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Temporary and permanent changes to the defect equilibrium due to ultraviolet exposure: Surface and bulk effects on ZnO nanostructures

Sesha Vempati^{a,*}, Sefika Ozcan^{a,b}, Tamer Uyar^{a,c}^a UNAM-National Nanotechnology Research Center, Bilkent University, Ankara 06800, Turkey^b Department of Polymer Science and Technology, Middle East Technical University, Ankara 06800, Turkey^c Institute of Materials Science & Nanotechnology, Bilkent University, Ankara 06800, Turkey

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ABSTRACT

We report on the influence of prolonged exposure of above band gap illumination (UV) on the surface electronic structure (core and valence band) and bulk defect equilibrium of ZnO nanorods. We investigated two samples (ZnO1 and ZnO2) of mutually contrasting surface electronic structure as well as photoluminescence responses. The changes due to the above gap exposure were juxtaposed of as-prepared, UV-treated and healed samples. As prepared samples consist of CC, COC and COOH groups at the surface. The intrinsic surface/defect mediated photocatalytic activity under UV-illumination regenerated the lattice oxygen, oxidized the excess zinc and increased the COC fraction. The surface of ZnO2 was catalytically more active than that of ZnO1 due to zinc interstitials (Zn_is) and extended Zn_is (ex- Zn_is). Also, we identify chemisorbed oxygen species, interstitial hydrogen (H_i^+), multidentate complexes and disassociated O_2 molecule at oxygen vacancies (V_O). As a result of the catalytic activity severe changes occurred to the valence band (VB) edge and deeper-VB structure. After the course of healing, the VB edge for ZnO1 recovered to its pristine condition, unlike ZnO2. Additionally, we note increased fraction of O_2s component for both the samples which, after healing did not recover to their as prepared condition. In the context of defect equilibrium the UV-treatment reduced the density of charged oxygen vacancy (V_O^δ) and the thickness of the depletion layer which we attribute to the desorption of some chemisorbed gases and reconstruction of lattice oxygen. For ZnO1, ex- Zn_is are induced after UV-treatment, which subdued to an extent in the course of healing. In sharp contrast, for ZnO2 the UV-treatment subdued the ex- Zn_i related emission, which slightly recovered after healing in addition to a further loss of V_O^δ related emission. The slow recovery and reorganization of intrinsic defects are attributed to the diffusivity of H_i^+ and the associated lattice distortion, and Zn_is in the neighborhood of $\text{V}_\text{O}\text{s}$. Furthermore, the non-Coulombic attractive interaction between neutral $\text{V}_\text{O}\text{s}$ and Zn_is mediate the migration of defects and subsequent stabilization on slower timescales. The changes due to UV illumination on the electronic structure and defect equilibrium enhance the applicability and understanding of ZnO nanostructures in optoelectronic applications.

1. Introduction

Zinc oxide is an important wide band gap semiconductor which is extensively studied for applications ranging from biology [1], optoelectronics [2–4], photocatalysis [5–9], etc. Indeed, the applicability is crucially dependent on the harvesting the photogenerated charge carriers as modulated by the optoelectronic response. Under above band gap illumination, electrons are excited into the conduction band (CB) leaving the holes in the valence band (VB). The photogenerated charge carriers are extracted at the surface [10] or at interface for catalytic or optoelectronic applications, respectively. i.e. the photogenerated charge carriers are utilized when ZnO is submerged in a test solution

[7–9], interfaced [1,4] or in other conditions [1,6], under prolonged exposure of above band gap illumination (UV-light in the case of ZnO). Furthermore, the applicability of ZnO crucially hinges on the density and distribution of intrinsic defects and their effects on optoelectronic properties, where the photogenerated charge carriers can be trapped at a localized intrinsic defect [2,5–9]. The intrinsic defects include zinc interstitials (Zn_is) extended zinc interstitials (ex- Zn_is), oxygen vacancies ($\text{V}_\text{O}\text{s}$) to name a few [11]. In any case, understanding the defect equilibrium, electronic structure and optoelectronic properties are inevitable when ZnO is subjected to prolonged exposure to above gap illumination. This can be studied at two contexts, such as ‘surface’ and ‘bulk’. Under extended above gap illumination, various photon-assisted

* Corresponding author.

E-mail address: svempati01@qub.ac.uk (S. Vempati).<https://doi.org/10.1016/j.apsusc.2018.05.214>

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Fig. 1. Micrographs of ZnO nanorods recorded (a) and (b) with SEM, while (c) and (d) under TEM. Inset of (c) shows FFT image of (d). (e) XRD pattern with various diffraction planes of ZnO annotated and (f) compares the probe depths, δ_{PES} and δ_{PL} , respectively from photoelectron spectroscopy (PES) and photoluminescence (PL). λ_{ex} -excitation wavelength, E_{kin} kinetic energy of electrons and λ_{detect} - detection range of emission wavelength.

surface reactions were discussed in the literature, as noted in the following. These include (a). desorption of the surface oxygen and decrease of the surface depletion depth [12,13], (b). release of captured electrons from surface states [14–16], generating V_O s [14,17,18], (c). lattice decomposition and formation of Zn-rich surface [19] etc. Notably, points (b) and (c) depend on the catalytic activity of the surface, where defect density [7,8], type of defect [8], reactivity [8], play a crucial role. In summary, the effects of the UV treatment are believed to be surface limited, however, we find that the effects can be extended into the *bulk* and alters the defect equilibrium as well as surface electronic structure.

In this study, we compared samples of mutually contrasting optical character, which differ in the relative concentration of Zn_s and V_O s. In both the samples, the changes to the electronic structure as well as the defect equilibrium were two fold. We find that some of the changes were reversible to that of as-prepared condition, while others were permanent after one week of healing process. We showed that the UV-treatment oxidizes the Zn-rich surface with a regeneration of lattice oxygen and COC functional groups in addition to some significant changes to the VB structure and core-levels. This study unveiled various permanent and temporary effects of prolonged exposure of above band gap illumination on the surface and bulk optoelectronic properties, thereby enhancing applicability of zinc oxide.

