

Interaction of light with the ZnO surface: Photon induced oxygen “breathing,” oxygen vacancies, persistent photoconductivity, and persistent photovoltage

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ZnO surfaces adsorb oxygen in the dark and emit CO₂ when exposed to white light, reminiscent of the lungs of living creatures. We find that this exchange of oxygen with the ambient affects the integrity of the ZnO surface. Thus, it forms a basis for several interesting surface phenomena in ZnO, such as photoconductivity, photovoltage, and gas sensing, and has a role in ZnO electrical conduction. Using x-ray photoelectron spectroscopy on ZnO nanowires, we observed a decomposition of ZnO under white light and formation of oxygen-depleted surface, which explains photoconductivity by the electron donation of oxygen vacancies. Our findings suggest that the observed decomposition of the ZnO lattice may *only* take place due to photon-induced reduction of ZnO by carbon containing molecules (or carbo-photonic reduction), possibly from the ambient gas, accounting in a consistent way for both the reduced demands on the energy required for decomposition and for the observed emission of lattice oxygen in the form of CO₂. The formation of oxygen-vacancy rich surface is suggested to induce surface delta doping, causing accumulation of electrons at the surface, which accounts for both the increase in conductivity and the flattening of the energy bands. Using surface photovoltage spectroscopy in ultra high vacuum, we monitored changes in the deep level spectrum. We observe a wide optical transition from a deep acceptor to the conduction band, which energy position coincides with the position of the so called “green luminescence” in ZnO. This green transition disappears with the formation of surface oxygen vacancies. Since the oxygen vacancies are donors, while the green transition involves surface acceptors, the results suggest that the initial emission of oxygen originates at the defect sites of the latter, thereby eliminating each other. This suggests that the green transition originates at surface Zn vacancy acceptors. Removing an oxygen atom from a Zn vacancy completes the vacancy to become a full ZnO molecule vacancy, which does not produce deep levels. Our results explain why ZnO finds use as an electrical detector for oxygen and for carbon containing gas molecules. They may also shed new light on photocatalytic uses of ZnO. It is suggested that similar surface phenomena may affect other semiconducting oxides. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4861413>]

I. INTRODUCTION

ZnO, an emerging candidate for oxide electronics and photonics,^{1–4} was the first semiconductor found to emit gas upon exposure to white light.⁵ This effect was studied in an attempt to explain several electrical surface-related phenomena in ZnO, most notably photoconductivity,⁵ surface photovoltage (SPV),^{6,7} and gas sensing.^{8–14} In this paper, we tie all of these effects with a new observation of illumination induced surface oxygen vacancies in a single self-consistent model, accounting for several superficial physical phenomena which make this material useful for gas sensing electronic devices as well as photochemical and catalytic uses.

While photoconductivity, the increase of conductivity in the presence of light, observed in ZnO, has commonly been associated with emission of CO₂, the opposite process in which the photoconductivity gradually diminishes, used in

oxygen sensing, has been convincingly related to a regain of oxygen by the ZnO surface.¹⁵ It is well established that only oxygen, and not CO₂, can cause the photoconductivity to disappear.^{16–18} However, the reverse process has been a subject of controversy, with several reports claiming emission of CO₂ alone,^{19,20} and one other report claiming emission of O₂.²¹

In spite of the evidence for CO₂ emission, the fact that the reverse process can only take place with O₂, made many scientists adopt the belief that under “clean” conditions, O₂ should be the only species emitted, and that observations of CO₂ are likely a coincidental result of a non-pure or non-clean material, emission from a metal sample holder, etc. The emitted CO₂ gas was also believed to originate at physically adsorbed oxygen in powdered ZnO.^{19,21} This belief leaned on a single report of flash photolysis that showed O₂ emission.²¹ Nonetheless, when the typical irradiation conditions for the photoconductivity experiment are reproduced (i.e., no highly energetic flashes), CO₂ is emitted rather than O₂. Using a residual gas analyzer in ultra high

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vacuum on various samples of bulk ZnO and of ZnO nanowires, we reproduced the emission of CO₂ under white light illumination.

Notably, even the highest photon energy that was typically used in all those experiments ($h\nu < 4\text{ eV}$) is well below the energy that binds together the ZnO lattice ($\sim 7.5\text{ eV}$); and therefore, a single such photon may not be enough to cleave a ZnO molecule. This fact has not raised any questions as it has so far been commonly assumed that the emitted gas originated at oxygen, or oxygen-containing molecules, that were *physically adsorbed*, i.e., weakly attached on the surface.¹⁹ In parallel with this illumination-related gas emission, the ZnO conductivity increases.¹⁵ However, the relatively small quantity of physically adsorbed oxygen alone may not be enough to account for photoconductivity that may keep on increasing for days. Figure 1 shows the time evolution of the photoconductivity as observed in our ZnO nanowire resistors. Interestingly, the photoconductivity in air quickly saturates, since in air, oxygen is gained back simultaneously, so the rise can only proceed until a balance is reached between the two opposing processes. However, in vacuum, the photoconductivity may rise on for days, making it hard to believe that this emission is only due to the limited quantity of adsorbed species. This observation led us to suspect that much more oxygen than just physically adsorbed oxygen is involved in the process, likely lattice oxygen.

ZnO is but one of a list of semiconducting oxides receiving increasing attention in recent years. Many oxides are used in catalytic processes in which the chemistry and photochemistry of the surface are critical. Many semiconducting oxides are finding use in electronic devices, most notably in solar cells and thermoelectric applications. For example, CuO, which is the basis for many superconductive compounds, shows similar phenomena.^{22,23} Similar behavior is reported on other semiconducting oxides.^{24–27} From the electronic application point of view, the appearance of a surface shunting layer under illumination could be a problem on the one hand, but could also lead to new applications.²⁸

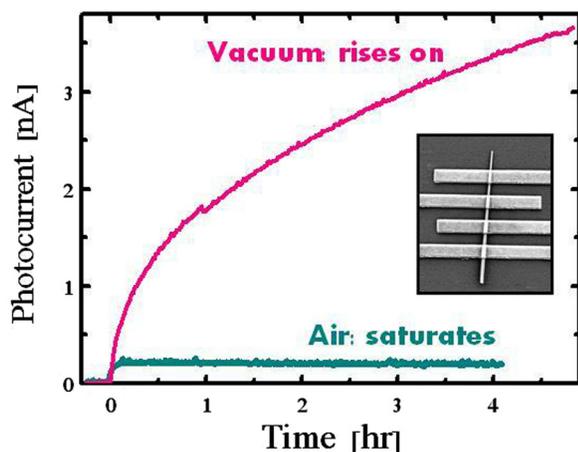


FIG. 1. Comparison of time evolution of photoconductivity in a ZnO nanowire in air and in vacuum. The photoconductivity was measured using a four-contact nanowire device (inset shows a scanning electron microscope image of such device; bar is $2\ \mu\text{m}$) to eliminate contributions from contact resistivity. It shows that as the air photoresponse saturates immediately, the vacuum photoresponse rises on for hours.

