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ARTICLE TYPE

Tailoring the charge carrier dynamics in ZnO nanowires: the role of surface hole/electron traps

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Post-fabrication thermal-annealed ZnO nanowires (NWs) in an oxidizing (or a reducing) ambient were investigated using transient photoluminescence and X-ray photoelectron spectroscopy. Our findings reveal an ultrafast hole-transfer process to the surface adsorbed oxygen species (e.g., O_2^-) occurring within a few hundred picoseconds (ps) in the air-annealed samples; and an ultrafast electron-transfer process to charged oxygen vacancies (i.e., V_O^{2+}) occurring within tens of ps in the H_2 -annealed samples. Contrary to the common perception that the bandedge emission (BE) dynamics are strongly influenced by the carrier trapping to the green emission related defect states (i.e., V_{Zn}), these above processes compete effectively with the ZnO BE. Hole trapping by ionized V_{Zn} , which occurs in an ultrashort sub-ps-to-ps timescale (and hence limits its effective hole capture radius), however, has less influence on the BE dynamics. Importantly, our findings shed new light on the photoinduced charge transfer processes that underpins the novel properties of enhanced photocatalytic activity, photovoltaic performance, and photoconductivity response of ZnO NWs; thereby suggesting a strategy for tailoring the ultrafast carrier dynamics in ZnO NW-based devices.

20 Introduction

One-dimensional (1-D) systems and quasi 1-D systems such as nanowires and nanorods have attracted much attention in the recent years due to their potential as building blocks for nanoscale transistors, sensors and optoelectronic devices. In particular, ZnO nanowires (NWs) have received considerable attention due to their unique properties (i.e., wide bandgap, large exciton binding energy etc.). Their meteoric rise to prominence could also be attributed to the significant advances in nanofabrication techniques which have afforded excellent control over the growth of dislocation free, highly faceted, single crystal ZnO NWs.¹ Potential applications for ZnO NWs include areas of optoelectronics,^{2,3} photovoltaics,^{4,5} photocatalysis,^{6,7} photonics,^{8,9} and photodetectors^{10,11} etc. To optimize device properties such as power consumption and modulation speed etc. for fast response, high sensitivity UV detectors, high efficiency solar cells and photocatalysts, a detailed understanding of the photoinduced carrier dynamics in light of the various competing radiative and non-radiative pathways is essential.

With a high surface to volume ratio in NWs, surface defects, near surface traps and surface adsorbed species, offering alternative relaxation pathways for the deexcitation of photo-excited carriers, will play a significant role in the carrier relaxation dynamics of these 1-D systems.¹² Many of the native point defects (oxygen vacancies (V_O), Zn vacancies (V_{Zn}),

oxygen antisites (O_{Zn}), Zn interstitials (Zn_i), etc)¹³ are formed during the NW growth and their concentrations are highly dependent on the growth conditions and post-fabrication treatments. Post-fabrication thermal annealing of ZnO NWs in an oxidizing/reducing gas ambient is commonly used to tune the intrinsic (or native) defects, modify the surface states and modulate the carrier concentrations; effecting changes to the optical and electrical properties of these NWs that result in enhanced gas sensitivity, field emission properties, photoconductivity, and photocatalytic activity¹⁴⁻¹⁹.

Typically, in an oxidizing ambient,²⁰ adsorbates like O_2 molecules undergo chemisorption on the NW's surface by capturing a free electron from the n-type ZnO (i.e., likely $O_2(g) + e^- \rightarrow O_2^-(ad)$),¹⁰ resulting in an upward band bending as shown in Fig. 1a. Conversely, in a reducing ambient,²⁰ adsorbates like atomic hydrogen (H) or intrinsic electron donors like V_O at the surface, transfers their electrons to the semiconductor (i.e., likely $H(g) \rightarrow H^+(ad) + e^-$ or $V_O \rightarrow V_O^{2+} + 2e^-$), giving rise to a positively charged surface; resulting in a downward band bending that moves the conduction band below the Fermi level, E_F (see Fig. 1b). These contrasting scenarios are commonly known to give rise to electron depletion and electron accumulation respectively at the semiconductor NW surface.²⁰ Upon illumination with photon energies above the band gap energy, photo-excited holes (electrons) in the former (latter) will migrate to the surface traps along the potential slope produced by the band-bending. Such photo-induced charge

transfer (CT) processes that ensue forms the basis of the enhanced field emitting properties, photoconductivity response, photocatalytic and photovoltaic performance of ZnO NWs.²¹⁻²³ A detailed understanding of the influence of the surface traps on the CT processes and the lifetime of photogenerated carriers in ZnO NWs is still lacking. Elucidating these ultrafast CT mechanisms that reflect the dynamic interplay between various trapping sites introduced by post-fabrication thermal annealing in ZnO NWs are the main foci of this paper.

