UV and Oxygen Sensing Properties of ZnO nanowires Grown on Glass using Ultrasound

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Abstract:

Here we report on a room ambient, sonochemical process to synthesize Zinc Oxide (ZnO) nanowires for the production of a UV photodetector. To see a trend in conduction (with and without UV light) we vary temperature and pressure to understand the adsorption mechanism at the nanowire surface. The samples are characterized by scanning electron microscopy (SEM), and spectroscopy setup. The results show that even without a seeding layer of ZnO, highly uniform, dense nanowires can be grown with the use of ultrasound. UV photodetectors and gas sensors have been shown as practical applications. We observe non-linear space charge limited current (SCLC) persistent in the nanowires at room ambient conditions. We attribute this SCLC to the readily incorporated traps during the sonochemical growth.

Keywords: Space charge limited current (SCLC), Sonochemistry, Zinc oxide nanowires, UV Photodetector, Oxygen gas sensor.

Introduction:

Among the II-VI semiconductor material, ZnO has a band gap of 3.37eV and a high excitation binding energy of ~60meV. This inherent property of ZnO allow for a wide range of applications such as photo-detectors and photoconductors in the UV-visible spectral regions. The excellent transparent conducting characteristics of ZnO make it a good candidate for applications such as solar cells[1], photodetectors[2], and flexible electronics[3].

Several methods such as chemical vapor deposition (CVD)[4], sol-gel method[5], spray-pyrolysis[6], and the hydrothermal method[7] 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.[8, 9] 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 resistance dependence of these ZnO nanowires over various temperature and pressure ranges. As grown ZnO nanowires are n-type semiconductors due to the oxygen vacancies and other native defects such as interstitial Zn ions can also act as donors in the ZnO nanomaterial. Although many have reported on the measurement of photoconductivity in ZnO thin films, nanowires, and nanoparticles, we report for the first time the production of ZnO UV photodetectors using ultrasound cavitation.

Experimental:

A glass slide was cleaned with methanol, acetone and isopropanol before immersing it into an aqueous solution with equimolar concentration (0.02M) of zinc nitrate hexahydrate ($Zn(NO_3)_2•6H_2O$) and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$). The solution was sonicated for 1 hour at an intensity of $19W^{\cdot}cm^{-2}$ at 20 kHz. 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 N_2 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.

All chemical reagents used in this report were used without further purification.

Results and discussion:

ZnO nanowires were coated on the sample after the first and second coating. The transmission results are shown in figure 1. 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 allows for ZnO nanowires to be extremely effective in blocking UV rays and protecting the skin from both sun damage and the chance of developing skin cancer.[10]

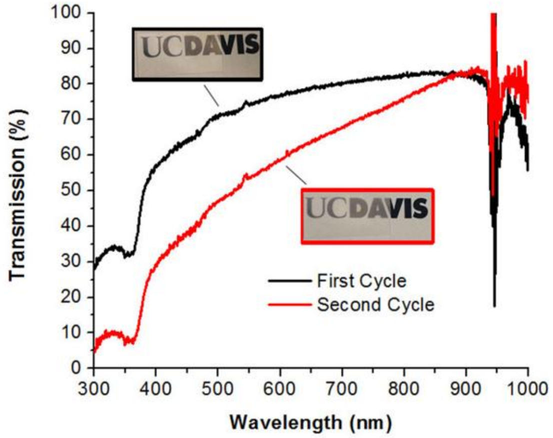

Figure 1. Transmittance spectra of ZnO nanowires grown on glass for the first and second growth cycles.

The absorbance at 368nm (corresponding to 3.37eV) is observed for the ZnO nanowires. This absorption study also revealed that the as-prepared ZnO nanowire arrays are transparent in the visible region. The inset of figure 1 shows the optical images of the glass slides that these ZnO nanowires were deposited on.

The SEM images of the nanowires are shown in figure 2. The formation of these nanowires is due to the decomposition of zinc nitrate hexahydrate ($Zn(NO_3)_2 \bullet 6H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$) in water. The chemical reaction that takes place during ultrasound excitation has been reported elsewhere.[11]

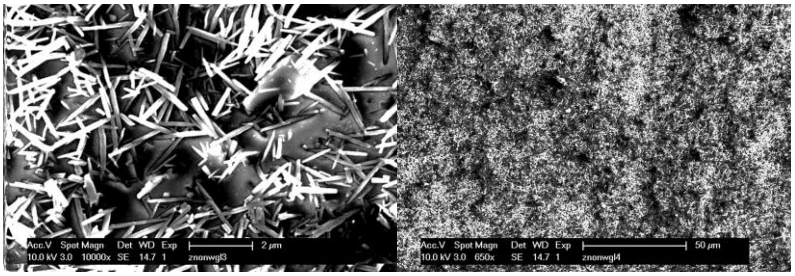

Figure 2. SEM images of ZnO nanowires grown on glass.