The recent emergence of nanostructures, where effects of surfaces are emphasized due to increased surface to volume ratio, has excited renewed interest in these old and mainly unsolved questions on the behavior of some oxide surfaces. The results we present here suggest a single mechanism underlies all of the above phenomena.

II. EXPERIMENTAL DETAILS

Undoped n-type ZnO nanowires were grown by CVD on Si(100) substrates using Au catalyst (for details, see Ref. 39). ZnO nanowire resistor devices were prepared on oxidized silicon substrates. ZnO nanowires were dry-transferred to the device substrate by contacting the growth substrate with the device substrate. Ti(5 nm)/Pt(250 nm) was deposited on e-beam lithography defined contacts. Four contacts were defined for each nanowire. The two outmost contacts were used to introduce constant current. The two inner contacts were used to measure voltage. The current was divided by the voltage and multiplied by the nanowire cross-sectional area divided by the length to obtain the conductivity. This method was used to eliminate contribution of the contact resistivity. The dark conductivity was subtracted to obtain the photoconductivity, $\Delta\sigma$. The photoconductivity was then divided by the dark conductivity to obtain the relative change, $\Delta\sigma/\sigma$. SPV was measured by monitoring changes in the surface work function. These changes were monitored using the Kelvin probe technique. The latter measures the contact potential difference (CPD), i.e., the difference in work function, between the semiconductor free surface and a vibrating reference probe. A commercial Kelvin probe (Besocke Delta Phi, Germany), with a sensitivity of $\sim 1\text{ mV}$, was used in all measurements. The physics of the technique is discussed further on in the context of its data. We refer the reader to a thorough review of the method that may be found in Ref. 29.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis Ultra X-ray photoelectron spectrometer. Spectra were acquired using a monochromatic Al K α (1486.7 eV) X-ray source. The pressure in the test chamber was maintained at better than 1×10^{-9} Torr during acquisition. The XPS binding energy was calibrated relative to the peak position of Fe⁰ 2p_{3/2} at 707.0 eV.³⁰ Exposures to white light were done using Newport 66986 Xe Arc lamp, illuminating the sample in vacuum through a CaF window. Fig. 2(A) shows a schematic cartoon of the XPS technique. Monochromatic X-ray photons excite photoemission of electrons from the sample. The electrons are collected by an electron energy analyzer that counts the electrons it collects per binding energy. Fig. 2(B) gives the energetics of the excitation/photoemission process. The absorbed x-ray photons are energetic enough to excite electrons from bond orbitals. Each element in the sample produces a set of characteristic peaks at characteristic energies. A chemical bond affects the electron configuration of the bonding orbitals producing a shift of the characteristic binding energy peaks. This shift is characteristic of the bonding element and is used to identify the bonding elements, and their chemical and electronic state. The electron analyzer counts the photoelectrons by their kinetic energy, which is

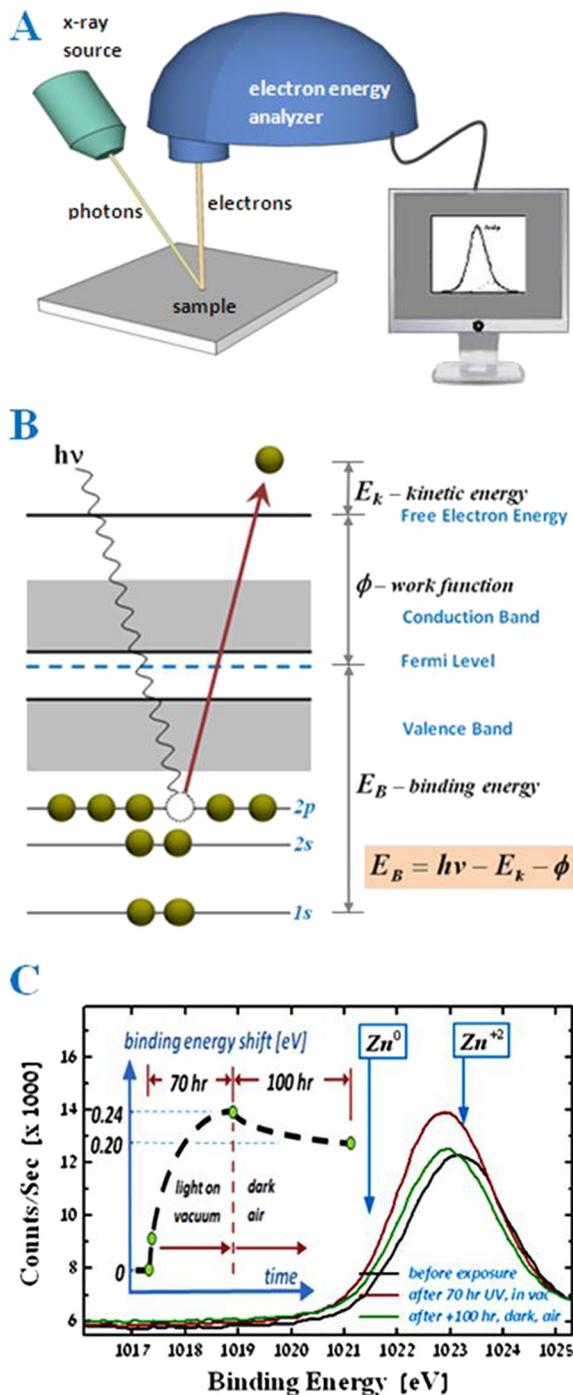


FIG. 2. (A) Schematic cartoon of the X-ray photoelectron spectroscopy setup. (B) Schematic band diagram showing the energetic of the photoemission process. (C) X-ray photoelectron spectra of the Zn2p core level before and after 70 h of exposure to white light (Xe lamp) in vacuum, and after 100 h in air in the dark. The peak shifts to lower binding energy upon exposure to light in vacuum, and shifts back, in a slower manner, after exposure to air in the dark. Two arrows mark the binding energy of metallic Zn and that in our ZnO. The inset shows that the amount of shift as a function of time follows the typical persistence time evolution commonly observed in photoconductivity (the green circles are the data, while the dashed lines are added for guidance).

then used to calculate binding energy according to the equation $E_B = h\nu - \phi - E_k$, where $h\nu$ is the photon energy, ϕ is the work function, and E_k is the kinetic energy. In our case, we look at ZnO and scan electron energies in the typical

energy range of the 2p orbital of the Zn element. The Zn2p peak typically assumes higher binding energies when the Zn is bonded to oxygen.

