Superior Functionality by Design: Selective Ozone Sensing Realized by Rationally Constructed High-Index ZnO Surfaces

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A new technique is reported for the transformation of smooth nonpolar ZnO nanowire surfaces to zigzagged high-index polar surfaces using polycrystalline ZnO thin films deposited by atomic layer deposition (ALD). The c-axis-oriented ZnO nanowires with smooth nonpolar surfaces are fabricated using vapor deposition method and subsequently coated by ALD with a ZnO particulate thin film. The synthesized ZnO–ZnO core–shell nanostructures are annealed at 800 °C to transform the smooth ZnO nanowires to zigzagged nanowires with high-index polar surfaces. Ozone sensing response is compared for all three types of fabricated nanowire morphologies, namely nanowires with smooth surfaces, ZnO–ZnO core–shell nanowires, and zigzagged ZnO nanowires to determine the role of crystallographic surface planes on gas response. While the smooth and core–shell nanowires are largely non-responsive to varying O₃ concentrations in the experiments, zigzagged nanowires show a significantly higher sensitivity (ppb level) owing to inherent defect-rich high-index polar surfaces.

1. Introduction
Readily synthesizable low-cost metal oxide nanostructures have been the focus of intense research in recent years due to their superior physical and electronic properties. In particular, ZnO, a II–VI compound semiconductor with a bandgap of 3.3 eV and room temperature exciton binding energy of 60 meV, has attracted a fair bit of attention in particular.[1] ZnO nanowires have been suggested as a prime candidate for the fabrication of various high-performance devices, including but not limited to transistors, light emitting diodes, and chemical and optical sensors.[2–4]

Thermodynamically stable high-aspect-ratio ZnO crystals (i.e., nanowires) can be easily synthesized either using a solution or gas phase growth route.[5,6] ZnO nanowires produced by these methods usually have a hexagonal wurtzite structure with alternating, close-packed zinc and oxygen layers stacked along the c-axis.[7] The reason for preferential c-axis growth is that under thermodynamic equilibrium,
crystal planes with higher surface energies occupy a smaller area on the crystal.\[8\] In the case of ZnO, the polar surfaces such as (0001) have higher surface energies than the charge neutral nonpolar crystal facets such as (0110) and (2110). Therefore, ZnO crystal growth occurs mostly in the [0001] direction. The side surfaces of the final products are enclosed by nonpolar planes. However, there have been a few studies reporting transformation of outer nonpolar ZnO surfaces to structured polar surfaces by post-processing. For instance, Han et al. used oleic acid and 1-octylamine to selectively etch the nonpolar surfaces of ZnO nanowires to create pagoda-like and hexagonal pyramidal nanostructures.\[9\] The exposed ZnO planes were low-index (0001) and (1011) polar surfaces which were resistant to the chemical etchant. In another study, Cho and co-workers first deposited a polycrystalline ZnSe layer on ZnO nanostructures by a solution-based reaction. Upon calcination at high temperatures, non-symmetrical and non-evenly-textured ZnO nanostructures with polar surfaces were obtained.\[10\]

In this research, we report a simple method for the rational formation of zigzagged ZnO nanowires with high-index polar surfaces. In the first step, ZnO nanowires were coated with highly conformal ZnO films by atomic layer deposition (ALD). The resulting ZnO (monocrystalline–ZnO (polycrystalline) core–shell nanowires were then annealed at an elevated temperature to create highly ordered, symmetrical single-crystalline zigzagged nanowires with high-index polar crystal facets exposed on the surface. By modulating the thickness of the deposited ALD ZnO film, highly porous zigzagged nanowires can also be created due to the quasi-Kirkendall effect, which is observed for the first time. Finally, we employed the zigzagged nanowires with high-index polar surfaces as room temperature ozone sensors which showed superior sensitivity toward ozone as compared to smooth and only coated nanowires.