Time resolved photoluminescence (TRPL) spectroscopy is a powerful probe of carrier dynamics and their relaxation pathways in semiconductor NWs.²⁴ Together with complementary chemical sensitive techniques such as X-ray photoelectron spectroscopy (XPS), an insight into the microscopic origins of the trapping centers and their characteristic trapping timescales can be elucidated. Herein, we report on the ultrafast CT processes in ZnO NWs with post-fabrication thermal annealing in an/a oxidizing/reducing gas ambient (and with UV-treatment) following above E_g photoexcitation. We found evidences of a hole transfer time constant of $\tau_{\text{ht-air-annealed}} \approx 400 \pm 80$ ps to the surface adsorbed oxygen species (O_2^-) in the air-annealed sample and an electron transfer time constant of $\tau_{\text{et-H}_2\text{-annealed}} \approx 60 \pm 10$ ps to V_O^{2+} in the H_2 -annealed sample. Furthermore, our studies reveal an ultrafast, localized hole transfer (in the sub-ps-to-ps timescale) to the green emission (GE) related defect states. Unlike the other two CT processes (to O_2^- and V_O^{2+}), these hole traps have limited influence over the ZnO band-edge emission (BE) lifetimes. This is contrary to the common perception that the ZnO BE dynamics are strongly influenced by the carrier trapping to the GE-related defects. Importantly, our findings shed new light on the photoinduced CT processes that underpins the novel properties of enhanced photocatalytic activity, photovoltaic performance, and photoconductivity response of ZnO NWs; thereby suggesting a strategy for tailoring the ultrafast carrier dynamics in ZnO NW-based devices.

Experimental

Sample preparation and post-fabrication thermal annealing.

In our experiments, vertically aligned ZnO NWs with diameters ranging from 80–100 nm and lengths of ~ 1 μm , were grown on c-plane sapphire by a chemical vapor transport method previously reported.²⁵ Briefly, the substrates were first carefully cleaned before depositing a Au film (with 2 nm nominal thickness) on them. For the growth, a mixture of high purity ZnO powder (99.999%) and graphite powder (99.999%) with a weight ratio of 1:1 ZnO/C was used as the source, which was heated at a ramping rate of 50 $^\circ\text{C min}^{-1}$. The substrate temperature was kept at about 850 $^\circ\text{C}$ for 15 mins for NW growth. High-purity argon mixed with 5% oxygen with a constant flow rate of 50 sccm was used as the carrying gas. The as-grown sample was then divided into three pieces: one piece was kept without any further treatment – *as-grown*; one piece was annealed in air at 600 $^\circ\text{C}$ for 30 mins (at atmospheric pressure) – *air-annealed* and another piece was annealed in forming gas at (90% Ar + 10% H_2) at 420 $^\circ\text{C}$ for 30 mins (H_2 pressure: 25mbar) – *H₂-annealed*. The fresh H_2 -annealed sample was kept in a vacuum desiccator to minimize

its contact with air prior to the optical and XPS measurements. These annealing conditions (at temperatures $< 850^\circ\text{C}$) were chosen to allow modulation of the surface properties and defect content without severely altering the sample composition.

Transmission electron microscopy and X-ray photoelectron spectroscopy.

The surface morphologies of the ZnO NWs were examined using a transmission electron microscope (JEOL 2100 TEM) operating at 200 KV. XPS measurements were performed using a VG ESCALAB 220i-XL system with a monochromatic Al K_α (1486.6 eV) X-ray source.

Steady state and time-resolved photoluminescence spectroscopy.

Time-integrated photoluminescence (TIPL) and time-resolved photoluminescence (TRPL) measurements were performed using 325 nm, 150 fs excitation pulses generated from a Coherent TOPAS-CTM optical parametric amplifier that was pumped by a 1kHz Coherent LegendTM regenerative amplifier, which was seeded by a 80 MHz Coherent VitesseTM oscillator. Typically, the samples were photoexcited with a pump fluence of 50 $\mu\text{J}/\text{cm}^2$ and the PL signals were collected in a conventional backscattering geometry and detected by a charge-coupled device array (Princeton Instruments, PixisTM 400B) coupled to a monochromator (Acton, Spectra ProTM 2500i). The temporal evolution of PL was resolved by an Optronis OptoscopeTM streak camera system which has an ultimate temporal resolution of ~ 10 ps when operated at the shortest time window of 330 ps. The BE TRPL measurements were typically performed with a time window of 1 ns and a time resolution of ~ 30 ps. However, for faster decays, shorter temporal settings of the streak camera were used. To remove the chemisorbed species, the samples were illuminated with 325nm, 100 $\mu\text{J}/\text{cm}^2$ fluence UV light for 20 mins in a continually evacuated optical cryostat (at a pressure of 10^{-5} Pa) at room temperature. Prior to UV-illumination, all the samples were measured at room temperature in air ambient, while the PL measurements of the UV-illuminated samples were performed under vacuum.

Results and discussion

TEM & XPS characterization of ZnO NWs.

Transmission emission microscopy (TEM) reveals a roughened polycrystalline surface with small ZnO particulates (~ 2.5 nm in diameter) that was formed in the H_2 -annealed samples (Fig. 2c), while there are no observable changes to the surface of the air-annealed samples (Fig. 2b) compared to the as-grown sample (Fig. 2a). The XPS spectra of O1s peak of the as-grown, air-annealed and H_2 -annealed ZnO NWs and their deconvoluted peaks are shown in Figure 2d – f; which exhibit distinct differences. The O1 1s peak (530.27 eV) present in all three samples has been attributed to originate from the O^{2-} ions in the ZnO lattice sites.²⁶ The middle O_{II} 1s peak located at slightly higher binding energy of 531.23 eV, which is present in both the as-grown and the H_2 -annealed samples, is attributed to O^{2-} ions in the oxygen deficient regions.²⁶ This binding energy shift arises from a reduced screening of the nearest neighbor O 1s electrons from their nucleus by an electron charge density when a V_O is created;

thereby raising the effective nuclear charge Z_{eff} (i.e., the binding energy) of an O_{II} 1s electron relative to that of an O_{I} 1s electron. Hence, the peak intensity variations of O_{II} 1s peak can be correlated with the surface V_{O} concentration in the sample. The relative increase in the intensity of this peak in the H_2 -annealed sample suggests an increased V_{O} concentration on the surface of ZnO NWs after H_2 -annealing.