III. RESULTS AND DISCUSSION

To test our hypothesis of lattice decomposition, we used XPS. X-ray photoelectron spectra were used to assess the energy position of the Zn2p core level, before and after exposure to white light in vacuum, followed by exposure to air in the dark. We expected that if ZnO indeed decomposed, the Zn2p peak would shift from its binding energy position in the O-Zn bond towards its position in metallic Zn. The results in Figure 2(C) indeed show this expected shift, in support of lattice decomposition. The shift is not a full shift, because most of the Zn underneath the surface remains bound to oxygen, while only a small volume of oxygen-vacancy-rich ZnO is actually formed at the very surface. Regardless of the core level studied, the shift is very small compared to the peak width. However, the trend is clearly observed in the position of the peak center. An initial shift of the peak center was observed already after hours of irradiation, but the sample was left irradiated for the duration of a weekend to obtain a notable shift. After illumination was turned off, the position of the Zn2p core level did not shift, neither up nor down, in energy, as long as ultra high vacuum was maintained. After exposure to air, the Zn2p core level gradually shifted back to its original position at a slow rate, presenting a clear *persistence* of the Zn core level shift. Thus, the binding energy shift of the Zn2p core level, upon exposure to white light, followed by the reverse shift, upon exposure to air in the dark, present similar persistence pattern to that which is observed in photoconductivity experiments on ZnO for many years.

Since the surface of ZnO is gradually depleted of oxygen upon exposure to white light, a layer with increasing density of oxygen vacancies (donors) must be formed at the surface. Based on *ab-initio* calculations, it has been suggested that the oxygen vacancy *in the bulk* of ZnO is a deep donor, and therefore, can contribute to conduction while still exposed to white light.¹ However, when the light is turned off, the donated electrons should be trapped back and the photoconductivity should thus gradually diminish, which is not what we observe in ultra high vacuum. At any event, upon illumination, an oxygen vacancy will donate an electron. Thus, the effective doping at the surface should increase, gradually reducing the resistance between the device contacts, resulting in the observed increase of the conductivity. Such effective doping at the surface is bound to cause accumulation of electrons near the surface. Indeed, a 2D electron-gas with electron densities of up to $5 \times 10^{13} \text{ cm}^{-2}$ was observed upon UV illumination of ZnO.³¹ When the light is turned off and an oxygen-containing gas, like air, is let in, the Zn-rich surface gradually oxidizes back, slowly eliminating the highly conductive quantum well at the surface layer and reducing the photocurrent.

We are therefore presented with two puzzling questions: (1) How can the illumination-related gas emission that accompanies the decomposition of surface ZnO contain

carbon and not consist of free oxygen, when on the other hand, only oxygen can cause the inverse process of relaxation of photoconductivity in the dark? and (2) How can the ZnO lattice decompose at a photon energy that is roughly half the energy that binds it together?

These two questions appear to be critical for the understanding of surface effects that seem to govern both the electronic and the optical behavior of this semiconducting oxide. Could these two questions be inter-related and consistently answered?

It is worth noting that an atom will not leave the ZnO lattice with any less than the energy that binds it since the probability of an atom tunneling off through the cohesive energy potential barrier at the surface is negligible in the absence of an external field.

Carbon is known to reduce oxides. This means that in the presence of carbon, oxygen may require smaller energy to detach itself from the oxide compound. When the energy source is thermal, this effect is commonly dubbed “carbothermal reduction.”³² The question we ask is could photons replace phonons giving rise to the same process?

If this is the case, than the presence of carbon compounds on ZnO surfaces (or otherwise adsorption of carbon-containing gas molecules) may permit lattice decomposition, where it is otherwise unlikely. The question is what could be the source for so much carbon if one uses cleaned ZnO surfaces in ultra-high vacuum.

Light hydrocarbons are a common component of air and their relative concentration even increases in the residual gas in ultra high vacuum systems due to differential pumping.³³ Users of transmission electron microscopes often witness growth of amorphous carbon layers on the borders of their samples as they are imaged, as a result of the high-energy electron beam decomposing residual hydrocarbons.³⁴ Let us then examine the possible energetic effect of various carbon species on ZnO decomposition.

We first note that when a material consists of separate molecules, as in gas, each photon affects a single molecule (Stark-Einstein Law). An absorbed photon causes an electron to transfer to a higher orbital. When the excited state is an antibonding orbital, cleavage of the molecule may occur. However, in crystals, orbitals of individual molecules unite with those of others into energy bands. A photon absorbed below the surface of a semiconductor crystal causes an electron to be excited from the valence band, over the forbidden energy gap, into the conduction band or higher. In extreme cases, which do not apply to the white light sources considered here, an electron may obtain enough energy to leave the lattice altogether. However, in the cases relevant to our experiment, the excited electron is scattered many times by the lattice, emitting phonons, and thereby thermalizing into the conduction band bottom. In direct semiconductors, it will then typically return to the ground state (the valence band) emitting a photon the size of the energy gap. As a result, we need to subtract the energy of the emitted photon from that of the absorbed photon, in order to obtain an idea of the energy that actually turns into heat.

As absorption takes place near surfaces, the heat obtained in the above process is produced near the surface.

In good conductors, such as semiconductors, it is then dissipated rapidly. Thus, with the little energy dissipating fast, the chances of accumulating enough energy to decompose the lattice are rather small. Typically, to obtain such decomposition, fast and powerful light sources are used in what has been dubbed “flash photolysis,” where the flux of photons is high enough to cause double photon absorption.

However, if the crystal is an oxide and carbon-containing compounds are available, the energy requirements for decomposition become modest.

Enthalpy values are not available for photolysis processes. We may only get a qualitative idea by examining the values for related thermolysis processes with and without carbon.