2. Experimental

ZnO nanorods (ZnO-NRs) were deposited on clean ITO coated polyethylene terephthalate (60 Ω /sq, Sigma Aldrich) substrates via electrodeposition as described in Ref. [20] Briefly, equimolar hexamethyl tetramine (HMT) and $Zn(NO_3)_2 \cdot 6H_2O$ aqueous solution is heated to $\sim 94^\circ C$. Typically, about 10 mm along the length of ITO substrate was immersed into the electrolyte. The distance between ITO and counter electrode (10 $\times$ 15 mm²) was set to ~ 15 mm. The deposition was carried out at -2.5 V followed by -2.1 V (with respect to a stainless steel counter electrode) to facilitate the formation of a seed layer (0.5 min) and the growth of nanorod (5 min), respectively.

Surface morphology of the ZnO-NRs was studied using a scanning electron microscope (SEM, FEI-Quanta 200 FEG). For transmission electron microscopy (TEM, FEI-Tecna G2F30) imaging, ZnO-NRs were

removed from the substrate by scratching with a sharp blade. The collected powder-like substance was sonicated in ethanol for < 1 min. A drop of this dispersion is collected on a holey carbon coated TEM grid and subjected to analyses. Fast Fourier Transform (FFT) of HR-TEM image was obtained with Image J 1.42q software. X-ray diffraction (XRD) patterns were collected ($2\theta = 30^\circ$ – 75°) using PANalytical X'Pert Pro MPD X-ray Diffractometer using $CuK\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Valence and core-level photoelectron spectroscopy (PES) was performed with AlK α line ($h\nu = 1486.6 \text{ eV}$ or $\sim 0.83 \text{ nm}$, ThermoScientific, K-Alpha) in the presence of a charge neutralizer. During the XPS data acquisition, a metal clip connected the sample to the sample holder via the uncoated ITO surface. Note that the sample holder is in contact with the ground. All photoelectron spectra were angle-integrated, i.e. each spectrum contains contributions from photoelectrons of all escape angles and various crystal planes of the almost vertically standing nanorods. For peak deconvolution (Avantage software) the number of peaks was chosen based on the chemistry of the surface while the spectral location and full width at half maximum (FWHM) were allowed to vary. Photoluminescence (PL) spectra were recorded (Horiba Scientific FL-1057 TCSPC) at an excitation wavelength (λ_{ex}) of 355 nm. Peak-fits were performed on the normalized PL spectra with Origin 8.5. Peak centers for charged V_O (V_O^δ)-related emission (527 nm and 571 nm) were fixed based on the literature and other parameters were allowed to vary [3,11]. After deconvolution, the centres of the other peaks contain a finite error of about ± 2 nm. We have investigated zinc oxide samples of two different PL characteristics which were referred to as ZnO1 and ZnO2. Above band gap or UV-Vis illumination (300 W, Ultra-Vitalux lamp, Osram) was carried out for 30 min from a distance of 12 cm from the source through ~ 5 cm of water column to eliminate the IR component. XPS and PL analyses were performed on pristine samples, UV treated counterparts and after one week of healing in ambient atmosphere. These samples are referred to as ZnO1(2), aUV ZnO1(2) and hUV ZnO1(2), respectively. aUV ZnO1 and aUV ZnO2 samples were transferred into the XPS analyses chamber almost immediately after the UV treatment. The difference PL response was defined as $\Delta^{a(h)UV}ZnO1(2) = {}^{a(h)UV}ZnO1(2) - ZnO(1)2$ and implemented on normalized spectra.

Table 1
Elemental composition shown in atomic percent as obtained from XPS survey spectra.

Elements	Sample 1			Net change after healing	Sample 2			Net change after healing
	ZnO1	aUVZnO1	hUVZnO1		ZnO2	aUVZnO2	hUVZnO2	
Zn (%)	74.01 ± 2.22	73.56 ± 2.20	69.57 ± 2.08	Decrease	76.56 ± 2.29	69.22 ± 2.08	70.95 ± 2.13	Decrease
O (%)	15.74 ± 0.47	16.57 ± 0.47	17.43 ± 0.53	Increase	15.87 ± 0.48	21.97 ± 0.66	18.67 ± 0.56	Increase
C (%)	10.23 ± 0.31	9.88 ± 0.29	13.00 ± 0.39	Increase	7.57 ± 0.23	8.81 ± 0.26	10.38 ± 0.31	Increase

3. Results and discussion

3.1. Morphology and crystal structure

Representative SEM images from ZnO1 are shown in Fig. 1a and b at two different magnifications. These nanorods showed a well-defined hexagonal shape with a width varying from 180 nm to 240 nm. SEM image with higher magnification depicted grain like features on top of the nanorod which is typical and expected in nanostructures grown via electrodeposition. HR-TEM imaging is performed on the nanorods which unveiled the growth direction to be the *c*-axis of the ZnO (Fig. 1c and d). Furthermore, Fig. 1d is recorded at much higher magnification depicting well resolved lattice planes. We have generated a FFT image of Fig. 1d and shown as an inset of 1c. The rectangular symmetry of the spots is an indication of well developed lattice along *c*-axis of ZnO, which is comparable to that of an earlier observation from ZnO nanorods [7]. Although TEM is a local probe, nicely resolved lattice planes is a clear indication of well developed crystal structure. Also, the interplanar spacing of ~0.5 nm is consistent with the literature [7]. We have compared ZnO1 and ZnO2 samples and we find that the morphology and surface coverage of are indistinguishable (results not shown here).

XRD patterns from ZnO-NRs and ITO substrate are shown in Fig. 1e, where the diffraction planes for the former are annotated. The diffraction peaks represent a hexagonal wurtzite structure, which is consistent with the data base (ICDD 01-074-9940). XRD pattern from nanostructures needs a precise inspection in terms of lattice parameters, especially when grown on substrates with large lattice mismatch such as ITO, silicon etc. The calculated lattice parameters are, $a = 3.266 \text{ \AA}$ and $c = 5.229 \text{ \AA}$, yielding a ratio of $(c/a) = 1.601$ in line with wurtzite crystal structure (cf theoretical value = $\sqrt{8/3}$). We compared the lattice parameters with that of literature which suggested some ‘stress’ that is associated with the defects and/or the substrate (ITO/PET) [7]. It is important to note the presence of the seed layer just underneath the nanorods (directly grown on the ITO substrate). The diffraction pattern has contribution from the seed layer as well, where perhaps the strain is maximum. However, in the present context, we cannot either confirm or deny any strain within nanorods. In any case, the changes to the lattice parameters are attributed to the effect from the substrate. Also, within the detection limits of XRD, we did not observe diffraction peaks associated with impurities or reactants.