2. Results and Discussion

2.1. Fabrication of Zigzagged Nanowires

Figure 1a schematically highlights the fabrication strategy for zigzagged ZnO nanowires. Non-textured, smooth ZnO nanowires are grown using a gas-transport technique in a horizontal tube furnace between 875–939 °C on a Si substrate. The smooth monocrystalline ZnO nanowires are then coated with a very thin (5 nm) polycrystalline ZnO layer by ALD at 150 °C using diethylzinc (DEZ) and water as the precursors. Finally, the ZnO–ZnO core–shell structures are annealed at 800 °C for 3 h in air to form the zigzagged ZnO nanowires. In this fabrication scheme, the most critical process is the conformal coating of the ZnO nanowires by ALD. ALD is a sequential chemical vapor deposition (CVD) technique which allows deposition of very high quality nitride, oxide, sulfide, elemental thin films over a wide temperature window.\[11,12\] The reactant gases during ALD are released into the deposition chamber in an alternating manner dividing the gas reactions into two separate surface reactions. This ensures precise monolayer thickness control and conformal coverage of even highly complex three dimensional structures with high aspect ratios. In the case of ZnO thin films, the ALD process always yields polycrystalline layers regardless of the deposition temperature or thickness. However, when the films are too thin, 5 nm in our case, a particulate film is formed with particles of a uniform size rather than a continuous layer. Figure 1b–d displays a set of scanning electron microscopy (SEM) images of ZnO nanowires at different stages of the fabrication process. Figure 1b is a high-magnification SEM image of bare ZnO nanowires. The as-grown ZnO nanowires have very smooth surfaces as anticipated. Once the nanowires were coated with a 5 nm ALD ZnO thin film (Figure 1c), their surfaces were roughened as a result of tiny ZnO crystallites of approximately 5 nm in size surrounding the nanowires. A core–shell structure consisting of a single-crystalline ZnO nanowire core and a polycrystalline ZnO shell was thus formed. The ZnO particles were distributed evenly and conformally over all nanowires. Upon annealing at 800 °C for 3 h in air, the initially rough ZnO–ZnO core–shell structures were transformed into single-crystalline zigzagged nanowires as shown in Figure 1d where the polycrystalline coating was no longer visible.

We investigated the influence of each step on the room temperature photoluminescence (PL) properties of the synthesized nanostructures. ZnO nanowire samples were sonicated...
in isopropyl alcohol and dispersed onto a Si substrate for micro-photoluminescence analysis. The measurement setup had a spatial resolution of 300 nm and was equipped with a moving xyz table for locating individually isolated nanowires. Located nanowires were excited by an Ar-ion laser with a wavelength of 334 nm and the emission spectra from the nanowires were recorded by a 550 nm focal length spectrometer with a 150 g/mm grating charge-coupled-device (CCD)-based sensor. Figure 2 (left) exhibits the recorded spectra from individual ZnO nanowires extracted from the samples. All spectra are normalized to the near band edge (NBE) peak. PL of ZnO typically consists of two distinct emission bands. The first one is the higher energy NBE peak centered at ~380 nm. Emissions at this wavelength are due to excitonic transitions caused by shallow donors inside the bandgap.\(^{[13]}\) The second band is the deep level emission (DLE) also known as defect luminescence band, which ranges from 450 to 900 nm and originates from various intrinsic and extrinsic defects in ZnO crystals and also influenced by defects, impurities and absorbed molecules on the nanowire surface.\(^{[14]}\) However, DLE emission is accepted to mostly originate from the nanowire surface and it’s generally agreed that DLE is largely related to oxygen vacancies \((V_o)\).\(^{[15]}\) Therefore, the DLE profile can be treated as a direct measure of the surface defect profile of ZnO nanowires. Figure 2 (right) displays a bar graph containing the DLE to NBE ratio of ZnO nanowires from four nanowire samples. Expectedly as-grown and annealed nanowires had comparable DLE to NBE ratios as the surface is practically unaltered, though annealing in air slightly increased DLE/NBE through high-temperature oxygen adsorption on the surface and upward band bending. ALD-coated nanowires showed a higher concentration of surface defects as a result of small ZnO particulates sitting on the nanowire surface. But most notably zigzagged ZnO nanowires showed the highest defect emission. This is attributed to high concentration of inherent surface defects (i.e., oxygen vacancies) contained in the high-index polar surfaces.