We first note that the term cohesive energy, used so far, relates to the energy binding the lattice together at the absolute zero temperature, which is required to decompose the lattice into its constituents in their gas form. However, the typical photoconductivity experiment is carried out at room temperature; and therefore, the Zn constituent does not go into vapor. Hence, we can subtract the Zn enthalpy of vaporization, 115.3 kJ/mol, or 1.19 eV per atom, from the cohesive energy, and remain with about 6.3 eV per molecule as the energy required for the reaction



If, for example, plain carbon is somehow available, the reaction may take the following path:



The CO product reacts again with ZnO, before it is emitted



and thus CO₂ will be emitted, not O₂, which is indeed what we observe. The energetic balance for Eq. (2) is $\Delta_f H^0 = 350.2 - 110.5 = 239.7 \text{ kJmol}^{-1}$ or 2.48 eV per molecule, which is less than a half.³⁵ Similarly, we get for Methane (CH₄) 2.86 eV/molecule.³⁵ For the typical solvents used in cleaning of semiconductor surfaces, such as methanol and acetone, the energy requirements are less than 1 eV/molecule.

The energy required to drive the reaction in Eq. (3) is rather small $\Delta_f H^0 = 320.5 + 137.2 - 393.5 = 64.2 \text{ kJmol}^{-1} = 0.66 \text{ eV/molecule}$.³⁵

The above considerations show how much more energetically favorable is the thermal decomposition of ZnO at the presence of carbon. If carbon is present, nature is bound to use it, because it is bound to always take the low energy path. At least qualitatively, it is very likely to work the same for *photolysis*, where we change the energy source from phonons to photons.

There could yet be another possible scenario of the outmost layer of the crystal. In this case, it could be that a single atom connected to the crystal, especially in the vicinity of defects, may be viewed to a certain extent as a part of a crystal-atom molecule (crystal on the one side, atom on the other side, chemical bond in-between) in which a photon may

excite an electron to an antibonding orbital resulting in separation of that atom from the crystal. Here as well, the presence of carbon species could reduce the energy requirements.

In the ZnO photoconductivity literature, it is commonly assumed that ultra-violet (UV) light at photon energies above the ZnO bandgap is required for the observed gas emission, for the reason described above.³⁶ However, as the light absorption and lattice decomposition take place at surfaces, and as surfaces host high concentration of electronic states in the forbidden gap (“surface states”), it is possible to excite electrons trapped at such surface states into the conduction band with much less than the energy of the gap. If carbon can reduce oxides by photolysis as it does by thermolysis, one should be able to cause lattice decomposition and photoconductivity in ZnO with light of wavelengths much longer than the ultra-violet, well into the visible range. This means that if one measures photoconductivity as a function of irradiation wavelength, the current should start rising above dark values somewhere between 500 and 650 nm. Indeed, in most of the reported photoconductivity spectra of ZnO, one can see that the onset of photoconductivity is typically between 500 and 650 nm.^{37,38}

Figure 3 shows a typical photoconductivity spectrum we obtained using an individual ZnO nanowire. Scanning from long to short wavelengths, the spectrum is indeed observed to rise above the noise level at the red part of the spectrum, around 650 nm. It then mildly rises further as we proceed to shorter wavelengths. This rise could be explained by the fact that more and more carbon species may get enough energy to reduce the oxide. As the scan reaches the wavelength that corresponds to the ZnO bandgap energy, the photoconductivity increases sharply. This reflects the sharp increase in absorption of light above the bandgap. Absorption is a critical condition on which the photonic energy transfer depends. Where there is no absorption, there can be no decomposition. States for electrons are fewer in the forbidden gap and are limited in their spectral range, depending on the presence of defect deep levels. For this reason, the photoconductivity is generally smaller within the forbidden gap. Nonetheless, this

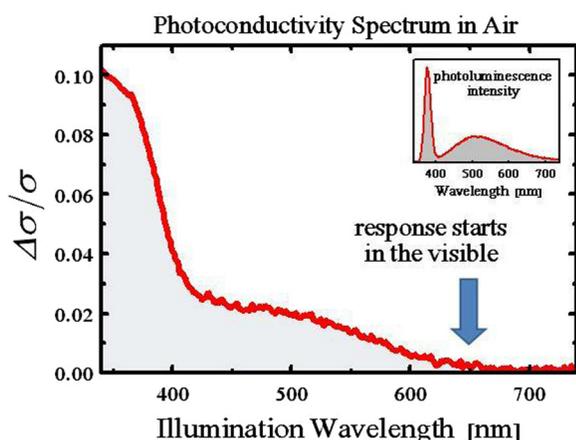


FIG. 3. Photoconductivity spectrum measured in air shows clearly that the response to light takes place at photon energies well below UV, at the red part of the visible spectrum. In the absence of carbon, this photon energy might not be enough for the lattice decomposition evidenced in Fig. 2. Inset shows photoluminescence from same sample.

result supports our prediction, suggesting that UV light is not altogether necessary to cause the proposed *carbo-photonic decomposition* of ZnO.

Absorption of photons below the ZnO bandgap energy, where the ZnO is typically transparent, requires the presence of electronic states in the forbidden gap. Indeed, a wide band of surface states is commonly observed in ZnO, giving rise to its ubiquitous green luminescence.³⁹ Green luminescence was also observed in the material used in this study (see inset in Fig. 3). Obviously, the density of the related electronic states is much smaller than the density of states in the valence band. Therefore, as the photon energy increases above the gap, the photoconductivity sharply increases, due to a similar increase in the absorption of light.⁴⁰

Finally, the same argument that applies to the oxygen source (i.e., that physisorbed oxygen alone may not be enough to support many hours of rising photoconductivity) may also apply to the amount of residual carbon on the surface. For this reason, it seems likely that, under illumination, the ZnO surface actively consumes carbon-containing gas molecules from the environment. This is also in line with the fact that the irradiated ZnO surface provides a thermodynamic sink, where impinging carbon-containing molecules turn into the more stable CO₂. As a matter of fact, ZnO-nanowire-based sensors, in which the energy source was heat, were shown to sense ethanol by reduction of the nanowire resistivity.¹⁰ In that study, they used an integral heater as a power source, instead of the light used in our case. However, except for this difference in the energy source, the mechanism there is identical to our case. The “sensed” ethanol reduces the ZnO, while in parallel, oxygen is causing the reverse process. The resulting conductivity reflects the balance between these two processes. This also means that ethanol was consumed from the environment, i.e., the mechanism we suggest has actually been observed and reported, though explained differently.

As mentioned before, if carbon or hydrocarbons are involved, the reaction in Eq. (1) is unlikely to take place *at all* (even at a suitable wavelength), as nature is always bound to take the lowest energy path. Therefore, it seems fairly unlikely that, under the typical conditions, and using a typical white light source, as commonly used in photoconductivity experiments, anyone could ever observe significant emission of O₂ from ZnO. Nonetheless, there is actually one report of such emission that requires scrutiny.