As motivated in the introduction, we would like to investigate the changes to the surface electronic structure and bulk optical properties of ZnO-NRs. Hence the probe depths of PES and PL techniques need to be discussed. In Fig. 1f, δ_{PES} and δ_{PL} indicate probe depths of PES and PL, respectively. In the context of XPS photoemitted electrons are detected. The relatively short escape depth (δ_{PES}) of photoelectrons makes the PES rather surface sensitive. δ_{PES} is derived from the universal curve of photoelectrons with reference to their kinetic energy, E_{kin} [21]. For core-level and valence band, the δ_{PES} varies from 1 nm ($E_{\text{kin}} \approx 1 \text{ keV}$) to 3 nm ($E_{\text{kin}} \approx 8 \text{ eV}$), respectively. In both the cases, the core and valence electronic structures are limited to the surface, where the role of adsorbants, functional groups, changes to the atomic composition can be studied. On the other hand, for PL, λ_{ex} of 355 nm penetrates as deep as ~50 nm below the surface (characteristic length for an optical absorption coefficient of $2 \times 10^5 \text{ cm}^{-1}$ at 355 nm, Ref. [22]). Hence, the

isotropic luminescence occurs from > 50 nm below the surface. Radiative transitions and changes to the surface depletion layer associated with intrinsic defects can be probed with PL spectroscopy [3,11]. Now, we start our discussion with surface electronic structure and then move on to the bulk-related-properties.

3.2. Surface electronic structure

Changes to the surface composition after UV treatment and subsequent healing are discussed in the following, before going into the details of the electronic structure. The atomic percentages of various elements were evaluated from the XPS survey spectra (not shown here) and the results are tabulated in Table 1. From Table 1, we note a loss (gain) of Zn(O) at% after UV treatment and subsequent healing process. The increase of oxygen content is generally ascribed to a net increase of defect density at the surface. However, we will see from the core-level spectra that the increase is indeed associated with lattice oxygen. Note that the survey-analysis does not distinguish lattice oxygen from that of chemisorbed species. Nevertheless, these defects host $-\text{OH}$, $-\text{CO}$, $\text{CO}_2^{-\alpha}$, adsorbed H_2O and/or O_2 or O^- and O^{2-} ions [6,8]. Interestingly, after UV irradiation the carbon contamination at the surface is decreased (increased) in the case of ZnO1 (ZnO2). The carbon at% includes chemisorbed gases like $\text{CO}_2^{-\alpha}$ and other strongly bound functional groups, which will be discussed further in relation to the core-level analyses.

Fig. 2 shows C1s-spectral region for three cases, viz pristine, UV-treated and healed samples. The core-level spectra depict three-peak structures irrespective of the course of the treatment, where the peak BE values are annotated on the spectra. The spectral feature at lower energy (~285 eV) with relatively higher intensity is attributed to C–C bonds, while the other two lower intensity peaks at ~286 and ~288 eV are attributed to C–O–C and O–C=O, respectively. The binding energy values are consistent with the data base [23]. The fractional

Fig. 2. C1s core-level spectra from ZnO nanorods. Spectral locations of the peaks and their shift with reference to untreated samples are indicated in eV. Atomic percentage of each functional group is annotated in italics.

contribution (%) of each of the functional groups is annotated on the spectra in italics. The atomic percentage of C–C group is decreased after UV-treatment for both the samples; however, ZnO2 exhibited higher initial carbon content. On the other hand, C–O–C at% increased after UV-treatment. Shapira et al. [24] argued that lattice oxygen desorbs in the form of CO₂ upon above band gap excitation of ZnO, for which the carbon at the surface should be catalytically active. The catalytic activity of the ZnO surface is already known, and indeed C–O–C groups might have generated from the oxidation of C–C (the exact oxidation mechanism is still to be unveiled). Interestingly, the O–C=O at% did not vary significantly on the surface of ZnO1 which is in contrast to that of ZnO2. The regeneration and variation to the density of oxygeneous groups are clear indications of the catalytically active surfaces, where the surface defects and their densities play a crucial role [9]. The differences in the chemical nature of catalytically active sites determine the strength of the bond, where for instance, ZnS mediate chemisorption of acidic groups more strongly than that of stoichiometric surface [25]. The consequences of catalytic activity of ZnO2 will be further explicit in the context of O1s-level and valence band spectra. The variation in the ionic environment is observed as shift of the peak-BE which differ across the samples and also with reference to the UV-treatment. The functional groups depict varying degrees of electron withdrawing nature due to the presence of oxygen with some electronegative character. In general, the blue shift can be attributed to relatively stronger binding of electron to the nucleus. This is true for both the samples after UV-treatment. However, after UV treatment, the magnitude of the blue shift increases for C–C, C–O–C and O–C=O for both the samples, where the largest shift is observed for O–C=O group. On the other hand, the red-shift is due to increased density or delocalization of electrons on the functional group. After healing, interestingly, the magnitude of red shift for ZnO1 increases for O–C=O, C–O–C and C–C, where the highest shift is recorded for C–C group. In sharp contrast, C1s from ZnO2 depicted a systematic blue-shift upon UV-treatment and then after healing.

O1s spectra from ZnO1 and ZnO2 are shown in Fig. 3, along with atomic percentages for lattice oxygen (O_{ZnO}) and chemisorbed oxygeneous groups (O_{Ch}) annotated in italics. The peak binding energy of O1s from ZnO lattice (O_{ZnO}) is consistent with the literature which confirms the tetrahedral coordination [23]. For ZnO1, the intensity of O_{ZnO} depicted a slight increase (decrease) after UV-treatment (healing course). The peak intensity of O_{ZnO} component consistently increased in the case

of ZnO2 and ZnO1 during the complete course of UV treatment and healing. This is an indication of reconstructed ZnO lattice due to the catalytic activity of the surface. Notably, the surface of ZnO1 is also catalytically active however, lower than that of ZnO2 (higher fractional increase of O_{ZnO} in ZnO2). The O_{Ch} component represents a number of chemisorbed oxygeneous functional groups at the surface and defects. The presence of multiple oxygeneous groups constituting the O_{Ch} is reflected in significantly larger FWHM values. These groups include V_{OS}, adsorbed H₂O, COC and –COOH. Importantly, these groups also consist the species of hydrogen-related, where the hydrogen binds to lattice-oxygen directly (interstitial hydrogen (H_i⁺)) [2]. Apart from the electron capturing molecules, the oxygen vacancy sites are attractive places for the chemisorption where O₂ undergoes a spontaneous and dissociative chemisorption at room temperature (at non-polar surfaces) [26,27]. Essentially V_O is filled when an oxygen molecule donates one oxygen atom to the lattice. Furthermore, it is also found that a mixture of CO₂ and H₂ produce peaks at 532.9 and 531.7 eV with the formation of ‘formate’ at the surface [28]. CO₂ chemisorbs at ZnO surface in a tridentate configuration mediated by a charge transfer process from the CB of ZnO [6]. Upon chemisorption, the binding energy of electron from O1s orbital of CO₂ decreases. Also some contribution to the broadening of FWHM occurs from molecules bound in multidentate configuration [29].