Figure 3a displays a transmission electron microscopy (TEM) image of a 5 nm ALD ZnO-coated ZnO nanowire along with a simple schematic view. As mentioned earlier, the 5 nm ALD film is not continuous and consists of small ZnO islands. This was confirmed by the presence of multiple diffraction rings in the electron diffraction pattern shown next to the structure. When this sample was annealed at 800 °C for 3 h, the starting core–shell nanowires were transformed into series of zigzagged nanowires, as shown in Figure 3b. It can be clearly seen that the produced nanowires are highly symmetric and have sharp zigzagged surfaces formed evenly throughout the nanostructures. Expectedly, as the diameter of the nanowires shrinks, the zigzagged morphology becomes more obvious since the surface-area-to-volume ratio is higher for thinner nanowires. Using our fabrication scheme, zigzagged nanowires of different sizes can be created as displayed in Figure S1 (see Supporting Information, SI).
Figure 3c and d exhibit high-resolution TEM (HRTEM) images of an original as-grown nanowire and a zigzagged nanowire, respectively. Both nanowires are monocristalline and c-axis-oriented as indicated by the lattice spacing of 5.2 and 2.6 Å. The as-grown nanowire has the usual nonpolar sidewalls with atomic smoothness perpendicular to the [0001] plane whereas, the zigzagged nanowire has a polar side surface with high-index exposed ZnO facets. One of these planes is schemed in Figure 3e. The marked facet is indexed approximately at (013 135) which is an unusually high-index plane. We consider that the zigzagged surfaces formed during the annealing process based on two major mechanisms: 1) Ostwald ripening caused by thermodynamic energy minimization and 2) electrostatic interactions caused by the charged polar surfaces. When annealed, the small ZnO particulates situated on the ZnO nanowires are inclined to fuse into the inner core to minimize their surface energies. The nonpolar surfaces (e.g., (0110)) have a smaller surface energy compared to polar surfaces. Therefore, at elevated temperatures such as 800 °C, atomic diffusion takes place to create aligned (0110) layers stacked parallel to the nanowire surface. However, during the alignment process each nanocrystal contains only a limited amount of material which is not enough to flatten around the entire nanowire surface. Hence, the aligned layers are stacked up on top of each other like a triangle to minimize the surface energy with high-index exposed facets. As a result, the highest growth rate is in the high-index directions. The preferential formation of high-index facets is also consistent with the Bravais–Friedel–K überling–Smith law (later modified by Donnay and Harker) which states that high-index crystal planes with small interplanar spacing grow faster than low-index planes. The stacking geometry of the (0110) planes precisely follows this law of crystal growth. This is the reason why high-index planes are rarely observed in final crystals under a steady atomic flux (such as in gas-phase ZnO nanowire growth). Furthermore, high-index polar crystal planes in ZnO are known to possess surface charge. For this reason, electrostatic interactions are expected to influence the surface reconfiguration process to compensate the induced electric field. The surfaces with the same electrostatic charge would repulse each other while the opposite charge would attract. We believe that this is the reason why all the projective triangles on the surface are of the same height but with different wall lengths as shown in Figure 3d, rendering the overall surface charge neutral which quenches the induced electric field. For tracing the surface evolution, the initial ZnO nanowires coated by a 5 nm ALD ZnO shell were also annealed by rapid thermal processing (RTP) at 800 °C for 5 min. However, the zigzagged surface morphology did not abundantly develop, confirming that the surface reconfiguration is a slower process (SI, Figure S2). Therefore, for fabricating the zigzagged ZnO nanowires by this strategy, a long-time annealing process is necessary.