Examining the one and only paper ever reporting experimentally observed photon induced oxygen emission from ZnO (Cunningham 1974),²¹ we find the authors used a mercury-xenon *flash* lamp with extremely energetic flashes of 200 Joules per 30 μs. Therefore, this experiment clearly falls into the category of *flash photolysis* where *two-photon absorption* obviously tilts the energy balance.

Our XPS results show that upon irradiation with white light, the ZnO crystal surface is depleted of oxygen, i.e., oxygen vacancies are generated, contrary to the previous belief that the emitted oxygen originated at physisorbed oxygen.¹⁵ This process of oxygen emission is long known to be associated with the occurrence of persistent photoconductivity and persistent surface photovoltage. Figure 4 (top) shows the

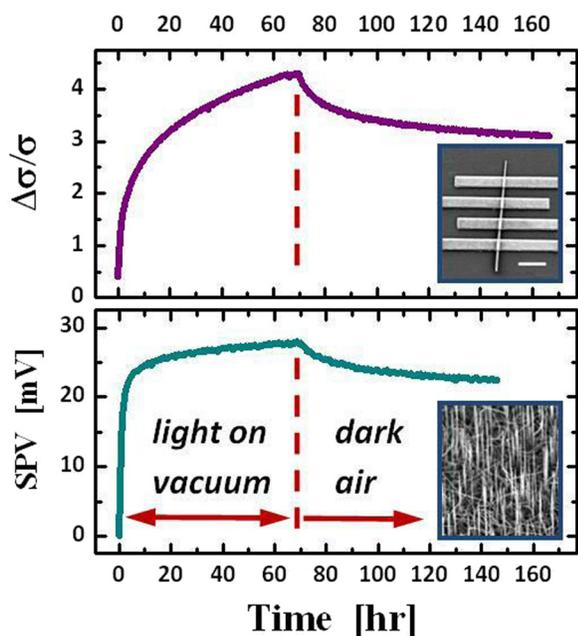


FIG. 4. Time-evolution of photoconductivity (top) with inset showing the nanowire resistor measured, and surface photovoltage (bottom), with inset showing the ZnO nanowire sample measured. In both cases, samples were exposed to light under identical conditions for 70 h in vacuum, followed by exposure to air in the dark.

persistence pattern of the photoconductivity in a single ZnO nanowire (inset shows the device) under the same conditions as in Fig. 2 (XPS results).

Figure 4 (bottom) shows a similar persistence in the surface photovoltage obtained from the nanowire-covered Si substrate, under the same conditions. The surface photovoltage is proportional to the change in surface band-bending induced by the absorbed light.²⁹ One may argue that the surface photovoltage should be reflected in the XPS core level shift. However, the photovoltage does not exceed 0.03 V, whereas the core level shifts by 0.24 V. Therefore, the photovoltage may only account for less than 15% of the core level shift, while most of it is due to an accumulation of neutral Zn at the expense of Zn^{+2} . The correlation between the Zn2p core level shift, the photoconductivity, and the surface photovoltage indicates that a common mechanism underlies all the three phenomena. Understanding the physical mechanism underlying the surface photovoltage experiment is a key to understanding the interaction of light with the ZnO surface.

The surface photovoltage is measured using a Kelvin probe. The probe forms one side of a parallel plate capacitor of which the material of interest (in our case, a ZnO semiconductor nanowires on Si) serves as the other plate (see schematic in Fig. 5(A)). Both sides are initially grounded and the surface voltage is the contact potential difference between the plates of the capacitor, which equals the difference in work function between the latter. The Kelvin probe is attached to a piezoelectric crystal plate driven by an alternating voltage at a constant frequency, so that the gap between the capacitor plates varies sinusoidally. An alternating current is formed in the capacitor, the amplitude of which is proportional to the capacitor charge. Applying an external

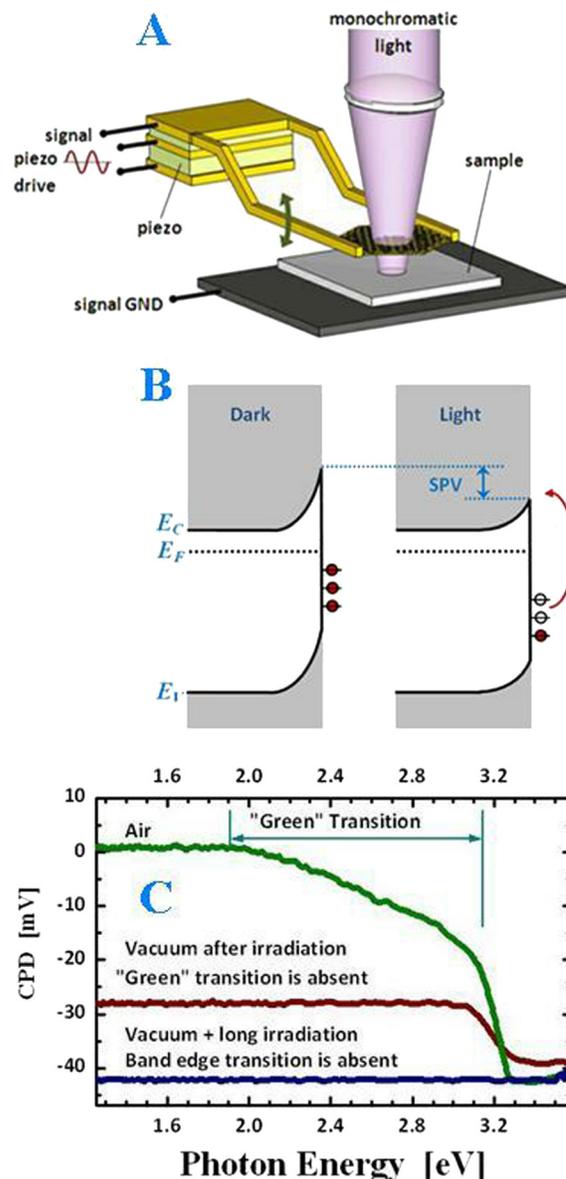


FIG. 5. (A) Schematic cartoon of the surface photovoltage setup. (B) Schematic band diagram showing an ionization of deep surface acceptors giving rise to a reduction of the surface band bending, the change of which is the surface photovoltage. (C) Surface photovoltage spectra acquired in air, in vacuum after short white light exposure, and in vacuum after long exposure. In air, no exposure to white light has taken place yet and oxygen is available to replace any emitted oxygen—the green transition is therefore unaffected. In vacuum after a short exposure, the oxygen that has been emitted is pumped away and no oxygen is available to replace it—the green transition is eliminated. After additional long exposure in vacuum, the band bending is totally eliminated and no photovoltage is observed.

voltage to the Kelvin side of the capacitor, to match the internal voltage, reduces the capacitor charge to zero and nulls the current. Therefore, the voltage required to null the current is the surface voltage. However, certain parasitic capacitances render this measurement inaccurate. In our experiment, we measure the illumination-induced variation in the surface voltage (hence, the surface photovoltage). Since the parasitic capacitances are illumination independent, they cancel out in the subtraction. The absorbed photons charge or discharge deep levels, changing the surface voltage, or the surface band-bending, as illustrated in the band

diagrams in Fig. 5(B). This way one can monitor photon-induced changes in the surface band bending of semiconductors.

