UV and Oxygen Sensing Properties and Space Charge Limited Transport of Sonochemically Grown ZnO Nanowires

Avinash P. Nayak¹, Ta-Chun Lin¹, Daniel Lam¹, Savas Kaya², and M. Saif Islam¹,*

¹Department of Electrical and Computer Engineering, University of California Davis, Davis 95616, USA
²School of Electrical Engineering and Computer Science, Ohio University, Athens, Ohio 45701, USA

We report on a room ambient sonochemical process to synthesize Zinc Oxide (ZnO) nanowires for fabricating UV photodetectors and gas sensors on an amorphous substrate. We investigated the conduction properties and the adsorption mechanism at the nanowire surface with and without UV exposure with variation in atmospheric pressure. Optical spectroscopy, scanning electron microscopy (SEM) and current–voltage measurements were used to characterize these samples. The results show that highly dense nanowires can be grown with the use of ultrasound at ambient conditions without a seeding layer of ZnO. We observe non-linear space charge limited current (SCLC) in the nanowires which is attributed to the readily incorporated traps during the sonochemical growth. UV photodetectors and gas sensors have been shown as practical applications of these nanowires grown with this simple method.

Keywords: Sonochemistry, Zinc Oxide Nanowire, UV Photodetector, Gas Sensor, Space Charge Limited Current (SCLC).

1. INTRODUCTION

Among the II–VI semiconductor material, ZnO has a direct band gap of 3.37 eV and a high excitation binding energy of ~60 meV. This inherent property of ZnO allows for a wide range of applications such as photodetectors and photoconductors in the UV-visible spectral regions. The transparent conducting characteristics of ZnO make it a good candidate for applications including solar cells, photodetectors, and flexible electronics.

Several methods such as chemical vapor deposition (CVD), sol–gel method, spray-pyrolysis, and the hydrothermal method have been used to synthesize ZnO nanowires. Unlike these conventional methods, we resort to using a sonochemical method to produce ZnO nanowires at room ambient conditions. The sonochemical method, when compared to the more conventional approach such as hydrothermal, the growth rate of ZnO increases by a factor of ten due to the fast hydrolysis rate caused by cavitation bubbles imploding. This method offers a promising alternative growth technique to synthesize these nanowires.

In this report, we present the transmittance spectra, photocurrent, dark current and the correlation between the resistance dependence of these ZnO nanowires over various atmospheric pressure ranges.

2. EXPERIMENTAL DETAILS

A glass slide was cleaned with methanol, acetone and isopropanol and dried with an N₂ gun before immersing it into an aqueous solution with equimolar concentration (0.02M) of zinc nitrate hexahydrate (ZNH, Zn(NO₃)₂·6H₂O) and hexamethylenetetramine (HMTA, C₆H₁₂N₄). The solution was sonicated for 1 hour at an intensity of 19 W·cm⁻² at 20 kHz. The horn tip was placed 1 cm above the glass substrate. After this first cycle, the glass slide was rinsed with DI water and sonicated under the same conditions for another hour. The sample was then dried with an N₂ gun. The conductivity characterization was done by using a HP 4156B parameter analyzer. All samples were imaged with FEI XL30 field emission Scanning Electron Microscopes. Ocean Optics SpectraSuit was used to obtain optical transmission results. A 0.1 W/cm² SUNRAY 400 SM UV light source (Uvitron International) was used for as the UV light source for the UV measurements.
All chemical reagents used in this report were used without further purification and purchased at Sigma Aldrich (CAS number 100-97-0, 10196-18-6 for HMTA and ZNH respectively).

3. RESULTS AND DISCUSSION

The SEM images of the nanowires are shown in Figure 1. The formation of these nanowires is due to the decomposition of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and hexamethylenetetramine (C₆H₁₂N₄) in water. The chemical reaction that takes place during ultrasound excitation has been reported elsewhere. In the sonochemical technique, high frequency ultrasound waves supply the high energy needed for chemical reactions to occur at a fast rate. The acoustic cavitation inside the solution forms micron sized bubbles that implode in microseconds. This implosion allows for intense local heating which results in high-velocity interparticle collisions.

We find the average aspect ratio of our nanowires to be 6.5 and the average growth rate to be 600 nm hour⁻¹. The aspect ratio and density of nanowires are comparable to the hydrothermal synthesis method but the sonochemical method used in this report has a substantially faster growth rate.

3.1. Photo-Response Characteristics

ZnO nanowires were coated on the sample after the first and second growth process cycle. The room temperature transmission measurement results are shown in Figure 2. We find that there is a 26.7% transmission decrease between the first and second coating cycles in the visible spectral range. This low transmission in the UV range can allow ZnO nanowires to be extremely effective in blocking UV rays and protecting the skin from both sun damage reducing the risk of developing skin cancer.