Zn2p core-level spectra are shown in Fig. 4. Peak positions and shifts with respect to pristine sample are indicated on the spectra. Peaks around 1021 and 1045 eV are attributed to 2p_{3/2} and 2p_{1/2}, respectively. The magnitude of the blue shift is the highest for UV-treated samples (ZnO1 and 2). After healing, we note that the magnitude of the blue shift decreased. The blue shift of Zn2p spectra is attributed to the increased degree of oxidation. Indeed the largest shift, after UV-treatment is consistent with the highest fraction of O_{Ch} as well as O_{ZnO}. The fraction of O_{Ch} and O_{ZnO} decreased after healing, as corroborated by the results from O1s spectra. The magnitude of the blue shift is also decreased after healing process. There is in fact, no indication of increased metallic zinc (Zn⁰) content, in which case a red shift is expected. Our results are in sharp contrast to the literature. Gurwitz et al. [19] reported oxygen breathing mechanism of ZnO, upon exposure to white light (Xe arc lamp) under UHV conditions. They have evidenced the formation of Zn rich surface, which is in fact discussed in the literature much earlier in 1958 [12]. We acknowledge the fact that if the surface is turned richer in Zn, it may be explicit with XPS as we reported earlier [3]. Currently, within the probe depth there is no indication for the

Fig. 3. O1s core-level spectra from ZnO nanorods. Spectral locations of the peaks and their shift with reference to untreated samples are indicated in eV. Atomic percentage of each functional group is annotated in italics. O_{Ch}-chemisorbed oxygen and O_{ZnO}-lattice oxygen from ZnO.

Fig. 4. Zn2p core-level spectra from ZnO nanorods. Spectral locations of the peaks are indicated in eV, and the shift is annotated with respect to that of pristine counterpart.

Fig. 5. Valence band spectra from ZnO nanorods. Fermi level is set to 'zero' on the binding energy axis. Majorly contributing atomic orbitals and spectral shift with reference to the pristine samples are indicated.

increase of metallic zinc, or Zn_s. Nevertheless, we will see their presence and changes to their density in the context of bulk optical properties for both the samples.

Furthermore, we have also investigated valence band region until 35 eV below the E_F , and spectra are shown in Fig. 5 for ZnO1 and ZnO2 samples [30]. Peak positions and shift with respect to untreated samples are annotated on the spectra. The peak centers contributing to the VB edges are at 4.64 and 5.45 eV for ZnO1 and ZnO2, respectively, where the difference is attributed to multiple factors, as discussed in the following. VB edge has a major contribution from O2p orbitals however, hybridized with Zn3d/4sp orbitals. The hybridized states extend until about 5 eV below VB edge. The structure of VB edge is, of course dependent on the stoichiometry at the surface, where notably the surface of ZnO2 is slightly Zn-rich than that of ZnO1 (Table 1). On the other hand, the surface defects, adsorbants and chemisorbed functional groups [25] contribute to the VB edge, where the peak at 4.64/5.45 eV (ZnO1/ZnO2) is attributed to the dangling orbitals of surface O atoms [31]. In the previous sections, we have discussed the oxygeneous functional groups at the surface in O1s and C1s core-level spectra. By given these factors, the difference in the spectral location of peak contributing to the VB edge among the two samples is convincing. Moving away from the edge, until Zn3d band the spectral components originate from relatively sub-surface region [31], however, within the limit of the electron escape depth as discussed with reference to Fig. 1f.

In the case of ZnO1, upon UV-treatment the peak contributing to the VB edge is blue shifted about 0.31 eV, apart from a loss of relative intensity. In the case of pristine samples, the formation of the depletion layer at the surface bends the VB and CB (relatively) upward. Upon UV exposure, the photoholes recapture the trapped electrons reducing the bent of the band edge, see Fig. 6g part ①. It must be emphasized that the surface is catalytically active upon photoexcitation, which regenerated COC and COOH functional groups, see the discussion on C1s spectra. After healing, the edge recovered to a scenario that is comparable to its untreated counterpart. Also, we note an increased intensity of O2s (peak around 19 eV). As mentioned earlier, the higher BE peaks (lying above binding energy of 8 eV) occur from slightly sub-surface region of the nanorod [31]. The increased O2s intensity is a clear indication of changes to the lattice integrity/structure [32]. Nevertheless, this could have multiple origins, such as changes to the atomic composition due to the catalytic activity or the intrinsic property of the lattice and defects. For ZnO2, in sharp contrast to that of ZnO1, the VB edge shifted towards lower BE. The chemisorbed gases leave the surface under above

band gap illumination for both ZnO1 and ZnO2. However, under UV-treatment significant changes took place at the surface, where ZnO2 is catalytically more active than that of ZnO1 (see O1s and C1s spectra and discussion therein). This is reflected in an increased intensity of O2s which is relatively higher for ZnO2 than that of ZnO1 [32]. Indeed from O1s spectra of ZnO2 it should be noted that the O_{Ch} (O_{ZnO}) component decreases (increases) after UV-treatment/healing which confirms that O2s peak has major contribution from the lattice than that of O_{Ch} -groups. In contrast, for ZnO1 the O_{Ch} (O_{ZnO}) component depicted nominal change in the intensity. After the course of healing, the VB edge was recovered for ZnO1 with a slight red-shift and lower intensity of O2s. For ZnO2 the VB edge depicted a net red shift of about 0.48 eV with a slight loss of intensity from O2s. Furthermore, the peak centered at 22.7 eV (ZnO1) depicted some blue-shift and slightly loss in its intensity upon UV-treatment. This also true for ZnO2 with reference to peaks at 19.4 eV. Peaks at 22.7 and 23.6 eV are tentatively attributed to O2p and/or Zn4s atomic orbitals. Indeed, DFT like theoretical studies are required to accurately disentangle the changes to O2s with reference to O2p/Zn4s. For ZnO1 sample, the Zn3d peak at 10.56 eV depicted some blue-shift after UV-treatment and sustained its intensity and shift after healing [23]. For ZnO2 this feature appeared at 11.48 eV with an apparent blue shift of about 1 eV with respect to ZnO1. Shift within the sample might be due to the variation in the degree of oxidation of Zn atom, as evidenced from the O1s and Zn2p spectra. Furthermore, the formation of $ZnCO_3^{2-}$ surface complex could be observed on surfaces with point defects after CO₂ exposure at 300 K. This surface complex is most probably the reason for the shift of O_{Ch} under multidentate configuration.