As evidenced in the XPS data, exposure to white light in vacuum results in a decomposition of the ZnO lattice and oxygen emission. The emitted oxygen can only originate at the very surface and cannot be emitted from within the lattice. This generates *surface* oxygen vacancies. To affect the conductivity, these oxygen vacancies must be *shallow donors*. As shallow donors, they form a very thin layer of n-type doping at the very surface. A gradual formation of n-type doping at the surface should work to gradually decrease the band-bending at the surface, which is the trend we observe in the surface photovoltage (Fig. 4 (bottom)).

Oxygen vacancies in ZnO were believed for many years to act as shallow donors.⁴¹ Recent *ab-initio* studies by Lany and Zunger and by Janotti and van de Walle showed that, when situated *in the bulk*, the oxygen vacancy is a deep donor and cannot contribute to conduction.^{42,43} Dalpian and Chelikowsky have shown that nanocrystals, such as nanowires, follow a principle of “self-purification,” according to which point defects migrate, during the growth, to the surface (extremely small distance to diffuse and very high temperature), leaving the structure mostly devoid of point defects.⁴⁴ Hence in principle, straight nanowires will contain *little to no* bulk oxygen vacancies. By choosing to experiment with ZnO nanowires, we intended to avoid bulk vacancies as much as possible. When we expose ZnO nanowires to white light, we can only create *surface* vacancies. The use of nanowires thus provides a relatively “clean” experiment that helps to isolate the effect of surface vacancies.

Evidently, the surface oxygen vacancies we generate have an immediate and considerable effect on the conduction. Under illumination, any donor would give away its electron. However, if the donor is deep it will re-trap its electron, sometime after the light is turned off. To contribute to the conduction in the dark, it must be a shallow donor. An oxygen vacancy can be in one of three charging states: neutral, singly ionized, and doubly ionized. *Ab-initio* studies of vacancies in the bulk have shown that, in its neutral state, the oxygen vacancy is a deep donor; while in its singly ionized state, it is a shallow donor.^{42,43} It was also suggested that under illumination, it may be possible to generate vacancies in the singly ionized charging state. This state, however, is metastable, but since each of the charging states involves a different lattice relaxation, there exists an energy barrier that prevents this metastable state from changing immediately into the stable neutral state. Given enough time, the singly ionized state will eventually decay into the neutral state. The important point here is that this decay *does not require* ambient oxygen. Hence, it should make no difference whether we place our sample in vacuum or expose it to air. All of these considerations refer to the *bulk*. Assuming that the energetic relations between these three states are roughly the same at the surface with certain small variations, it may well be that by illumination, we indeed create singly ionized oxygen vacancies on the surface, which start off as shallow donors and contribute immediately to the conduction, explaining the photoconductivity.

If this is indeed the case, then once we turn off the light and expose to oxygen, our surface oxygen vacancies have two alternative paths for decay. One path is to absorb oxygen from the ambient gas and cease to exist. The rate of this process should strongly depend on the pressure of ambient oxygen, and this actually fits the common experience with ZnO photoconductivity. The other path is to decay into the neutral state. This process does not require oxygen and may take place in vacuum. However, in ultra high vacuum ($\sim 1 \times 10^{-10}$ Torr), we did not observe any noticeable variation seven hours after we turned off the light.⁴⁵ We also could not find a report of such observation in the literature. This latter process must therefore be rather slow and this may be the reason why it has not been noticed experimentally.

To further examine the oxygen-independent decay path, we exposed a ZnO nanowire sample to white light in ultra-high vacuum and then kept the sample in the dark, in vacuum, for three days. As the chamber is continuously pumped, practically no oxygen is available to fill in the vacancies, and therefore their density should not change. If the expected transition (between the oxygen vacancy charging states) takes place, some of the vacancies that were created by light will go back from the shallow donor state to the deep donor state, and this deep level should be noticed as a transition in the surface photovoltage spectrum. Contrary to our expectation, we did not notice any new deep level transition.⁴⁶ We note that in surface photovoltage spectroscopy, it is difficult to distinguish shallow states from their adjacent band.²⁹ This means there may still exist shallow levels that are not manifested in the photovoltage spectra. Hence practically, our illumination-induced oxygen vacancy donors remained shallow for the duration of our experiment.

To examine the dynamics of the deep levels in response to light, we examine surface photovoltage spectra before and after irradiation with white light. Figure 5(C) shows a reference surface photovoltage spectrum obtained from the ZnO nanowire sample in air, after a 48 h relaxation in the dark. The contact potential difference drops sharply around the band edge (3.3 eV) confirming the n-type conductivity of the material.²⁹ Another transition is observed over the wide energy range between 1.8 and 3.2 eV. This transition matches the range of the commonly observed green luminescence in ZnO. It has been shown that the green luminescence in ZnO nanowires originated from surface states,³⁹ and therefore the polarity of the surface photovoltage transition reveals a transition between a deep acceptor and the bottom of the conduction band. The green luminescence has been suggested to originate at Zn vacancies forming deep acceptors, which is in line with the interpretation of the SPV spectra.^{47,48} We emphasize that other than this deep acceptor, there is no other deep level observed, and this is a most typical photovoltage spectrum of ZnO in all its forms, bulk or particles (in our case nanowires). After a short (1 h) exposure to white light in vacuum followed by a long (24 h) relaxation in the dark and in vacuum, the surface photovoltage spectrum is missing the green transition. After additional exposure to white light for a long time (8 h) followed by a long (36 h) relaxation in the dark in vacuum, the band-edge transition disappears as well from the photovoltage spectrum,

i.e., there is no photovoltage at any photon energy. After three additional days of relaxation in the dark, the spectrum remained featureless with *no trace of a deep donor* (not shown as there was no change). The only way to reconcile this absence of a deep donor, with the theoretical works suggesting oxygen vacancy to be a deep donor, is to conclude that the ZnO superficial oxygen vacancy has no optical cross-section, i.e., it does not respond to light (may perhaps be detected by thermal methods). More plausible, however, is the possibility that the surface oxygen vacancy is simply a shallow donor, having a different configuration than the calculated bulk vacancies.