The O_{III} 1s peak, located at $\sim 532.01 - 532.69$ eV for the three samples is attributed to the presence of loosely bound oxygen species on the surface of ZnO NWs (e.g., adsorbed O_2 , $-CO_3$ or H_2O).^{27, 28} Oxygen chemisorption on the surface of ZnO NW is likely to be more prevalent in the air-annealed samples than in the as-grown and the H_2 -annealed samples. Previously, it was reported that the rate of O_2 chemisorption increases with increasing temperature^{29,30} and the chemisorbed O_2 could diffuse into the bulk during annealing to induce a high density of acceptor-like defects (i.e., V_{Zn} , O_{Zn}). This would result in the compensation of the donor-like defects (i.e. V_{O} , Zn_i) and the depletion of the carrier density.³⁰⁻³³ Therefore, the substantive increase of the O_{III} 1s peak relative to the O_{I} peak, as well as the absence of the V_{O} -related O_{II} 1s peak in the air-annealed sample (from Fig 2(e)) are consistent with this interpretation (i.e. a dominant presence of chemisorbed O_2 species on the surface of the air-annealed ZnO NWs). Identification of the specific species (e.g., adsorbed O_2 , $-CO_3$ or H_2O) on the surface of the ZnO NWs is beyond the scope of this work and we shall term these loosely bound oxygen species as chemisorbed O_2 species (O_2^-).

Variation in PL and TRPL properties of ZnO NWs with different treatments.

Fig. 3a shows the room-temperature TIPL spectra for the three samples which exhibit a BE peak at ~ 3.28 eV and a broad defect-related GE band centered at ~ 2.45 eV of varying intensities. This GE band is typical of ZnO nanostructures prepared by the vapor transport method; and was believed to have originated from on/near surface defects.^{3,34-37} Nonetheless, the identity of the defect responsible for the GE remains entwined with controversies.³⁴ Previously, it was commonly believed that this defect is V_{O} .³⁸ However, recent theoretical and experimental works have identified that the V_{Zn} deep acceptor state as a more likely source of the GE.^{13,39,40} From first principles calculations, amongst all the native point defects in n-type ZnO, V_{Zn} possesses the lowest formation energy on the ZnO surface (under O-rich conditions)⁴¹ and this energy is sufficiently low for negatively charged Zn vacancies (e.g., V_{Zn}^{2-}) to exist in appreciable concentrations in n-type ZnO, functioning as compensating centers.¹³ Possible charge state configurations of V_{Zn} -related defects include: V_{Zn}^0 , V_{Zn}^- and V_{Zn}^{2-} . Our experimental data from the air-annealed sample is consistent with the recent finding about alternative origins of the GE as our results show that there is an inverse relation between a decrease in V_{O} concentration (from XPS) and an increase in GE intensity (from PL) compared to the as-grown sample. Similarly, this inverse relation is also evident from the H_2 -annealed sample where the converse is evident: i.e., an increase in V_{O} concentration (from XPS) and a decrease in GE intensity (from PL). The decrease in GE intensity following H_2 annealing is attributed to the passivation of V_{Zn} through the formation of $V_{\text{Zn}}-H_2$ complexes.⁴² We therefore attribute the GE to originate from the recombination between the

electrons in the conduction band/shallow donors and the holes trapped by acceptor states (i.e., $CB \rightarrow$ acceptor or from donor acceptor pair (DAP) recombination), in a mechanism similar to that of the yellow band in GaN epitaxial layers.⁴³ The mechanism and the carrier dynamics of the GE band in ZnO NWs will be discussed in another paper.

Next, we shall turn our attention to the dynamical aspects of the BE recombination in relation to the influence from the various defects. Fig. 3b shows the BE PL decay curves for three samples that are fitted with bi-exponential components: $I(t) = A_f \exp(-t/\tau_f) + A_s \exp(-t/\tau_s)$, where A_f and A_s refer to the decay amplitudes (i.e., weighting factors) of the fit and τ_f and τ_s refer to the decay time constants of the fast and slow components respectively. The former and latter time constants were attributed to arise from the recombination of the excitons near the surface and the bulk respectively,⁴⁴ or more generally, from the defect-rich regions (i.e., dominated by the non-radiative component) and the defect-free regions (i.e., dominated by the radiative component) respectively in $1/\tau_{\text{PL}} = 1/\tau_R + 1/\tau_{\text{NR}}$; thereby yielding two different decay time constants in our ensemble-averaged measurements. Table 1 lists the BE decay time constants and their respective weighting factors (in %) for the various samples.

Hole-trapping time by chemisorbed O_2^- in as-grown and air-annealed ZnO NWs.