3.3. Bulk optical properties

In the previous sections, we have discussed the effect of prolonged UV exposure on the surface electronic structure of ZnO nanorods, now we focus on a bulk optical property, namely photoluminescence which unfolds the intrinsic and radiative defect density. Fig. 6a and b depict PL spectra from ZnO1 and ZnO2, respectively, where the spectral locations and attributions are annotated. Free exciton recombination and various relevant defect-emissions were schematized in Fig. 6c, see Ref. [11] and citations therein. Schematic of ZnO crystal with various planes is shown in Fig. 6d. Here we choose a non-polar surface (10–10) for the clarity of the discussion, refer to Fig. 6d for various planes.

Fig. 6. Photoluminescence spectra from ZnO nanorods (a) ZnO1, (b) ZnO2, (c) schematic band diagram depicting the relative energies of intrinsic radiative defects, where the emission wavelengths are in nm unless otherwise specified. Insets in (a) and (b) show magnified region of the spectra while the spectral positions are annotated in nm. (d) shows a schematic crystal structure of ZnO. The difference spectra from ZnO1 and ZnO2 are shown (e) and (f), respectively. (g) shows schematic of various processes. ① and ② show the surface reactions for above gap excitation, while ③ indicates the attractive interaction between Zn_i s and neutral V_o s.

The effect of UV exposure on the PL is unveiled via difference spectra as shown in Fig. 6e and f for ZnO1 and ZnO2, respectively. Fig. 6g ① and ② show surface and slightly subsurface reactions upon above band gap excitation. Part ③ depicts interaction between intrinsic defects in the bulk of the material. These schematics will be referred to in the discussion, contextually. The PL spectra were deconvoluted into 5 bands including free exciton recombination (FX) which occurred at ~ 380 and ~ 384 nm for ZnO1 and ZnO2, respectively [11]. The other three bands are attributed to various intrinsic defects such as Zn_i s, ex- Zn_i s, V_o s and/or V_{Zn} s. The differences in the spectral features are indications of variations in the defect densities for ZnO1 and ZnO2 samples [11]. The intensity ratio of interband transition to that of defect emission is an index of the optical quality of the material. Indeed, this ratio is higher for ZnO1 than that of ZnO2, suggesting better optical quality of the former.

Going into the defect related emission, we start with the green emission which is attributed to oxygen vacancies. Oxygen molecule undergoes a spontaneous and dissociative chemisorption at a oxygen vacancy site [26,27]. Essentially the vacancy is filled when the oxygen molecule donates one oxygen atom to the lattice at room temperature (at non-polar surfaces). These are the sites at which oxygen-assisted recombination of electrons and holes take place. This is energetically located about 0.5 eV above the VB edge [33]. On the other hand, interestingly, hydrogen being ubiquitous in experimental conditions is also believed to occupy oxygen vacancy site (shallow donor, H_o^+) and forms a multicenter bond where H is equally shared between the four Zn nearest neighbors [2]. From the neutral state (with two electrons) V_o s are ionized by donating 1 or 2 electrons to the CB of ZnO transforming themselves into V_o^+ or V_o^{++} , respectively [34]. The emission due to charged oxygen vacancy (V_o^δ) consists of two components at 527 nm and 571 nm corresponding to singly (527 nm: $V_o^+ +$ photo-excited holes) and doubly (571 nm: $e_{CB} + V_o^{++}$, where e_{CB} -electron from conduction band) ionized defects, respectively (Fig. 6c) [3,4,34,35]. Although PL from zinc oxide is believed to occur from the bulk of the sample, the green emission has some interesting characteristics [3,4,34,35]. Indeed, in the case of as prepared samples, the

gaseous species such as CO_2 , O_2 form the depletion region (DR) by capturing an electron from CB (e_{cptr}), see Fig. 6g ① and ②. For above band gap illumination, electron hole pairs are created in CB and VB, respectively. The increased hole-population in the VB releases the chemisorbed gases by re-capturing the electron. The removal of such electron withdrawing species decreases the width of depletion region and relatively flattens the conduction and valence bands. Interestingly, the depletion region and grain boundaries at the surface are favourable conditions for the formation of V_o^{++} state [3,4,35], which is the case with as prepared samples. See the schematic shown in Fig. 6g part ②. Importantly, after the UV-exposure we observe a loss of intensity that is relatively higher for the band centred at 571 nm than that of 527 nm (Fig. 6e and f). i.e. UV-treatment subdued the intensity of V_o^{++} component, via removing the chemisorbed species. In our earlier investigation, we have observed a converse phenomenon, where upon increasing the width of the depletion layer, relatively V_o^{++} component is increased [3]. The width of the depletion region depends on the intrinsic carrier concentration(s). For ZnO2, the loss of V_o^{++} component is higher than that of ZnO1, as seen from Fig. 6f and e, respectively. Also, the curves $\Delta^{aUV}ZnO1$ and $\Delta^{hUV}ZnO1$ in Fig. 6e indicated a trend of retrieving the original green emission intensity. This is in contrast to that of ZnO2, where V_o^{++} component further lost its intensity after healing ($\Delta^{aUV}ZnO2$ vs $\Delta^{hUV}ZnO2$).

In the context of zinc-related defects, the energetic positions of Zn_i s, ex- Zn_i s and the corresponding emission wavelengths are indicated in Fig. 6c. The ex- Zn_i states can be ionized Zn_i s, complex defect or localized Zn_i states, however the origin of their formation is not completely understood yet [36]. Zn_i to VB transition occurred only in the case of ZnO1 sample, while ZnO2 exhibited ex- Zn_i related defect bands. For ZnO1, interestingly, after UV-treatment, not only the luminescence due to Zn_i is increased but also transitions from ex- Zn_i s to VB are observed. This indicates enhanced density of Zn_i -defects and formation of new ex- Zn_i states (grey box on Fig. 6e). However, after healing, ex- Zn_i s to VB transitions are almost subdued, with a net increase in the Zn_i to VB band emission. In clear contrast to this scenario, ZnO2 sample significantly lost the emission intensity from ex- Zn_i s ($\Delta^{aUV}ZnO2$, Fig. 6f).