2.2. Nanoscale Quasi-Kirkendall Effect

Additionally, we frequently encountered zigzagged ZnO nanowires with embedded small voids during TEM analysis. One of these nanowires is displayed in Figure 4a where several voids are encircled, and the inset shows a magnified view of a selected area on the nanowire. It appears that the voids are always formed beneath the surface, adjacent to the interface region between the surface zigzags and the original ZnO core. To understand the exact origin of the generated interfacial voids, we coated a new sample of as-grown nanowires with a thicker ALD ZnO film (15 nm) as shown in Figure 4b. With the ZnO thickness increased, the ALD-deposited film becomes a continuous polycrystalline layer instead of a particle film like the case of the 5 nm ZnO layer. Annealing this sample at 800 °C for 3 h resulted in the universal formation of significantly more porous zigzagged nanowires with clearly faceted larger interfacial voids (Figure 4c,d). A magnified version of these faceted voids can be seen in Figure S3 (SI). Moreover, the locations of the voids formed beneath the surface became deeper, conforming to the thickness of the as-deposited ZnO layer.

In binary material systems, differences in atomic diffusivities across an interface...
is often compensated by a vacancy flux where diffused lattice vacancies accumulate and supersaturate into voids in the interface region, on the side of the faster diffusing species. The formation of interfacial voids in this type of thermal diffusion couples has been attributed to the nanoscale Kirkendall effect.\cite{Kirkendall} Using this phenomenon, various hollow and porous nanospheres, nanowires, and even thin films have been fabricated with controlled porosity.\cite{PorousNanowires, PorousNanofibers, PorousNanotubes, PorousNanoparticles} It is known that the surface of ZnO can be thermally activated at temperatures higher than 800 °C, leading to a slight evaporation or desorption of ZnO during annealing. When the ALD ZnO-coated ZnO core–shell nanowires are annealed at this temperature, thermal diffusion of ZnO is likely to take place at both the surface and the core–shell interface. In particular, the kinetics-favorable grain boundary diffusion will dominate the migration of ZnO within the outer polycrystalline shell as well as at the single-crystalline/polycrystalline interface. At the ZnO–ZnO interface, the outward diffusion of the single crystal ZnO nanowire core is thus enhanced due to the presence of the abundant grain boundaries in the polycrystalline ZnO shell. As a result, the injected vacancies will gradually evolve into interfacial voids until the shell structure is finally transformed into the single-crystal component of the stems. The continuous coating of 15 nm ZnO can provide a more confined space for the accumulation and supersaturation of generated vacancies. Thus, vacancies positioned on the nanowire surface cannot be easily filled by the self-healing feature of ZnO\cite{SelfHealing} and more interfacial voids were produced.

2.3. Ozone Sensing Response

As mentioned before, the fabricated zigzagged nanowires have high-index polar surfaces as opposed to nonpolar surfaces as in the case of as-grown nanowires. Therefore, we expect a change in sensitivity versus gasses such as ozone (O₃) between different morphologies. We have selected O₃ in particular because in general ZnO shows low sensitivity to O₂ even at elevated temperatures (350 °C).\cite{ZnO_O2} In order to test this hypothesis, we fabricated a set of interdigitated gold electrodes or the so-called finger-grid structure which can be used to selectively grow ZnO nanowires for sensing applications.\cite{ZnO_Sensing} An SEM image of the fabricated finger-grid nanowire sensor is exhibited in Figure 5a where the inset shows the sensor architecture schematically. In this system, the gold electrodes are fabricated on an insulating 200 nm thick SiO₂ layer, fabricated by thermal oxidation of a Si (100) wafer, and act as a seed layer for ZnO nanowire growth during gas-phase deposition. Using this method, ZnO nanowires can be grown only on the patterned gold areas. A zoomed-in view of the finger-grid structure is shown in Figure 5b. In this figure, the lighter contrast areas correspond to the gold seed layer where the nanowires are nucleated and the darker areas are the insulating layer with no nanowire nucleation. Further magnification into the dark areas (Figure 5c) reveals that ZnO nanowires originating from the gold layers randomly come in contact with each other over the insulating areas forming electrically conductive junctions. This is also illustrated schematically in Figure 5d.