After air-annealing, the BE becomes quenched while the GE band becomes enhanced as shown in Fig. 3a, typical of oxygen-annealed ZnO materials prepared by physical methods (in thin films^{45, 46} or NWs^{35, 47}) reported previously. TRPL measurements (Fig. 3b) reveal a shortening of the BE lifetimes compared to the as-grown samples. This would arise from a competition from the alternative relaxation pathways: hole trapping by defects (e.g., V_{Zn} , DAP etc.) and by surface chemisorbed oxygen species (O_2^-). This latter pathway can be suppressed through ultraviolet (UV) illumination of the samples in vacuum, where neutralization by photo-generated holes will desorb the O_2 molecules (i.e., $h^+ + O_2(\text{ad}) \rightarrow O_2(\text{g})$).¹⁰ Upon UV illumination at 325 nm under vacuum in an optical cryostat, there is an enhancement of the BE for both the as-grown and air-annealed sample (Fig. 3a), together with a lengthening of the PL lifetimes (Fig. 3b) that is attributed to the suppression of the hole-trapping process. Furthermore, upon exposing the UV illuminated ZnO NWs back to the air ambient, their emission properties prior to UV illumination were recovered, due to the re-adsorption of O_2 molecules on the NW surface.

UV illumination has only a marginal effect on the GE band for both the as-grown and air-annealed samples (see Fig. 3a). The V_{Zn} concentration is unlikely to be drastically modified by UV illumination. Hence, we would expect that any contributions of V_{Zn} to the BE recombination dynamics to remain largely invariant following UV illumination. From these results, we can obtain the average hole-trapping time constant τ_{ht} by the chemisorbed O_2^- in as-grown and air-annealed samples after photo-excitation, using the following relations (See Fig. 1c):

$$\text{Before UV: } \frac{1}{\tau_{\text{PL}}} = \frac{1}{\tau_{\text{R}}} + \left(\frac{1}{\tau'_{\text{ht}}(\text{V}_{\text{Zn}})} + \frac{1}{\tau_{\text{ht}}(\text{O}_2^-)} \right)$$

$$\text{After UV: } \frac{1}{\tau'_{\text{PL}}} = \frac{1}{\tau_{\text{R}}} + \frac{1}{\tau'_{\text{ht}}(\text{V}_{\text{Zn}})};$$

where τ_{R} is the radiative lifetime of BE, $\tau'_{\text{ht}}(\text{V}_{\text{Zn}})$ and $\tau_{\text{ht}}(\text{O}_2^-)$ are the characteristic hole trapping time by GE related defect states (i.e., V_{Zn}) and chemisorbed O_2^- respectively, τ_{PL} and τ'_{PL} are the average exciton lifetimes measured before UV illumination in air and after UV illumination in vacuum respectively. From these, we obtain: $\tau_{\text{ht-as-grown}} = [1/\tau_{\text{PL}} - 1/\tau'_{\text{PL}}]_{\text{as-grown}}^{-1} \approx 900 \pm 200$ ps and $\tau_{\text{ht-air-annealed}} \approx 400 \pm 80$ ps. The larger $k_{\text{ht}(\text{O}_2^-)}$ of the air-annealed sample (i.e., faster $\tau_{\text{ht-air-annealed}}$) can be attributed to the higher concentration of chemisorbed O_2 species present following air-annealing, in agreement with our XPS results.

Electron-trapping pathways introduced by H_2 -annealing.

Hydrogen annealing has been previously reported to result in the passivation of the deep centers in ZnO ⁴⁸ as well as in the formation of non-radiative defects, such as V_{O} , Zn_i or OH groups through reactions with ZnO . Our results in Fig. 3d show that H_2 -annealing reduces both the BE intensity and the lifetime of BE, in agreement with previous reports.^{49,50} Through the formation of $\text{V}_{\text{Zn}}\text{-H}_2$ complexes, the GE band is also significantly reduced. XPS measurements indicate that there is an increase of V_{O} concentration after H_2 -annealing. A likely mechanism for the formation of V_{O} is: $\text{ZnO} + \text{H}_2 \rightarrow \text{Zn} + \text{H}_2\text{O} + \text{V}_{\text{O}}$. The removal of an oxygen atom from the ZnO lattice results in the breaking of four Zn-O bonds. The resulting four “dangling” bonds on the surrounding Zn atoms combine to form a fully symmetric a_1 state in the bandgap, and three near-degenerate states located above the conduction band minimum (CBM). For V_{O}^0 , the a_1 state is occupied by two electrons while the other three states above the CBM are always empty and need not be further considered.¹³ First principles investigation by Janotti and Van de Walle¹³ has shown that in ZnO , both the V_{O}^0 and V_{O}^{2+} charge states are more likely to be formed than V_{O}^+ . This is attributed to the unusually large local lattice relaxations (i.e., “negative- U ” behavior where U is the on-site Coulomb correlation energy) that significantly reduces the formation energies of V_{O}^0 and V_{O}^{2+} relative to V_{O}^+ . Recently, based on first principles density functional theory methods, it was also reported that the formation energy of V_{O}^{2+} is lowest at the surface of the ZnO NWs.⁴¹