Table 2

Changes to the defect concentration as observed from photoluminescence are juxtaposed for the two ZnO samples. The concentration of a defect in pristine sample is indicated in square brackets while the course of treatment is indicated with superscript aUV or hUV. Enumerated observations are discussed in the text.

Defect/Pristine case			After UV treatment	After healing	Net change after healing	Note
[V _O ^δ]	ZnO1	low	^{aUV} [V _O ^δ] < [V _O ^δ]	^{hUV} [V _O ^δ] ≈ ^{aUV} [V _O ^δ] < [V _O ^δ]	Decrease	(1)
	ZnO2	low	^{aUV} [V _O ^δ] < [V _O ^δ]	^{hUV} [V _O ^δ] < ^{aUV} [V _O ^δ] < [V _O ^δ]	Decrease	(2)
[ex-Zn _i]	ZnO1	≈ 0	^{aUV} [ex-Zn _i] > [ex-Zn _i]	^{hUV} [ex-Zn _i] ≈ [ex-Zn _i] ≈ 0	No change	(3)
	ZnO2	high	^{aUV} [ex-Zn _i] < [ex-Zn _i]	^{hUV} [ex-Zn _i] > ^{aUV} [ex-Zn _i] < [ex-Zn _i]	Decrease	(4)
[Zn _i]	ZnO1	low	^{aUV} [Zn _i] > [Zn _i]	^{hUV} [Zn _i] > [Zn _i]	Increase	(5)
	ZnO2	high	^{aUV} [Zn _i] < [Zn _i]	^{hUV} [Zn _i] < ^{aUV} [Zn _i] < [Zn _i]	Decreases	(6)

After healing in ambient, we observe a slight increase of ex- Zn_i emission, however, did not recover to its original intensity. Essentially, some of the changes are irreversible while the others continue to change over time, as discussed in the following. The changes to the defect concentrations are summarized in Table 2 for both the samples. To unveil the underlying mechanisms behind the non-retrieval and/or the trends of retrieved intensities from V_O, Zn_i, ex-Zn_i-related emission, deeper understanding of the interaction between these defects is essential. Generally, the intrinsic donor defects such as V_Os and Zn_s are predominantly ionic in nature which are formed due to Schottky and Frenkel reactions (followed by ionization), respectively [36]. V_O and Zn_i mainly originate from the Zn4s orbitals, where the former may be occupied by molecular oxygen or hydrogen [2,26,27]. Notably, Zn_s occupy octahedral sites [37], where the interstitial volume is higher to accommodate the Zn atom. Indeed, there are three equivalent octahedral sites around a V_O, which are spacious to accommodate the interstitial atoms and hence preferable sites for Zn_s. Both being donor type, Zn_i is attracted by neutral V_O via quantum mechanical hybridization between the respective electronic states as predicted by theory (see ③ in Fig. 6g) [38,39]. i.e. in charged state they are under Coulombic repulsion if nearby. As the distance between two defects decreases, the interaction significantly lowers the energy of the electronic donor orbital of V_O and the total energy of the system. Furthermore, for Zn_i-V_O pair the tensile and compressive strains are compensated which further supports a weak attractive interaction. Notably, the attractive interaction from the compensated-strain is weaker than that of quantum mechanical hybridization [38].

From the PL spectra, it is clear that the concentration of charged oxygen vacancy ([V_O^δ]) is certainly lowered as a consequence of UV-treatment (Table 1 and 2). Also, changes to the concentration of other intrinsic defects after the UV-treatment can be temporary or permanent, where in general, lattice stabilizes with some density of intrinsic defects while maintaining the charge neutrality. By given this background, our observations are enumerated in Table 2 and discussed in the following.

- (1) Desorption of chemisorbed species and decreased [V_O^δ] at the surface, as consistent with the intensity of O_{ZnO} (O1s spectra).
- (2) For the above band gap excitation, the catalytic activity of the surface not only decreased the [V_O^δ] but also improved the intensity of O_{ZnO} (O1s spectra). After healing, the intensity of O_{ZnO}/O1s further increased, which is consistent with the further loss of V_O^δ related emission. Note that the V_Os can be excited to a metastable charged state after a structural relaxation while a thermally activated barrier prevents the recapture of electrons [40]. The structural relaxation after defect reorganization determines the final density of defects.
- (3) ^{aUV}[ex-Zn_i] is a temporary response of the lattice due to the fluctuations in the [V_O^δ]. The Fermi level in the bulk determines the degree of ionization of V_Os at the surface for a constant surface [V_O] [41]. In this case, the [V_O] is decreased due to UV-treatment which effected the carrier concentration. This essentially changed the degree of ionization and perhaps increased the neutral [V_O]. Now the previously discussed attractive interaction between Zn_s and V_Os

should be considered, which may mediate the stabilization of Zn_s around neutral V_Os. Most probably, the lattice recovery/ reconstruction may take place on slower time scales preceded by the decreased defect concentration at the surface. This might happen via already existing H_i⁺ which binds with O in the ZnO lattice (see the discussion on O1s) [2] and/or diffusion of hydrogen in and out of the lattice (see Refs. 51–54 in Ref. [2]). This H_i⁺ is notably less stable than that of substituted counterpart at a V_O site, the H_O⁺. Also note that the H_i⁺ causes significant lattice relaxation in both bond-centre (BC) and ABO configurations. Especially, in BC configuration the Zn and O atoms move outward as much as 40% and 20% of the bond lengths, respectively. ABO configuration causes relaxation about 20% of the bond length for both the Zn and O atoms. Since H_i⁺ can occur in rather high concentrations, it leads to the formation of Zn_s followed by ex-Zn_i due to excessively high lattice distortion. However, after healing, the lattice further stabilizes via minimizing the ex-Zn_s and Zn_s.