After the sensor structure was constructed, we transformed the as-grown ZnO nanowires into zigzagged ZnO nanowires with high-index surface planes for room-temperature O₃ sensing. Additionally, the as-grown ZnO nanowires (annealed at 800 °C for 3 h in air) and ZnO–ZnO core–shell nanowires (first annealed at 800 °C for 3 h in air then coated) were also tested for comparison. The intention for employing the annealing process for the control samples is to reduce the systematic difference for all samples.\cite{Systematic_Difference} The smooth surface morphology of the as-grown ZnO nanowires was unchanged after the annealing process.

Resistance of the nanowires was measured using a two-probe method by attaching electrical contacts to the finger-grid structure on each end. The change in resistance was...
recorded when exposed to different concentrations of O$_3$ gas. The ozone concentration in the measurement chamber was adjusted using a mass flow controller. The adsorbed oxygen species are removed from nanowire surfaces for sensor recovery by illumination with UV light (3.5 eV) generated by a UV light-emitting diode (LED). The LED on the sensor was operated in a modulation mode, and regularly switched on (reactivation cycle) and off (ozone adsorption cycle) every 2 min resulting in the observable minima and maxima in the recorded resistance, respectively. The ratio between recorded on and off resistance is a measure of the ozone concentration and is displayed as O$_3$ response in Figure 6d. Further experimental conditions have already been introduced in a previous work. Figure 6a shows an overview of the measurement results at different O$_3$ concentrations between 0 and 600 ppb at room temperature. While the other two control samples were mostly insensitive to the varying O$_3$ concentrations, the resistance of the zigzagged nanowires approximately doubled when exposed to as high as 600 ppb of ozone even for short durations. Figure 6b and c shows the response curve of zigzagged nanowires in detail. It can be clearly seen that when the O$_3$ concentration is increased, resistivity of the zigzagged ZnO nanowires increased accordingly. At high concentrations, a baseline shift during operation is apparent, e.g. at 600 ppb from 2.06 × 10$^4$ Ω at the first cycle to 2.15 × 10$^4$ Ω at the sixth cycle (Figure 6c). However, the ratio between LED-on and LED-off resistance, i.e., the O$_3$ response, is stable already after two cycles. As a consequence, the zigzagged nanowire sensor is fully reversibly responsive to both increasing and decreasing gas concentrations, confirming the stability of the platform as an ozone sensor. The resulting O$_3$ response of all the three types of nanowires is summarized in Figure 6d. Obviously, the sensor shows also a response of 1.16 if no ozone is present due to a UV-induced photocurrent. This contribution to the sensor response is constant and independent of the ozone concentration and can be considered accordingly.

O$_3$ sensing using ZnO nanowires involves two stages. In the first stage, UV stimulation and consequent injection of high energy photons invokes desorption of oxygen from surface and release of free electrons, which reduces resistivity of the nanowires. Additionally, high energy photons with energies greater than the bandgap of ZnO would create electron-hole pairs and further increase conductivity of the nanowires. In the second stage, exposure to O$_3$ introduces oxygen species to the exposed surfaces. Adsorbed oxygen species capture and trap free electrons at the nanowire surface in the form of ions. The captured electrons on the surface will result in upward band bending and a corresponding depletion region, also known as the space-charge layer. The width of the space-charge layer is the width of the band bending region which is directly associated with the resistance of the nanowires. Thus, it’s also clear that with higher amounts of oxygen on the surface, increase in the resistance of the nanowires would be more significant. Oxygen adsorption in ZnO is generally related to the density of oxygen vacancies on the surface. Therefore, nanowires with higher $V_o$ defect densities, in our case zigzagged nanowires with high-index polar crystal planes, as confirmed in Figure 2, were expected to yield higher sensitivity towards ozone. In fact, Cheng et al. investigated oxygen desorption from high-index polar ZnO surfaces by annealing two ZnO bulk samples terminated with nonpolar (1010) and (001) polar high-index surfaces. The oxygen saturated samples were subsequently annealed and the thermal oxygen desorption profiles were recorded. While the nonpolar surface displayed only a single desorption peak, the high-index polar surface displayed two peaks at two different temperatures one of which was four times wider than the oxygen peak from the nonpolar surface. The authors concluded that the higher density of oxygen vacancies on the high-index polar planes was responsible for the increased oxygen desorption.