In the V_{O}^{2+} configuration, the empty a_1 state is located close to the CB and could thus function as an electron trap.¹³ Hence, we attribute the BE suppression to arise from a competition from photo-excited electron trapping by V_{O}^{2+} . UV illumination in vacuum has little or no effect on the freshly treated H_2 sample, with the PL spectrum and radiative recombination dynamics remaining invariant to that of the pre-illuminated case. This shows the deficiency of chemisorbed O_2^- after H_2 -annealing and the non-passivation of the V_{O}^{2+} state (with UV illumination) in vacuum. It is also highly likely that V_{O}^{2+} plays a more dominant role in the formation of the accumulation region than the adsorbed H atoms as any adsorbed H atoms would have been

desorbed from the NW surface following UV illumination. With the suppression of the relaxation pathways to both V_{Zn} and chemisorbed O_2^- in the H_2 -annealed NWs, the trapping of the photo-excited electrons to V_{O}^{2+} is therefore the dominant non-radiative process that competes with the BE (see Fig. 1d). Before we elucidate the average electron trapping time constant by V_{O}^{2+} , we would like to further examine the relative effects of the various non-radiative pathways (i.e., V_{Zn} -related defects, chemisorbed O_2^- and V_{O}^{2+}) on the BE dynamics of these ZnO NWs.

Relative effects of V_{Zn} -related defects, chemisorbed O_2^- and V_{O}^{2+} on the BE dynamics of ZnO NWs.

To examine the carrier trapping process to GE-related defects in the air-annealed samples, we shall focus on the UV-illuminated as-grown (grey line) and air-annealed (red line) samples (in Fig. 3) where the hole-trapping pathway by chemisorbed O_2^- is suppressed. The higher (lower) BE intensity of the former (latter) is commensurate with longer (shorter) BE decay lifetime. We propose that the decrease of BE for the air-annealed sample would arise from the trapping of the photo-excited holes to negatively charged V_{Zn} states (i.e., V_{Zn}^- or $\text{V}_{\text{Zn}}^{2-}$). An earlier study reported the enhancement of the GE and suppression of the BE of ZnO powder following annealing in air at 1000°C .⁵¹ The authors attributed the shortening of the BE lifetimes to exciton trapping by the GE related defects with a calculated exciton trapping lifetime comparable to the intrinsic exciton lifetime (i.e., ~ 2.0 ns).⁵² Our findings reveal an ultrashort sub-ps-to-ps hole trapping process to these ionized V_{Zn} states. Evidence of this can be found in the TRPL measurements of the BE and GE dynamics (shown in Fig. 4a) where both the rise times of the BE and GE exhibits a near-simultaneous onset of the spontaneous emission; indicating that the carriers are indeed rapidly trapped at these ionized V_{Zn} states. This finding is further corroborated by femtosecond differential transmission measurements where hole trapping times of < 1 ps were measured in all the samples (see Supplementary Information). In addition, as shown in Fig. 3b, following UV illumination, the BE dynamics of the air-annealed sample recover to approximately that of the UV illuminated as-grown sample. Although air-annealing increases the concentration of V_{Zn} in ZnO NWs, hole-trapping to the chemisorbed O_2^- plays a more significant non-radiative role in the BE dynamics compared to the hole-trapping process by the ionized V_{Zn} species in these air-annealed samples. The small difference in the BE dynamics between the as-grown and the air-annealed samples after UV illumination could be attributed to the introduction of other types of defects (e.g., O_{Zn}) as a consequence of the air-annealing.

Amongst the three main non-radiative relaxation pathways identified: V_{Zn} -related defects, chemisorbed O_2^- and V_{O}^{2+} , the first two are dominant in the air-annealed samples while V_{O}^{2+} is dominant in the H_2 -annealed samples. These contrasting scenarios allow us to further compare the relative effects of these non-radiative relaxation pathways on the BE recombination dynamics through a pump-fluence dependent study. Fig. 4b shows a plot of GE intensity as a function of pump fluence and Fig. 4c show plots the best fit parameters for the BE bi-exponential decay as a function of pump fluence for the air-annealed and H_2 -annealed samples respectively. The weighting factor of the fast decay component, A_f (or the fast decay

amplitude), was also plotted together with τ_f , which is associated with the recombination of the excitons from the defect-rich regions. With increasing pump intensities, a saturation of the defect states would be evident from an initial increase of the decay lifetimes or decrease of the decay amplitude and the eventual leveling of both the decay lifetimes and decay amplitude. Hence, the trend lines (i.e., the saturation or non-saturation behaviour) of A_f and τ_f as a function of the excitation pump fluence would be indicative of the concentration of the non-radiative centers present in the samples.

