2$] (HMTA) at a temperature of 90 °C. The quality, diameter, and length of the NRs was measured using a Gemini field emission scanning electron microscopy (SEM) Carl Zeiss SUPRATM 25. CBD introduces water based absorbates, which we controlled this parameter by comparing samples as-prepared not dried (ND), dried at 100 °C for 20 min on a hot plate, and left to dry over two weeks. Additionally, we annealed a sample at 600 °C for 30 min in O$_2$ to understand the role of V$_o$.

Resistance measurements were performed under exposure to 364 nm UV light. The samples were biased to force a current of 1 nA between two probes 1 mm apart to extract the resistance. This value was used to avoid compliance in the samples and gave a good overall response under UV exposure. PL measurements were performed by pumping at 1.5 mW the 325 nm line of a He-Cd laser chopped through an acousto-optic modulator at a frequency of 55 Hz. The PL signal was analyzed by a single grating monochromator, detected with a Hamamatsu visible photomultiplier, and recorded with a lock-in am-
plifier using the acousto-optic modulator frequency as a reference. PL spectra were taken in air or vacuum within a cryostat ($\sim 10^{-5}$ mbar), to ascertain the role of atmospheric O$_2$. The PL transient behaviour was measured by fixing the monochromator at each peak wavelength and monitoring the PL intensity as a function of time.

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 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 $V_0^{\pm}$, and create a $\pm 10$ nm shift in the DLS PL spectrum. These defect species can act as shallow donors, are easily removed after UV exposure$^{15}$, 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$^{13,15}$. 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$^{14}$. We believe that this assessment is premature as it does not segregate the role of different defects types in UV sensing.

FIG. 1. SEM image of the ZnO NRs showing their hexagonal crystal structure. Ref. 12 measured their wurtzite crystal structure.

FIG. 2. PL spectra showing the variation in the DLS peak intensity between air and vacuum for the dry, ND, and annealed samples. The inset shows the UV spectra for the dry, ND, and annealed samples in vacuum.
with a single component ≈ 80 s.

Finally, in Fig. 5 a comparison between sample resistance and PL intensity as a function of time under UV exposure is shown for the dried sample. The inset of Fig. 5 depicts the geometry of the electrical probes during the resistance measurements. The electrical probes force a current along the NR length perpendicular to the depletion extension. There are several factors that can affect the transient measurements, such as the intensity of the excitation source and sample quality. Nonetheless, we consistently measure an exponential decay time in the resistance ~ 20 → 25 s, which is well correlated with the first decay time of the 555 nm PL peak. Resistance measurement using a Au interdigitated mask grown atop the Si substrate prior to ZnO NR growth gives faster decay time of 5 s (not shown). While, in the annealed sample (not shown) we measured no variation in the resistance under UV exposure. We can explain these results with a simple model. 

The results reported above hint at a clear role for surface defects under UV excitation, depicted in Fig. 6. First, the depletion region results from accumulated electrons at the surface due to broken lattice order. In the flat band region, V_o is neutral (doubly occupied) below E_F. Upward band bending in the depletion region forces V_o above E_F, which ionizes the state to become V_o^+ (singly occupied) (see Fig. 6 'vacuum'). Atmospheric O_2 absorbs on the surface at the V_o^+ sites by polarizing surface electrons and forming O_2^−, thus further increasing the depletion region, represented by Δ 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_o^2+ (unoccupied) 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_o^2+ or V_o^+ (Ref. 9) and stabilizes the band bending, hence, we assume that the surface is mainly comprised of V_o^+ sites. Therefore, in air, we expect more V_o^+ and V_o PL centres 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} ≈ I_{610}. 

The bottom part of Fig. 5 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 spectra from the V_o^+ and V_o state at 2.25 and 2.03 eV, respectively, which is constant over time. While in air, the holes are free to migrate to 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_o^+ (→ V_o) reduces, thus reducing the number of radiative centres, 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
FIG. 6. Schematic illustration of the UV sensing mechanism (not drawn to scale). The top and bottom half represent the band configuration in air and vacuum before and after UV excitation, respectively. Band bending ionizes the V\textsubscript{o} state at the surface to V\textsuperscript{o}\textsuperscript{+}. In the air configuration, absorbed O\textsubscript{2} increases the band bending (represented by Δ) and the number of V\textsuperscript{o}\textsuperscript{+} sites. After UV excitation, two DLS PL bands are represented. In air, holes (open circles) migrate to the surface allowing O\textsubscript{2} to desorb decreasing the depletion region and the number of V\textsuperscript{o}\textsuperscript{+} sites, simultaneously electron (filled circles) conduction increases.

PL and resistance transient over the time scale of ~20 s in our samples, while the longer PL transient may be associated with the variation in the V\textsubscript{o} 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\textsubscript{2} desorption is not a significant process in PPC studies\textsuperscript{15,22,24} whereby, the metastable state model of Ref. 6 is favoured. However, these studies consider thin films\textsuperscript{15,22,24} which have a lower concentration of surface defects and thus a modified O\textsubscript{2} desorption rate compared with NRs\textsuperscript{15,22,24}. In our model, since conduction electrons accumulate at the surface V\textsubscript{o}\textsuperscript{+} state, response time is correlated with V\textsuperscript{o}\textsuperscript{+} due to surface band bending. Therefore, more band bending implies more V\textsubscript{o}\textsuperscript{+} states and promotes the V\textsuperscript{o}\textsuperscript{+} → V\textsubscript{o} transition, which can explain why better response was observed for gas sensors with reduced NR diameter\textsuperscript{25}. Furthermore, our model implies O\textsubscript{2} desorption is only one route to obtain charge separation through the V\textsuperscript{o}\textsuperscript{+} state. Many authors have found enhanced UV sensing by coating ZnO with a metal\textsuperscript{24} 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\textsuperscript{o}\textsuperscript{+}, and V\textsubscript{o}, respectively. The 555 nm PL intensity exhibits a transient in air ~ 20 s, which is well correlated with the change in resistance under UV excitation. This correlation arises because O\textsubscript{2} desorption decreases the band bending and thus the concentration of V\textsubscript{o}\textsuperscript{+} states, simultaneously charge separation reduces the sample resistance. The PL transient is suppressed in vacuum, because the depletion region is stable since O\textsubscript{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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ACKNOWLEDGMENTS

We would like to thank Kingsley Iwu for valuable discussions and insights regarding the chemical synthesis of ZnO NRs. The authors acknowledge MIUR projects, ENERGETIC (PON02_00355_3391233), and PLASTIC (PON02_00355_3416798).