Additionally, at room temperature, the physisorption process dominates the adsorption of gas species on the nanowire surface since chemisorption requires higher energies (e.g., higher temperatures) to create a chemical bond between the surface groups and the nanowire surface. However, sensing in metal oxides are mostly considered to be related to the chemisorption process which requires additional energy for the surface reactions. This energy barrier can be lowered by the introduction of high-index polar ZnO surfaces which act as catalytic surfaces for the reaction of ozone related species with oxygen vacancies on the nanowire surface. High-index crystal facets have already been shown to be catalytically more active.
due to high density of active sites comprised of low coordination atoms located in step, ledges and kinks of the high-index crystal surfaces.\textsuperscript{[31,32]} Different crystal facets can also display selective catalysis characteristics.\textsuperscript{[33]} Because of this reason, we have also checked sensitivity of all three nanowire sensors to NO\textsubscript{2} (SI, Figure S4) and O\textsubscript{2} gasses. Interestingly, none of the sensors showed visible sensitivity to these other oxygen-based gasses. An observable modulation of the sensor response is caused by UV-induced photocurrent. It is independent of the gas concentration and can be observed also in pure nitrogen. As mentioned before, by taking this constant contribution into account, it has no impact on the sensor’s sensitivity.

The results confirmed that the zigzagged nanowires with the high-index surfaces not only allow detection O\textsubscript{3} but also show selectivity for different gasses which can amplify its ability to selectively sense O\textsubscript{3} in the presence of other oxygen-based gasses. This gas-dependent sensing difference is considered to result from the relative instability of O\textsubscript{3} in oxygen-based gasses. An observable modulation of the sensor response is caused by UV-induced photocurrent. It is independent of the gas concentration and can be observed also in pure nitrogen. As mentioned before, by taking this constant contribution into account, it has no impact on the sensor’s sensitivity.

It should be mentioned that, contrary to expected, the ZnO–ZnO core–shell nanowires with abundant small crystals attached on the surface also showed no sensitivity to O\textsubscript{3}. It’s true that the introduction of smaller grains on the ZnO nanowire surface increased the overall surface area and surface defect concentration (Figure 2). However, the carrier depletion within the nanocrystals does not affect the depletion region within the inner core thus, not affecting the overall resistance of the single-crystalline ZnO nanowires. In contrast, the presence of surface nanocrystals severely prevented the adsorption of sensed gases on the nanowire stem surface. Thus, increasing surface area not automatically increases sensitivity to gases. Electronic coupling of the surface features to the nanostructures is an essential precondition for sensing behavior, which is realized optimally in the monocrystalline zigzagged ZnO nanowires.

3. Conclusion

In summary, we have demonstrated a new technique for the modification and transformation of ZnO nanowire surfaces from being smooth and nonporous into zigzagged and high-index polar surfaces attributed to Ostwald ripening in combination with electrostatic interactions. The zigzagged nanowires showed significantly higher sensitivity to ozone at room temperature owing to higher density of oxygen vacancies and catalytically active sites in the high-index polar surfaces. In addition, in our current sensor setup, zigzagged ZnO nanowires were highly selective toward ozone and showed no sensitivity for other oxygen-based gasses (i.e., O\textsubscript{2} and NO\textsubscript{2}). Our results demonstrate that by carefully engineering the crystallographic planes exposed on a nanostructure, non-functional surfaces can be functionalized for a specific task.