The absorbance at 368 nm (corresponding to 3.37 eV) is observed for our ZnO nanowires. This absorption data also revealed that the as-prepared ZnO nanowire arrays are mostly transparent in the visible region. The inset of Figure 2 shows the optical images of the glass slides that these ZnO nanowires were deposited on.

Conventional semiconductors have very quick photo-response which rapidly diminishes back down to base-level as soon as the illumination is turned off. ZnO materials however exhibit slow photosresponse which have their own advantages. The photoconduction in ZnO nanowires relies on fast carrier thermal excitation and trapping at the surface of the ZnO material and electron–hole recombination at extended and localized states. During the growth of ZnO nanowires, there is usually a high density of defects at the surface which traps holes and increases the photocurrent response. When UV light is present, the photon energy is larger than the band gap of ZnO and therefore electron–hole pairs are generated. While the high density surface trapping states are leaving the material, the photo-generated holes are trapped along the surface. The photo-generated electrons are left unpaired and therefore contribute to the rapid increase of photocurrent.

We see the change in conductivity with and without UV light in Figure 3. We observe a three order magnitude difference between UV light on and UV light off.

As shown in Figure 4, we see that upon illumination, conductivity increases. Our synthesis technique shows a three order charge in conductivity and a response time (τᵣₑₛ) of 33 seconds and a recovery time (τᵣₑ𝑐) of 244 seconds. The photosensitivity, S, is defined as $S = \sigma_{ph}/\sigma_d$ where $\sigma_{ph}$ is photoconductivity under illumination and $\sigma_d$ is dark conductivity. The photosensitivity was observed to be 89. This is relatively higher in comparison to hydrothermal UV on-off ratios. The UV light was applied for at least 60 seconds to make sure that the photochemical response reached a steady state. The device exhibits low dark currents with a resistance of 2GΩ at a bias of $V = 2$ V at standard temperature and pressure. In vacuum (2.4 mTorr), a constant voltage of $V = 2$ V was also applied to the device. We attribute this to the photo-excited...
Fig. 2. Transmittance spectra of ZnO nanowires grown on glass for one and two growth process cycles. Each growth cycle contribute to a higher density of nanowires. A local dip at 368 nm represents the characteristics of the ZnO band gap. A loss of 30% transmission in the visible spectrum is attributed to enhanced photon-nanowire interaction and photon trapping phenomenon observed in nanowire arrays. The inset shows the optical images of the glass samples after the synthesis process.

holes that are trapped by the adsorbed O₂ through the surface electron–hole recombination. The photo-excited unpaired electrons increase the conductivity due to their increased lifetime.

Comparing Figures 4(a) with (b), we see that while under vacuum (2.4 mTorr) the relaxation time is significantly higher. Since 30 minutes was not enough to reach 10% of the minimum value (τ_rec), we approximate the recovery time, at this rate (4.94 nA/sec), to be 40 minutes. In vacuum, the photo-to-dark ratio is significantly higher. The higher photocurrent and the slower decay time under vacuum are mainly due to the reduced probability of O₂ being adsorbed onto the nanowire surface and the lack of O₂ present in the chamber. The partial oxygen pressure in 1 atm is ∼150 Torr (assuming the humidity in air is 35%). Upon UV illumination, the current rises by 1% in air and 79% under vacuum but both the rise and decay rate are faster when compared to measurements done in vacuum. These properties have been well understood and have been attributed to carrier trapping and band bending. The average current before UV illumination...
(base current) at ambient conditions was measured over a period of 600 seconds and was found to be 1.78 nA for a constant bias of $V = 2 \text{ V}$.

### 3.2. Space Charge Limited Current Transport

To understand the non-linear $I$–$V$ behavior observed while in room ambient conditions, we examine the current decay over time after UV exposure. ZnO is known to be a wide band-gap material which has high charge carrier mobility in the bulk and is heavily intrinsically n-doped. Since these ZnO nanowires were grown on glass, understanding the electrical transport through the $n^+$/insulator$/n^+$ ($n-i-n$) interface is necessary. Semiconductors experience space charge limited current (SCLC) if the number of carriers injected into the sample is more than the number of traps or defects inherent in the material. The electric field applied to the sample becomes non-uniform, and the current no longer follows Ohm’s law. In Figure 5, we plot $I/V$ versus $V$ to determine that SCLC transport is the dominant current transport mechanism present in these ZnO nanowires. We attribute this SCLC behavior to charge traps that are readily incorporated during the growth and due to the $n-i-n$ interface.21–23 From Figure 5(b), the $I/V$–$V$ characteristics show that the ZnO nanowires undergo a transition from the recombination and generation current at low bias voltages to the space-charge-limited current at higher bias voltages.22 We observe a transition from Ohmic to SCLC between low and high biases. The separation between the Ohmic transport (before the indicated circles) and the observed SCLC transport (after the indicated circles) is shown in Figure 5(b).