With increasing pump fluence, the GE intensity of the air-annealed sample increases linearly, while that of the H₂-annealed sample becomes saturated (Fig. 4b). This clearly shows a saturation of the V_{Zn} defect states in the latter, while there is an abundance of such states in the former. However, the BE recombination dynamics indicate otherwise: the decay time constants τ_f and τ_s (i.e., fast and slow components of the radiative e-h recombination originating from the defect-rich and defect-poor regions respectively) of the air-annealed sample increases and approaches a plateau while that of the H₂-annealed sample merely shows an increasing (non-plateauing) trend. Furthermore, with increasing fluence, the A_f values of both samples decreases; but with that of the air-annealed sample exhibiting a sharp decrease that levels off to a plateau. These observations can be explained as follows: (a) for the air-annealed samples, the V_{Zn}-related defects are in abundance and are not saturated at these pump intensities. The BE decay lifetimes increase with the removal of the chemisorbed O₂⁻ by the photo-excited holes and approach a plateau as the desorption and readsorption of O₂ reach an equilibrium. (b) For the H₂-annealed sample, the saturation of the GE clearly shows that the V_{Zn} defect states have been saturated at these pump intensities. However, the V_O states which are in abundance are not saturated at these pump intensities and this is evident from the increasing (non-plateauing) trend of the BE decay lifetimes and the decreasing (non-plateauing) trend of the decay amplitude A_f . Hence, from these results and our earlier result that hole trapping to the negatively charged V_{Zn} occur on an ultrashort sub-ps-to-ps timescale, we can infer that these V_{Zn} deep defect states have a limited effective hole capture radius. Although hole trapping by V_{Zn}-related defects depopulates the bandedge carrier population, the ultrafast trapping exhibited by these states and their localized nature mean that the hole-trapping process to the ionized V_{Zn} species is essentially static in the timescale of the exciton lifetime and would have little influence on the BE dynamics. This is in contrast to the other two non-radiative relaxation pathways (i.e., chemisorbed O₂⁻ and V_O²⁺), which directly compete with the ZnO BE dynamics.

Electron-trapping time by V_O²⁺ in H₂-annealed ZnO NWs.

In view of our findings that H₂-annealing depletes the chemisorbed O₂⁻ on the ZnO NW surface and that V_{Zn} has little influence on the BE dynamics, we can proceed to estimate an upper limit for the average electron trapping time, τ_{et} , by the V_O²⁺ defects using the average BE lifetimes in Table 1 of the as-grown sample after UV illumination, τ'_{PL} , and that of the H₂-annealed sample, τ''_{PL} . Using the following relations:

$$\text{As-grown, after UV: } \frac{1}{\tau'_{PL}} = \frac{1}{\tau_R} + \frac{1}{\tau'_{\text{defects}}};$$

$$\text{H}_2\text{-annealed: } \frac{1}{\tau''_{PL}} = \frac{1}{\tau_R} + \left(\frac{1}{\tau''_{\text{defects}}} + \frac{1}{\tau_{et}(V_O^{2+})} \right)$$

where τ'_{defects} and τ''_{defects} are the characteristic trapping times by the other intrinsic defect states (i.e., O_i, Zn_i) apart for the dominating non-radiative channel V_O²⁺ in the as-grown (UV-illuminated) and the H₂-annealed samples, respectively. With $\tau_{et}(V_O^{2+})$ dominating the non-radiative component (i.e. in parentheses) in the latter equation, we can have the following approximation: $1/\tau''_{PL} = 1/\tau'_{PL} + 1/\tau_{et}(V_O^{2+})$, where we estimate $\tau_{et}(V_O^{2+}) \approx 60 \pm 10$ ps. We further emphasize that this estimate is an upper limit because even though τ'_{PL} is dominated by the radiative component, there exists a non-radiative contribution (i.e., $\tau'^{-1}_{\text{defects}}$) for the as-grown (UV-illuminated) sample. Therefore, the value of τ'_{PL} is smaller than that of the intrinsic τ_R . Hence, $\tau_{et}(V_O^{2+})$ would have been even shorter.

Conclusions

The dynamic interplay between various trapping centers in ZnO NWs following post-fabrication thermal annealing in an/oxidizing/reducing gas ambient was investigated using TIPL and TRPL spectroscopy and their microscopic origins being correlated using XPS. Our findings reveal the presence of a hole transfer time constant of $\tau_{ht-\text{air-annealed}} \approx 400 \pm 80$ ps to the surface adsorbed oxygen species (O₂⁻) in the air-annealed sample and an electron transfer time constant of $\tau_{et-\text{H}_2\text{-annealed}} \approx 60 \pm 10$ ps to the ionized oxygen vacancies (i.e., V_O²⁺) in the H₂-annealed sample. Comparatively, a hole transfer time constant of $\tau_{ht-\text{as-grown}} \approx 900 \pm 200$ ps was measured for the untreated as-grown samples. Contrary to the common perceptions that the ZnO BE are strongly influenced by carrier trapping at the GE related defect states (i.e., V_{Zn}), our findings reveal that the CT processes to O₂⁻ and V_O²⁺ compete effectively with the BE. Hole trapping to the ionized V_{Zn} occurs in an ultrashort sub-ps-to-ps timescale, which limits the effective hole capture radius of these GE-related defects. Hence, compared to the two CT processes, hole trapping at the GE related defects have less influence on the BE dynamics than previously perceived. Importantly, our findings shed new light on the dynamic interplay between various trapping centers in ZnO NWs; thereby suggesting a strategy for tailoring the ultrafast carrier dynamics of ZnO NWs, which is highly relevant to the development of improved ZnO NW-based photocatalysts, photovoltaic devices and photosensors.