We explain the photovoltage observations as follows. If the green-related surface states are indeed Zn vacancies, as is commonly suggested both by experiments⁴⁹ and by theory,⁴² then from the energetic point of view, oxygen should be more easily extracted from atoms surrounding a surface Zn vacancy, thereby neutralizing it. This may explain the disappearance of the green transition. After a long exposure, the density of oxygen vacancies exceeds that of the Zn vacancies, and the excess oxygen vacancies gradually produce an n-type surface delta doping, flattening the bands at the surface, and possibly even creating surface accumulation in extreme cases, resulting in a complete elimination of the band-edge photovoltage transition. The observation of white light induced *surface accumulation* in ZnO under similar conditions as reported by Eger *et al.*³¹ is therefore explained as well by our suggested model.

IV. CONCLUSION

In summary, it is evident by XPS that, under the common photoconductivity experimental conditions, the ZnO lattice decomposes at its very surface. This happens in spite of the fact that there is not enough photon energy for direct decomposition, apparently due to the participation of carbon or carbon containing molecules. Energy considerations suggest that both the ZnO decomposition and its related photoconductivity may be accounted for by photon-assisted reduction of ZnO by carbon species, whether residing on the ZnO surface or adsorbed onto it from the gas ambient. This decomposition forms oxygen vacancies that increase the free electron concentration at the surface creating a surface delta doping forming a surface accumulation layer acting as an electric shunt, reducing the electrical resistance at the surface. Gas environment of carbon containing molecules may favor decomposition, while oxygen environment may favor re-composition. Thus, each of these gasses changes the balance of composition/decomposition driving the observed resistance up or down, respectively. This makes the ZnO resistor a good sensor for certain carbon containing gas molecules, and for oxygen. The bottom line is that our results show that *the integrity of the ZnO surface is affected by white light*. This process is bound to affect *all* surface related phenomena in ZnO.

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- ¹L. J. Brillson, in *Surfaces and Interfaces of Zinc Oxide*, Semiconductors and Semimetals Vol. 88, edited by B. G. Svensson, S. J. Pearton, and C. Jagadish (Academic Press, Burlington, 2013), pp. 105–157.
- ²C. H. Swartz, “Transport and surface conductivity in ZnO,” *J. Mater. Res.* **27**, 2205 (2012).
- ³A. P. Ramirez, “Oxide electronics emerge,” *Science* **315**, 1377 (2007).
- ⁴M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. D. Yang, “Room-temperature ultraviolet nanowire nanolasers,” *Science* **292**, 1897 (2001).
- ⁵D. B. Medved, “Photodesorption in zinc oxide semiconductor,” *J. Chem. Phys.* **28**, 870 (1958).
- ⁶H. C. Gatos and J. Lagowski, “Surface photovoltage spectroscopy—A new approach to the study of high-gap semiconductor surfaces,” *J. Vac. Sci. Technol.* **10**, 130 (1973).
- ⁷L. Kronik and Y. Shapira, “Surface photovoltage spectroscopy of semiconductor structures: At the crossroads of physics, chemistry and electrical engineering,” *Surf. Interface Anal.* **31**, 954 (2001).
- ⁸J. C. Moore and C. V. Thompson, “Phenomenological model for the photocurrent transient relaxation observed in ZnO-based photodetector devices,” *Sensors* **13**, 9921 (2013).
- ⁹P. Mitra, A. P. Chatterjee, and H. S. Maiti, “ZnO thin film sensor,” *Mater. Lett.* **35**, 33 (1998).
- ¹⁰Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li, and C. L. Lin, “Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors,” *Appl. Phys. Lett.* **84**, 3654 (2004).
- ¹¹V. Kobrinsky, E. Fradkin, V. Lumelsky, A. Rothschild, Y. Komem, and Y. Lifshitz, “Tunable gas sensing properties of p- and n-doped ZnO thin films,” *Sens. Actuators B* **148**, 379 (2010).
- ¹²C. C. Li, Z. F. Du, L. M. Li, H. C. Yu, Q. Wan, and T. H. Wang, “Surface-depletion controlled gas sensing of ZnO nanorods grown at room temperature,” *Appl. Phys. Lett.* **91**, 032101 (2007).
- ¹³P. Sharma, K. Sreenivas, and K. V. Rao, “Analysis of ultraviolet photoconductivity in ZnO films prepared by unbalanced magnetron sputtering,” *J. Appl. Phys.* **93**, 3963 (2003).
- ¹⁴J. X. Wang, X. W. Sun, Y. Yang, H. Huang, Y. C. Lee, O. K. Tan, and L. Vayssieres, “Hydrothermally grown oriented ZnO nanorod arrays for gas sensing applications,” *Nanotechnology* **17**, 4995 (2006).
- ¹⁵Y. Shapira, R. B. McQuistan, and D. Lichtman, “Relationship between photodesorption and surface conductivity in ZnO,” *Phys. Rev. B* **15**, 2163 (1977).
- ¹⁶Y. Shapira, S. M. Cox, and D. Lichtman, “Chemisorption, photodesorption and conductivity measurements on ZnO surfaces,” *Surf. Sci.* **54**, 43 (1976).
- ¹⁷P. Ivanoff Reyes, C.-J. Ku, Z. Duan, Y. Xu, E. Garfunkel, and Y. Lu, “Reduction of persistent photoconductivity in ZnO thin film transistor-based UV photodetector,” *Appl. Phys. Lett.* **101**, 031118 (2012).
- ¹⁸Z. G. Yin, X. W. Zhang, Z. Fu, X. L. Yang, J. L. Wu, G. S. Wu, L. Gong, and P. K. Chu, “Persistent photoconductivity in ZnO nanostructures induced by surface oxygen vacancy,” *Phys. Status Solidi RRL* **6**, 117 (2012).
- ¹⁹Y. Shapira, S. M. Cox, and D. Lichtman, “Photodesorption from powdered ZnO,” *Surf. Sci.* **50**, 503 (1975).
- ²⁰P. Morgen, J. H. Onsgaard, and S. Tougaard, “Desorption from powdered ZnO during electron bombardment and interaction with atomic hydrogen,” *J. Appl. Phys.* **48**, 3443 (1977).
- ²¹J. Cunningham, E. Finn, and N. Samman, “Photo-assisted surface-reactions studied by dynamic mass-spectrometry,” *Faraday Discussions* **58**, 160 (1974).
- ²²L. Liao, B. Yan, Y. F. Hao, G. Z. Xing, J. P. Liu, B. C. Zhao, Z. X. Shen, T. Wu, L. Wang, J. T. L. Thong, C. M. Li, W. Huang, and T. Yu, “P-type electrical, photoconductive, and anomalous ferromagnetic properties of Cu₂O nanowires,” *Appl. Phys. Lett.* **94**, 113106 (2009).
- ²³M. T. S. Nair, L. Guerrero, O. L. Arenas, and P. K. Nair, “Chemically deposited copper oxide thin films: structural, optical and electrical characteristics,” *Appl. Surf. Sci.* **150**, 143 (1999).
- ²⁴D. Sporleder, D. P. Wilson, and M. G. White, “Final state distributions of O₂ photodesorbed from TiO₂,” *J. Phys. Chem. C* **113**, 13180 (2009).
- ²⁵R. S. Chen, C. A. Chen, H. Y. Tsai, W. C. Wang, and Y. S. Huang, “Photoconduction properties in single-crystalline titanium dioxide nanorods with ultrahigh normalized gain,” *J. Phys. Chem. C* **116**, 4267 (2012).
- ²⁶K. Huang and Q. Zhang, “Giant persistent photoconductivity of the WO₃ nanowires in vacuum condition,” *Nanoscale Res. Lett.* **6**, 52 (2011).
- ²⁷E. Comini, G. Faglia, and G. Sberveglieri, “UV light activation of tin oxide thin films for NO₂ sensing at low temperatures,” *Sens. Actuators B* **78**, 73 (2001).