4. Experimental Section

\textbf{ZnO Nanowires:} ZnO nanowires were grown by a vapor–solid gas-phase deposition method in a horizontal tube furnace on gold-coated Si substrates. For growth, ZnO (Sigma Aldrich 99.999) and graphite (Alfa/Aesar –200 mesh) powders were mixed in a 1:1 ratio and inserted inside a quartz tube along with the prepared substrate. Subsequently, the tube was pumped to 200 mbar and kept between 875 and 939 °C during the process. Ar (7 scm) and O\textsubscript{2} (0.001 scm) were used as the carrier and the oxidizing gas.

\textbf{Deposition:} ALD ZnO Films were deposited by reacting diethylzinc (DEZ) and water at 150 °C in a vertical-flow-type hot-wall reactor manufactured by Oxford Instruments (OpAL). The chamber was pumped down to 20 mTorr before deposition and was kept at 170–190 mTorr during the process. The residual gasses and reaction by-products were purged using N\textsubscript{2} to prevent parasitic CVD reactions. N\textsubscript{2} was also used as the carrier gas for the delivery of the precursors in the reactor. The thickness of the deposited ZnO layers could be tuned by adjusting the number of deposition cycles where the number of cycles is related to film thickness in a linear fashion.

\textbf{High-Temperature Annealing:} High-temperature annealing was carried out at 800 °C in an open box furnace (Carbolite) in air for 3 h. Short time anneals by RTP (Ijielec JetFirst 200C) was carried out for 5 min also at 800 °C in air.

\textbf{Spatially Resolved Micro-photoluminescence (micro-PL):} The micro-PL measurements were carried out using an Ar-ion excitation source (334 nm, 30 mW) manufactured by Spectra Physics. The light was focused using a Zeiss LD Plan - Neofluar 63x/0.75 Korr microscope objective. A xzy piezo stage equipped with an E712 type controller (Physik Instrumente) was used for spatial manipulation of the sample. The produced spectra were recorded using a Horiba Yobin Ivon IHR 550 spectrometer with a 150 g/mm grating and a Synapse CCD camera (CCD2048 × 512-BIU). For micro-PL measurements, different ZnO nanowire samples were first sonicated for 30 s in isopropyl alcohol and dispersed onto a 1 cm × 1 cm Si substrate. These samples were subsequently used for measurement.

\textbf{Gold Finger-Grid Structures:} The finger-grid were fabricated by patterning an AZ 5214 E image reversal photosist layer by standard lithography and thermally evaporating a 100 nm gold film. This was proceeded by lift-off in acetone.

\textbf{Microstructural Characterization:} Microstructure was determined using TEM (JEOL JEM-1010), HRTEM (JEOL JEM-4010) and HRSEM (FEI: Nova Nanosem) microscopes.

\textbf{Ozone Sensor Response of the ZnO Nanowires:} Ozone sensor response was measured at room temperature using a two-probe measurement setup. Temperature was not specifically controlled, however, determined by a sensor in the chamber to be nearly constant at −22 ± 1 °C. Dry synthetic air with a total flux of 1 lpm was set by mass flow controllers (800 scm N\textsubscript{2} + 200 scm O\textsubscript{2}) and was kept constant, when ozone was added. Humidity level was well below the measurement limit (<1%). Prior to sensing experiments, the setup was purged with dry synthetic air for 3 h. An ultraviolet LED (3.5 eV) was placed above the nanowires for UV stimulation of the nanowires and sensor recovery. The sensor response was recorded by a PC terminal running LabView program. When the UV LED was turned on, the measurement chamber was also purged with N\textsubscript{2} gas at the same time for removal of ozone from the measurement environment.
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