To further understand the relationship between current and voltage we examine the Ohmic and SCLC regions in detail. We use the coefficient of determination ($R^2$) to see the relationship between current and voltage in both the regions. As shown in Figure 6, the agreement with

![Fig. 5.](image)

(a) $I$–$V$ curves for ZnO nanowires to examine current decay over ten minutes with two minute intervals after UV exposure. We find the conductivity relaxation rate to be 0.15 $\mu$A/min. (b) $I/V$ versus $V$ plot to observe the Ohmic and SCLC transport present in these ZnO nanowires. The transition voltage from Ohmic to SCLC decreases by 0.1 V every two minutes from $V_{\text{trans}} = 1 \text{ V}$ at zero minutes and $V_{\text{trans}} = 1.4 \text{ V}$ at 10 minutes. This transition voltage at each two minute interval is indicated by the circles.

![Fig. 6.](image)

(a) $I$–$V$ curves for the ohmic region of electrical transport. The $R^2$ values show the Ohmic relationship before transition voltage ($V_{\text{trans}}$). (b) $I$–$V$ curves for the SCLC region of electrical transport. Even higher $R^2$ values are observed in the SCLC region. The respective transition voltage from Ohmic to SCLC from zero minutes to ten minutes in two minute intervals are $V_{\text{trans}} = 1, 1.1, 1.3, 1.2, 1.2, 1.4 \text{ V}$ respectively.
3.3. Gas Adsorption

On the surface of the ZnO nanowire, there is a finite density of electron donors or acceptors. The adsorption of gas molecules from the exposed environment results in an electronic charge transfer from the semiconductor forming ionized oxygen adsorbs such as $\text{O}^-$ and $\text{O}_2^-$. The negative trended curve and the experimental data shows the correlation between current and voltage is within 0.001% error. Figures 6(a) and (b) shows the Ohmic region and SCLC region respectively.

It is interesting to note the resistance decrease over time in both the Ohmic and SCLC region, it is expected that after the electron–hole recombination process that no photo-excited carriers are present, the Ohmic conduction is the dominant transport mechanism. The $I$–$V$ characteristic of ZnO nanowires, left in ambient conditions for 24 hours after being exposed to UV light is shown in Figure 7. It can be seen that the current is drastically lower (nA range) in comparison to the UV exposed nanowires ($\mu$A range).

Fig. 7. $I$–$V$ characteristics after leaving the sample in ambient conditions for 24 hours. No SCLC current transport is observed since UV excited carries have relaxed down to base current. Although the current is drastically lower (nA range), the electrical transport through the ZnO nanowires is observed to be Ohmic. The spacer distance was kept at 500 $\mu$m.

Fig. 8. Adsorption of oxygen gas molecules under vacuum. When pressure is in the (a) nano Torr range (with a pressure rate of 0.04 pTorr/sec) has a conductance rate of 0.01 pA/sec while in the (b) micro Torr range the range of conductance increases to 1 pA/sec. (c) $I$–$V$ characteristics changing with with pressure. (d) The same is shown with UV light on. No conductance trend is observed with increase in pressure suggesting that the major contributor to conduction is UV conduction and not oxygen adsorption.
charge is generated on the surface of the nanowire which then leads to the formation of a depletion region close to the surface. This in turn reduces the conductance of the ZnO nanowire. When the nanowire is exposed to a chemical gas species, the gas interacts with the pre-adsorbed oxygen ion which then modulates the space charge region.

The rate of change in conductance at low and high pressure over time can be seen in Figures 8(a) and (b) respectively. The change in conductance at stable pressures can be observed in Figure 8(c). We find that with low pressure, the rate of adsorption is less because of the limited amount of O₂ in the chamber. At atmospheric pressure, the rate of conductance is less because of the limited current (SCLC) was observed in the nanowires in room ambient conditions, however, this non-linearity was not persistent under vacuum. We find that the sonochemical approach to growing ZnO nanowires show distinct advantages over the various other synthesis techniques.

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References and Notes

1. S. A. Geetha et al., Nanotechnology 22, 29503 (2011).
5. H. Gullapalli et al., Small 6, 1641 (2010).

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