We find the average aspect ratio of our nanowires to be 6.5 and the average growth rate to be 600nm/hour. 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. [10] We see the change in conductivity with and without UV light in figure 3. We observe a 3 order magnitude difference between UV light on and UV light off.

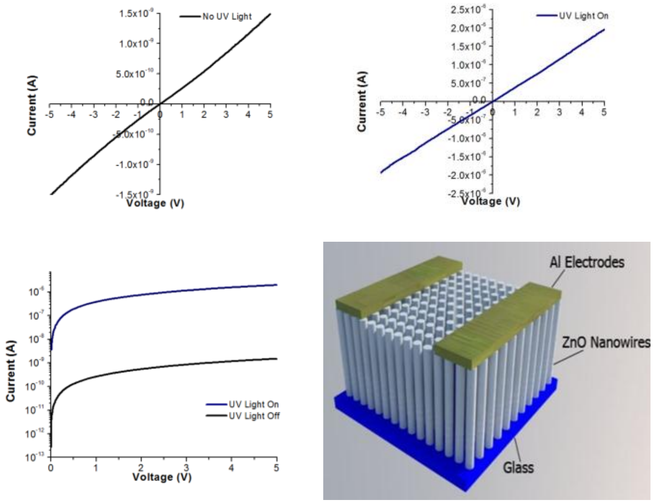

Figure 3. I-V curves for (a) ZnO nanowires without UV light (b) and with UV light on. (c) The magnitude current difference between UV illumination and dark current where current is plotted in the log scale. (d) The device schematic.

The photoconductivity in ZnO is attributed to the photo-generation of many electron-hole pairs in the material after adsorbing photons. This increases the carrier density and the conductivity of the material. Our synthesis technique shows a three order charge in conductivity and a response time (τ_{res}) of 33 seconds and a recovery time (τ_{rec}) of 244 seconds. The photo-to-dark current ratio was observed to be 89. This is significantly higher in comparison to hydrothermal UV on-off ratios.[9] The device exhibits low dark currents with a resistance of 2GΩ at a bias of 2V at standard temperature and pressure. In vacuum (2.4E-3 Torr), a constant voltage of 10V was applied to the device. As shown in figure 4, we see that upon illumination, conductivity increases. We attribute this to the photoexcited holes that are trapped by the adsorbed O_2 through the surface electron-hole recombination. The photoexcited unpaired electrons increases the conductivity due to their increased lifetime. [12]

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. The UV light was applied for at least 60 seconds as to make sure that the photochemical response reached a steady state.

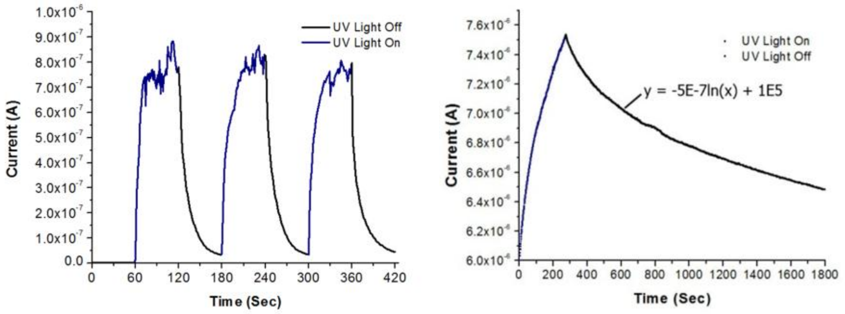

Figure 4. Current vs. Time for ZnO nanowire with (a) UV illumination every 60 seconds. A constant bias of 2 volts was applied. (b) UV light in vacuum. For measurements at standard pressure, 10 volts was applied at a pressure of 2.4E-3 Torr.

Comparing figure 4a with 4b, we see that while under vacuum (2.4E-4 Torr) 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 (-5E-7A/sec), to be 40 minutes. In vacuum, the photo-to-dark ratio is significantly higher. The growth decay is observed to be slower due to the smaller amount of O_2 present in the chamber.