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Notes and references

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1. C. Jagadish and S. J. Pearton, *Zinc Oxide Bulk, Thin Films and Nanostructures: Processing, Properties and Applications*, Elsevier, Oxford, UK, 2006.
2. M. Law, J. Goldberger and P. Yang, *Annu. Rev. Mater. Res.*, 2004, **34**, 83.
3. H. Kind, H. Yan, B. Messer, M. Law and P. Yang, *Adv. Mater.*, 2002, **14**, 158.
4. M. Law, L. Greene, J. C. Johnson, R. Saykally, P. Yang, *Nat. Mater.*, 2005, **4**, 455.
5. K. S. Leschkes, R. Divakar, J. Basu, E. Enache-Pommer, J. E. Boercker, C. B. Carter, U. Kortshagen, D. J. Norris and E. S. Aydi, *Nano Lett.*, 2007, **7**, 1793.
6. T.-J. Kuo, C.-N. Lin, C.-L. Kuo, and M. H. Huang, *Chem. Mater.*, 2007, **19**, 5143.
7. D. Deng, S. T. Martin and S. Ramanathan, *Nanoscale*, 2010, **2**, 2685.
8. M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo and P. Yang, *Science*, 2001, **292**, 1897.
9. P. J. Pauzauskie and P. Yang, *Mater. Today*, 2006, **9**, 36.
10. C. Soci, A. Zhang, B. Xiang, S. A. Dayeh, D. P. R. Aplin, J. Park, X. Y. Bao, Y. H. Lo, D. Wang, *Nano Lett.*, 2007, **7**, 1003.
11. D. Lin, H. Wu, W. Zhang, H. Li, and W. Pan, *Appl. Phys. Lett.*, 2009, **94**, 172103.
12. R. P. Prasankumar, P. C. Upadhyay, A. J. Taylor, *Phys. Status Solidi B*, 2009, **246**, 1973.
13. Janotti and C. G. Van de Walle, *Phys. Rev. B*, 2007, **76**, 165202.
14. S. H. Jo, J. Y. Lao, Z. F. Ren, R. A. Farrer, T. Baldacchini and J. T. Fourkas, *Appl. Phys. Lett.*, 2003, **83**, 4821.
15. Y. W. Heo, L. C. Tien, D. P. Norton, B. S. Kang, F. Ren, B. P. Gila and S. J. Pearton, *Appl. Phys. Lett.*, 2004, **85**, 2002.
16. M. W. Ahn, K. S. Park, J. H. Heo, J. G. Park, D. W. Kim, K. J. Choi, J. H. Lee and S. H. Hong, *Appl. Phys. Lett.*, 2008, **93**, 263103.
17. J. Bao, I. Shalish, Z. Su, R. Gurwitz, F. Capasso, X. Wang and Z. Ren, *Nanoscale Res. Lett.*, 2011, **6**, 404.
18. M. H. Mamat, Z. Khusaimi, M. M. Zahidi, and M. R. Mahmood, *Jpn. J. Appl. Phys.*, 2011, **50**, 06GF05.
19. Y. Zheng, C. Chen, Y. Zhan, X. Lin, Q. Zheng, K. Wei, J. Zhu, and Y. Zhu, *Inorg. Chem.*, 2007, **46**, 6675.
20. L. J. Brillson and Y. Lu, *J. Appl. Phys.*, 2011, **109**, 121301.
21. X. Chen, S. Shen, L. Guo, and S. S. Mao, *Chem. Rev.*, 2010, **110**, 6503.
22. I. Hochbaum and P. Yang, *Chem. Rev.*, 2010, **110**, 527.
23. Soci, A. Zhang, X.-Y. Bao, H. Kim, Y. Lo, D. Wang, *J. Nanosci. Nanotechnol.*, 2010, **10**, 1430.
24. M. Jones and G. D. Scholes, *J. Mater. Chem.*, 2010, **20**, 3533.
25. Z. Zhang, S. J. Wang, T. Yu and T. Wu, *J. Phys. Chem. C*, 2007, **111**, 17500.
26. J. C. C. Fan and J. B. Goodenough, *J. Appl. Phys.*, 1977, **48**, 3524.
27. S. Major, S. Kumar, M. Bhatnagar and K. L. Chopra, *Appl. Phys. Lett.*, 1986, **49**, 394.
28. B. Du. Ahn, S. H. Oh, C. H. Lee, G. H. Kim, H. J. Kim and S. Y. Lee, *J. Cryst. Growth*, 2007, **309**, 128.
29. J. Lagowski, E. S. Sproles, Jr., and H. C. Gatos, *J. Appl. Phys.*, 1977, **48**, 3566.
30. V. Khramovskyy, J. Eriksson, A. Lloyd-Spetz, R. Yakimova and L. Hultman, *Thin Solid Films*, 2009, **517**, 2073.