(4) ZnO2 depicted rather high levels of interstitial Zn which under catalytic reaction were oxidized (upon above gap illumination). This is explicit from the intensity of O_{ZnO} (O1s spectra) and the blue shift of Zn2p spectra. Hence, the subdued ex-Zn_i related emission is convincing as Zn_s are decreased. After the healing process, this emission is slightly recovered.

(5)/(6) The explanation given in point (3)/(4) in the context of ex-Zn_s is also true for Zn_s as the former can be ionized Zn_s, complex defect or localized Zn_i states [36].

4. Conclusions

This study unveils reversible and irreversible changes to the electronic structure of ZnO due to prolonged above band gap illumination. Here we choose nanorods of zinc oxide by given the higher surface area to volume ratio to enhance any surface/bulk effects due to above band gap illumination. We grew ZnO nanorods on PET/ITO substrate via electrodeposition. The width of the synthesized nanorods were in the range of 180–240 nm with a wurtzite crystal structure. HRTEM depicted well defined lattice planes and growth along the c-axis of ZnO. The surfaces of ZnO1 and ZnO2 were zinc rich, however, the latter has slightly higher zinc content. As prepared surfaces consisted of CC, COC and COOH groups. Upon UV-treatment, we found some regeneration of COC groups on the surface with an overall decrease in the carbon content. Specifically, the surface of ZnO2 was catalytically more active to produce COC functional groups than that of ZnO1. We have also observed systematic changes to the ionic nature of the surface where after UV-treatment the oxygeneous functional groups bind strongly to the surface. O1s spectra revealed some significant quantities of chemisorbed oxygen of various types (also complimented by C1s spectra). Multidentate surface complexes and other functional groups contributed to the relatively high FWHM of the peak corresponding to O_{CN}. Severe changes to the VB edge were indicative of desorption of some chemisorbed species in the case of ZnO1, and complex formation in the case of ZnO2. Also, importantly after the UV-treatment, the catalytic activity of the surface increased the fraction of the lattice oxygen, O_{ZnO}.

Furthermore, zinc rich surfaces were oxidized upon above band gap excitation due to the intrinsic surface/defect mediated catalytic activity. Deeper VB structure indicated an increased contribution of O2s orbitals, corroborating the changes to the VB edge as well as the observations in O1s spectra. It was clear at the end of healing process that the changes to the deeper VB are irreversible. The VB edge for ZnO1 recovered to its pristine condition unlike ZnO2. It is convincing by given the fact that ZnO2 is catalytically more active and changes were severe than that of ZnO1.

Investigation on the bulk optical properties revealed the effect of above band gap excitation is just not limited to the surface, but rather influences the bulk of the lattice and intrinsic defect equilibrium. Upon UV-treatment, we have observed a loss in the intensity of the PL bands corresponding to V_O^δ which is consistent with the desorption of surface chemisorbed species and decreased thickness of the depletion layer. In the case of ZnO1, the emission from ex-Zn_is appeared after UV-treatment which was subdued in the course of healing. After healing, ZnO1 sustained the emission from Zn_is. On the contrary, ZnO2 depicted rather peculiar behavior. After UV-treatment, severe loss of ex-Zn_i related emission was observed, which is consistent with the observation from XPS. When ZnO2 left for healing, a slight increase in the emission from ex-Zn_i was observed with a further loss of V_O^δ related emission. The slow recovery and reorganization of intrinsic defects were attributed to the diffusivity of H_i^+ and the associated lattice distortion. Furthermore, the attractive interaction between neutral V_O s and Zn_is also believed to mediate the migration of defects and subsequent stabilization. These findings related to alterations to the defect equilibrium under above band gap excitation are fundamentally important due to the applicability of ZnO based nanostructures in optoelectronic applications.