To understand the non-linear I-V behavior observed while in room ambient conditions, we examine the current decay over time after UV exposure. In figure 5, we plot I/V vs. V to determine if space charge limited current (SCLC) transport is the dominant current mechanism present in these ZnO nanowires. We attribute this SCLC behavior to charge traps that are readily incorporated during the growth. [13] From figure 5b, 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. We observe a transition from Ohmic to SCLC between low and high biases. From |2V|, we observe the Ohmic transport (region I), while from |2-5V| observe SCLC transport (region II).[13, 14]

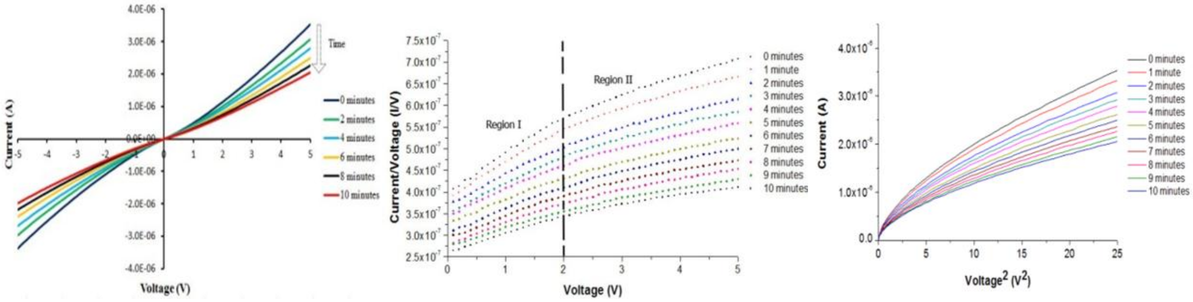

Figure 5. (a) I-V curves for ZnO nanowires to examine current decay over time after UV exposure. (b) I/V vs. V plot to observe the Ohmic and SCLC transport present in these ZnO nanowires. (c) I vs. V^2 plot to show the prodiminet SCLC at higher voltages.

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 O^- and O_2^-. The negative charge is generated on the surface of the nanowire (figure 6a) which then leads to the formation of a depletion region close to the surface (figure 6b). This in turn reduces the conductance of the ZnO nanowire. When the nanowire is exposed to a chemical gas species (figure 6c), the gas interacts with the pre-adsorbed oxygen ion which then modulates the space charge region.

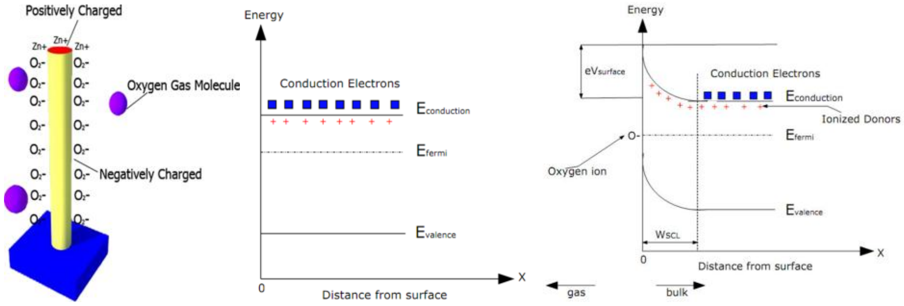

Figure 6. ZnO nanowire based (a) adsorbtion schematic. (b) The band diagram before ZnO is exposed to any gas species. (c) The band diagram of the adsorbtion process taking place when exposed to oxygen.

We find that with low pressure, the rate of adsorption is less because of the finite ammount of O_2 in the chamber. At a pressure increase rate of 4E-10 Torr/sec, we see the conductance rate is 1E-14A/sec. The rate of conductance increase to 1E-12A/sec at a pressure rate of 3E-8Torr/sec. The rate of change in conudctance at low and high pressure over time can be seen in figure 8a and 8b respectively. The change in coductance at stable pressusres can be observed in figure 8c. We find that when ZnO nanowires are exposed to UV light (figure 8d) the rate of conductance is independent of pressure change and mainly dependent on time.