- ²⁸V. Sabayev, D. Aronov, L. Oster, and G. Rosenman, "Electron-induced surface reactivity modification in zinc oxide-based thin films," *Appl. Phys. Lett.* **93**, 144104 (2008).
- ²⁹L. Kronik and Y. Shapira, *Surf. Sci. Rep.* **37**, 1 (1999).
- ³⁰J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, in *Handbook of X-ray Photoelectron Spectroscopy*, 2nd ed., edited by J. Chastain (Physical Electronics Division, Perkin-Elmer Corp., Eden Prairie, MN, 1992).
- ³¹D. Eger, Y. Goldstein, and A. Many, "Oxygen chemisorptions and photodesorption processes on ZnO surfaces," *RCA Rev.* **36**, 508 (1975).
- ³²H. T. Ng, B. Chen, J. Li, J. E. Han, M. Meyyappan, J. Wu, S. X. Li, and E. E. Haller, "Optical properties of single-crystalline ZnO nanowires on m-sapphire," *Appl. Phys. Lett.* **82**, 2023 (2003).
- ³³D. Lichtman, "Residual gas analysis: Past, present, and future," *J. Vac. Sci. Technol. A* **8**, 2810 (1990).
- ³⁴T. Ogawa, M. Akabori, J. Motohisa, and T. Fukui, "Real-time observation of electron-beam induced mass transport in strained InGaAs/AlGaAs layers on GaAs (100) and (311)B substrates," *Jpn. J. Appl. Phys., Part 1* **38**, 1040 (1999).
- ³⁵*CRC Handbook of Chemistry and Physics*, 87th ed., edited by D. R. Lide (CRC Press, Boca Raton, 2006), pp. 5-4.
- ³⁶K. Keem, H. Kim, G.-T. Kim, J. S. Lee, B. Min, K. Cho, M.-Y. Sung, and S. Kima, "Photocurrent in ZnO nanowires grown from Au electrodes," *Appl. Phys. Lett.* **84**, 4376 (2004).
- ³⁷D. B. Medved, "Photoconductivity and chemisorption kinetics in sintered zinc oxide semiconductor," *J. Phys. Chem. Solids* **20**, 255 (1961).
- ³⁸S. K. Mishra, R. K. Srivastava, S. G. Prakash, R. S. Yadav, and A. C. Panday, "Photoluminescence and photoconductive characteristics of hydrothermally synthesized ZnO nanoparticles," *Opto-Electron. Rev.* **18**, 467 (2010).
- ³⁹I. Shalish, H. Temkin, and V. Narayanamurti, "Size-dependent surface luminescence in ZnO nanowires," *Phys. Rev. B* **69**, 245401 (2004).
- ⁴⁰C. R. Gorla, N. W. Emanetoglu, S. Liang, W. E. Mayo, Y. Lua, M. Wraback, and H. Shen, "Structural, optical, and surface acoustic wave properties of epitaxial ZnO films grown on (0112) sapphire by metalorganic chemical vapor deposition," *J. Appl. Phys.* **85**, 2595 (1999).
- ⁴¹A. Janotti and C. G. Van de Walle, "Fundamentals of zinc oxide as a semiconductor," *Rep. Prog. Phys.* **72**, 126501 (2009).
- ⁴²A. Janotti and C. G. Van de Walle, "Oxygen vacancies in ZnO," *Appl. Phys. Lett.* **87**, 122102 (2005).
- ⁴³S. Lany and A. Zunger, "Anion vacancies as a source of persistent photoconductivity in II-VI and chalcopyrite semiconductors," *Phys. Rev. B* **72**, 035215 (2005).
- ⁴⁴G. M. Dalpian and J. R. Chelikowsky, "Self-purification in semiconductor nanocrystals," *Phys. Rev. Lett.* **96**, 226802 (2006).
- ⁴⁵In lower vacuum, around 10^{-8} Torr, we did observe a decay, but this clearly coincided with the increase in the residual oxygen in the chamber.
- ⁴⁶For a recent report of ZnO photoconductivity that persists for days in ultra high vacuum, see B. Claffin, D. C. Look, S. J. Park, and G. Cantwell, "Persistent n-type photoconductivity in p-type ZnO," *J. Cryst. Growth* **287**, 16 (2006).
- ⁴⁷D. C. Look, K. D. Leedy, L. Vines, B. G. Svensson, A. Zubiaga, F. Tuomisto, D. R. Doutt, and L. J. Brillson, "Self-compensation in semiconductors: The Zn vacancy in Ga-doped ZnO," *Phys. Rev. B* **84**, 115202 (2011).
- ⁴⁸Y. W. Heo, D. P. Norton, and S. J. Pearton, "Origin of green luminescence in ZnO thin film grown by molecular-beam epitaxy," *J. Appl. Phys.* **98**, 073502 (2005).
- ⁴⁹D. C. Reynolds, D. C. Look, B. Jogai, and H. Morkoc, "Similarities in the bandedge and deep-centre photoluminescence mechanisms of ZnO and GaN," *Solid State Commun.* **101**, 643 (1997).