31. G.-D. Yuan, W.-J. Zhang, J.-S. Jie, X. Fan, J.-X. Tang, I. Shafiq, Z.-Z. Ye, C.-S. Lee, and S.-T. Lee, *Adv. Mater.*, 2008, **20**, 168.
32. Mora-Seró, F. Fabregat-Santiago, B. Denier, and J. Bisquert, R. Tena-Zaera, J. Elias, and C. Lópy-Clément, *Appl. Phys. Lett.*, 2006, **89**, 203117.
33. V. E. Henrich and P. A. Cox, *The Surface Science of Metal Oxides*, Cambridge University Press, Cambridge, 1994.
34. A. B. Djurišić and Y. H. Leung, *Small*, 2006, **2**, 944.
35. D. Wang, H. W. Seo, C.-C. Tin, M. J. Bozack, J. R. Williams, M. Park, N. Sathitsuksanoh, A.-J. Cheng and T. H. Tzeng, *J. Appl. Phys.*, 2006, **99**, 113509.
36. X. Zhou, Q. Kuang, Z.-Y. Jiang, Z.-X. Xie, T. Xu, R.-B. Huang, and L.-S. Zheng, *J. Phys. Chem. C*, 2007, **111**, 12091.
37. N. E. Hsu, W. K. Hung and Y. F. Chen, *J. Appl. Phys.*, 2004, **96**, 4671.
38. K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, J. A. Voigt and B. E. Gnade, *J. Appl. Phys.*, 1996, **79**, 7983.
39. Q. X. Zhao, P. Klason, M. Willander, H. M. Zhong, W. Lu and J. H. Yang, *Appl. Phys. Lett.*, 2005, **87**, 211912.
40. H. Chen, Shu. Gu, K. Tang, S. Zhu, Z. Zhu, J. Ye, R. Zhang and Y. Zheng, *J. Lumin.*, 2011, **131**, 1189.
41. N. H. Moreira, B. Aradi, A. L. da Rosa, and T. Frauenheim, *J. Phys. Chem. C*, 2010, **114**, 18860.
42. E. V. Lavrov, J. Weber, F. Bärmert, C. G. Van de Walle and R. Helbig, *Phys. Rev. B*, 2002, **66**, 165205.
43. D. M. Hofmann, D. Kovalev, G. Steude, B. K. Meyer, A. Hoffmann, L. Eeckey, R. Heitz, T. Detchprom, H. Amano and I. Akasaki, *Phys. Rev. B*, 1995, **52**, 16702.
44. Q. X. Zhao, L. L. Yang, M. Willander, B. E. Sernelius and P. O. Holtz, *J. Appl. Phys.*, 2008, **104**, 073526.
45. H. S. Kang, J. S. Kang, J. W. Kim and S. Y. Lee, *J. Appl. Phys.*, 2004, **95**, 1246.
46. P.-T. Hsieh, H.-S. Chin, P.-K. Chang, C.-M. Wang, Y.-C. Chen and M.-P. Hough, *Physica B*, 2010, **405**, 2526.
47. X. Q. Meng, D. X. Zhao, J. Y. Zhang, D. Z. Shen, Y. M. Lu, L. Dong, Z. Y. Xiao, Y. C. Liu and X. W. Fan, *Chem. Phys. Lett.*, 2005, **413**, 450.
48. Y. M. Strzhemechny, J. Nemergut, P. E. Smith, J. Bae, D. C. Look and L. J. Brillson, *J. Appl. Phys.*, 2003, **94**, 4256.
49. K. H. Tam, C. K. Cheung, Y. H. Leung, A. B. Djurisić, C. C. Ling, C. D. Beling, S. Fung, W. M. Kwok, W. K. Chan, D. L. Phillips, L. Ding and W. K. Ge, *J. Phys. Chem. B*, 2006, **110**, 20865.
50. S. Choi, B.-Y. Park and H.-K. Jung, *Mater. Res. Bull.*, 2011, **46**, 810.
51. J. V. Foreman, H. O. Everitt, J. Yang and J. Liu, *Appl. Phys. Lett.*, 2007, **91**, 011902.
52. J. V. Foreman, H. O. Everitt, J. Yang, T. McNicholas and J. Liu, *Phys. Rev. B*, 2010, **81**, 115318.

Table 1. A summary of the fitting parameters for the as-grown, air-annealed and H₂-annealed samples. The average life time (τ_{avg}) is calculated by: $\tau_{\text{avg}} = (A_f \tau_f^2 + A_s \tau_s^2) / (A_f \tau_f + A_s \tau_s)$.²⁴

Samples	τ_f (ps)	τ_s (ps)	τ_{avg} (ps)
As-grown	43 (13%)	286 (87%)	280
As-grown (After UV)	93 (22%)	440 (78%)	420
Air-annealed	36 (20%)	190 (80%)	183
Air-annealed (After UV)	71 (23%)	355 (77%)	338
H ₂ -annealed	30 (92%)	113 (8%)	50

Figures

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Fig. 1 (Color online) A schematic illustrating the band bending in the cases of (a) electron depletion and (b) electron accumulation at the NW surface. (c) and (d) shows the corresponding phenomenological model of the trapping pathways in a two-particle picture.

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Fig. 2 (Color online) High resolution TEM images of the sample edges of the (a) as-grown, (b) air-annealed and (c) H₂-annealed ZnO NWs. (d) Insets show the region where the close-up TEM images were taken (black scale bar: 100 nm). (d), (e) and (f) show the corresponding XPS spectra of the respective samples.

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Fig. 3 (Color online) (a) Room-temperature TIPL spectra of the as-grown, air-annealed, and H₂-annealed ZnO NWs measured in air ambient. These spectra were overlaid by spectra from the as-grown and air-annealed samples measured in vacuum, following 20 mins of UV illumination in vacuum. All the spectra were obtained in the same experiment geometry. (b) Normalized BE PL decay transients of the corresponding samples in (a). The solid lines are bi-exponential fits to the data with the system temporal response deconvolved. The fitted time constants and the respective weighting factors (in %) are compiled in Table 1.