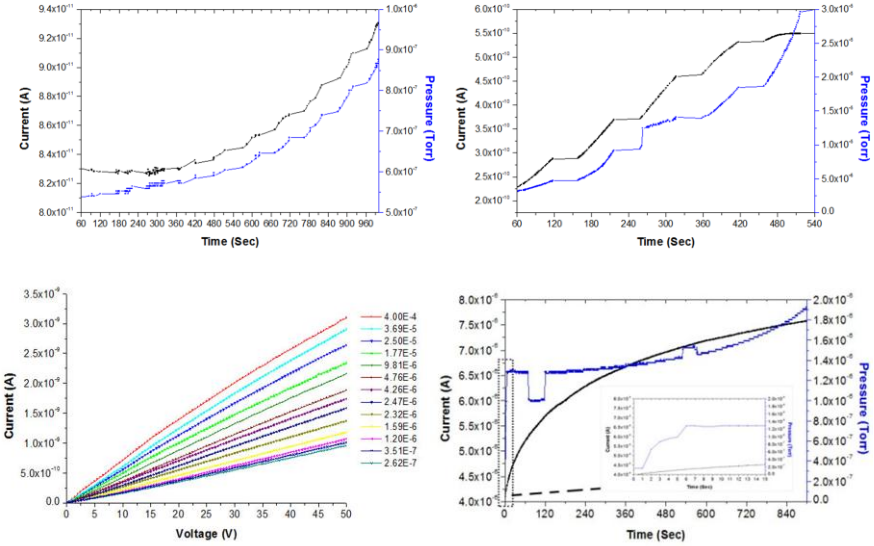

Figure 8. Adsorption of oxygen gas molecules in air under vaccum. When pressure is in the (a) E-7 Torr range and in the (b) E-5 Torr range. (c) We see thatshow that the conductivity is decreasing with pressure. (d) The same is shown with UV light on.

The initial change in pressure (shown in the inset of figure 8d) within the first 6 seconds is due to the high energy photons from the UV source. These high energy photons cause molecules to move rapidly and as a result the pressure inside the chamber increase. Even after the first 6 seconds, we do not observe a relationship between pressure and current. This is a good indication that UV enhanced photo-conductivity is the dominant contributer to increasing conductivity and not O_2 molecules adsorbing onto the surface of the ZnO nanowires. It is also known that a high-energy UV irradiation (>3.2eV) can easily break the oxygen bonds on the surface of the nanowires. The UV radiation also causes the generated holes to migrate toward the surface of the nanowire t react to the charged O_2 molecules and escape them from the surface of the nanowires. This generation of the extra electron helps increase the conductivity of the nanowires.[15]

Resistance characteristics also vary with substrate temperature as shown in Figure 9. With increasing temperature we see that the current flowing through the ZnO nanowires also increases therefore decreasing resistance.

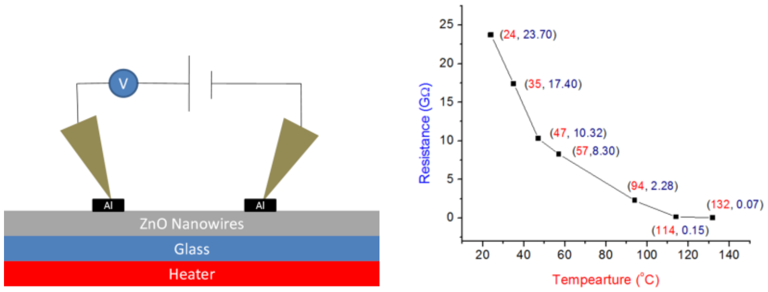

Figure 9. (a) Probing schematic for testing ZnO nanowires with variation in temperature. (b) ZnO resistnace dependence over temperature at a constant bias of 10V.

The current is increased due to thermal activation energy which is given by $I=I_0exp(-E_a/kTd)$. Where Ea is the activation energy, k is boltzmann's constant, and T is the absolute measurement temperature. The resistance decreased by four orders of magnitude with higher temperature. This shows that there is good agreement with typical resistance-temperature curves for ZnO nanowires used for gas sensing. [16]

Conclusion:

Here we have reported on a sonochemical method for growing ZnO nanowires for UV and gas sensing. The adsorption process of oxygen and the electron-hole pair generation from UV high energy photons have also been studied. We conclude that UV enhanced photo-conductivity is the dominant contributer to increasing conductivity while in vacuum since no trend in adspoption is observed. It was found that the rate of conductance was proportional to the rate of pressure increase when no UV immumination was present. Non-linear space charge limited current (SCLC) was observed in the nanowires in room ambient conditions. This non-linearity was not persistent under vacuum. Temperature was also varied to examine the change in resistance over different temperatures for future high sensitive gas sensitive applications.

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