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References

- J. Liu, M.D. Rojas-Andrade, G. Chata, Y. Peng, G. Roseman, J.-E. Lu, G.L. Millhauser, C. Saltikov, S. Chen, Photo-enhanced antibacterial activity of ZnO/graphene quantum dot nanocomposites, *Nanoscale* 10 (2018) 158–166.
- A. Janotti, C.G.V. Walle, Fundamentals of zinc oxide as a semiconductor, *Rep. Prog. Phys.* 72 (2009) 126501.
- S. Vempati, A. Celebioglu, T. Uyar, Defect related emission versus intersystem crossing: blue emitting ZnO/graphene oxide quantum dots, *Nanoscale* 7 (2015) 16110.
- S. Vempati, S. Chirakkara, J. Mitra, P. Dawson, K.K. Nanda, S.B. Krupanidhi, Unusual photoresponse of indium doped ZnO/organic thin film heterojunction, *Appl. Phys. Lett.* 100 (2012) 162104.
- S.Y. Sawant, J.Y. Kim, H.T. Hiep, S.A. Ansari, M.H. Cho, Electrochemically active biofilm-assisted biogenic synthesis of Ag-decorated ZnO@C core-shell ternary plasmonic photocatalyst with enhanced visible-photocatalytic activity, *New J. Chem.* (2017).
- Y. Wang, R. Kováčik, B. Meyer, K. Kotsis, D. Stodt, V. Staemmler, H. Qiu, F. Traeger, D. Langenberg, M. Muhler, C. Wöll, CO₂ activation by ZnO through the formation of an unusual tridentate surface carbonate, *Angew. Chem. Int. Ed.* 46 (2007) 5624.
- F. Kayaci, S. Vempati, C.O. Akgun, N. Biyikli, T. Uyar, Enhanced photocatalytic activity of homoassembled ZnO nanostructures on electrospun polymeric nanofibers: a combination of atomic layer deposition and hydrothermal growth, *Appl. Catal. B* 156–157 (2014) 173–183.
- F. Kayaci, S. Vempati, I. Donmez, N. Biyikli, T. Uyar, Role of zinc interstitials and oxygen vacancies of ZnO in photocatalysis: a bottom-up approach to control defect density, *Nanoscale* 6 (2014) 10224–10234.
- F. Kayaci, S. Vempati, C.O. Akgun, I. Donmez, N. Biyikli, T. Uyar, Transformation of polymer-ZnO core-shell nanofibers into ZnO hollow nanofibers: Intrinsic defect reorganization in ZnO and its influence on the photocatalysis, *Appl. Catal. B* 176–177 (2015) 646–653.
- M.R. Hoffmann, S.T. Martin, W. Choi, D. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* 95 (1995) 69–96.
- S. Vempati, J. Mitra, P. Dawson, One-step synthesis of ZnO nanosheets: a blue-white fluorophore, *Nanoscale Res. Lett.* 7 (2012) 470.
- R.J. Collins, D.G. Thomas, Photoconduction and surface effects with zinc oxide crystal, *Phys. Rev.* 112 (1958) 388.
- J. Bao, I. Shalish, Z. Su, R. Gurwitz, F. Capasso, X. Wang, Z. Ren, Photoinduced oxygen release and persistent photoconductivity in ZnO nanowires, *Nanoscale Res. Lett.* 6 (2011) 1.
- S.A. Studenikin, N. Golego, M. Cocivera, Carrier mobility and density contributions to photoconductivity transients in polycrystalline ZnO films, *J. Appl. Phys.* 87 (2000) 2413.
- P. Sharma, K. Sreenivas, K.V. Rao, Analysis of ultraviolet photoconductivity in ZnO films prepared by unbalanced magnetron sputtering, *J. Appl. Phys.* 93 (2003) 3963–3970.
- J. Reemts, A. Kittel, Persistent photoconductivity in highly porous ZnO films, *J. Appl. Phys.* 101 (2007) 013709.
- D.A. Melnick, Zinc oxide photoconduction, an oxygen adsorption process, *J. Chem. Phys.* 26 (1957) 1136–1146.
- B. Clafin, D.C. Look, D.R. Norton, Changes in electrical characteristics of ZnO Thin Films Due to Environmental Factors, *J. Electron. Mater.* 36 (2007) 442–445.
- R. Gurwitz, R. Cohen, I. Shalish, Interaction of light with the ZnO surface: photon induced oxygen “breathing”, oxygen vacancies, persistent photoconductivity, and persistent photovoltage, *J. Appl. Phys.* 115 (2014) 033701.
- Y.-Y. Lin, C.-W. Chen, W.-C. Yen, W.-F. Su, C.-H. Ku, J.-J. Wu, Near-ultraviolet photodetector based on hybrid polymer/zinc oxide nanorods by low-temperature solution processes, *Appl. Phys. Lett.* 92 (2008) 233301.
- S. Hüfner, *Photoelectron Spectroscopy: Principles and Applications*, Springer, Berlin Heidelberg, Berlin, Heidelberg, 1996.
- G.E. Jellison, L.A. Boatner, Optical functions of uniaxial ZnO determined by generalized ellipsometry, *Phys. Rev. B* 58 (1998) 3586.
- A.V. Naumkin, A.K. Vass, S.W. Gaarenstroom, C.J. Powell, NIST X-ray Photoelectron Spectroscopy Database, Version 4.1, in: U.S. Secretary of Commerce, 2012.
- Y. Shapira, S.M. Cox, D. Lichtman, Chemisorption, photodesorption and conductivity measurements on ZnO surfaces, *Surf. Sci.* 54 (1976) 43–59.
- V.E. Henrich, P.A. Cox, *The Surface Science of Metal Oxides*, Cambridge University Press, Cambridge, 1996.
- W. An, X. Wu, X.C. Zeng, Adsorption of O₂, H₂, CO, NH₃, and NO₂ on ZnO nanotube: a density functional theory study, *J. Phys. Chem. C* 112 (2008) 5747–5757.
- Y. Yan, M.M. Al-Jassim, Oxygen-vacancy mediated adsorption and reactions of molecular oxygen on the ZnO(10–10) surface, *Phys. Rev. B* 72 (2005) 235406.
- C.T. Au, W. Hirsch, W. Hirschwald, Adsorption and interaction of carbon dioxide, formic acid and hydrogen/carbon dioxide mixtures on (10–10) zinc oxide surfaces studied by photoelectron spectroscopy (XPS and UPS), *Surf. Sci.* 199 (1988) 507–517.
- W. Hotan, W. Göpel, R. Haul, Interaction of CO₂ and CO with nonpolar zinc oxide surfaces, *Surf. Sci.* 83 (1979) 162–180.
- We have recorded angle integrated photoelectron spectrum that was an average from the almost vertically standing nanorods of various planes, see Figure 6d.
- K. Ozawa, K. Sawada, Y. Shirotori, K. Edamoto, Angle-resolved photoemission study of the valence band structure of ZnO(10–10), *J. Phys.: Condens. Matter* 17 (2005) 1271–1278.
- We have tentatively attributed O2s to the lattice oxygen based on an indirect support that we obtained from photoluminescence, where the oxygen vacancies are in fact decreased after UV treatment. However, further studies, e.g. angle resolved photoelectron spectroscopy, are required to disentangle if the O2s states occur from COC and/or COOH groups that were at the surface. See Ref. 31.
- J.D. Prades, A. Cirera, J.R. Morante, A. Cornet, Ab initio insights into the visible luminescent properties of ZnO, *Thin Solid Films* 515 (2007) 8670–8673.
- A. Janotti, C.G.V. deWalle, Oxygen vacancies in ZnO, *Appl. Phys. Lett.* 87 (2005) 122102.
- J.D. Ye, S.L. Gu, F. Qin, S.M. Zhu, S.M. Liu, X. Zhou, W. Liu, L.Q. Hu, R. Zhang, Y. Shi, Y.D. Zheng, Correlation between green luminescence and morphology evolution of ZnO films, *Appl. Phys. A: Mater. Sci. Process* 81 (2005) 759.
- H. Zeng, G. Duan, Y. Li, S. Yang, X. Xu, W. Cai, Blue Luminescence of ZnO nanoparticles based on non-equilibrium processes: defect origins and emission controls, *Adv. Funct. Mater.* 20 (2010) 561.
- A. Janotti, C.G.V. deWalle, Native point defects in ZnO, *Phys. Rev. B* 76 (2007) 165202.
- Y.-S. Kim, C.H. Park, Rich variety of defects in ZnO via an attractive interaction between O vacancies and Zn interstitials: Origin of n-type doping, *Phys Rev Lett* 102 (2009) 086403.
- Zn_i was shown to be inside the CB of ZnO for high level of donor defect density which determines the Fermi level. However it could exist about 0.22 eV below the CB minimum depending on the Fermi level (see cross references 28 and 29 Ref. 11).
- S. Lany, A. Zunger, Anion vacancies as a source of persistent photoconductivity in II-VI and chalcopyrite semiconductors, *Phys. Rev. B* 72 (2005) 035215.
- W. Göpel, Reactions of oxygen with ZnO–1010-surfaces, *J. Vac. Sci. Technol.* 15 (1978) 1298–1310.