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Anomalous Electrical Response in Ethanol-Adsorbed Zinc Oxide Thin Films Under Visible Light*

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***Abstract*— In this paper we report a unique electrical response of ethanol-adsorbed ZnO films subjected to a constant potential difference. Current measurements were obtained in both dark and illuminated conditions. A significant delay in achieving saturation current was observed indicating a nonlinear and time varying effective resistance; a time-dependent equation describing this behavior was developed, allowing the calculation of a time constant for the transition regime. To determine the role of the surface properties in this behavior, microwave plasma was used to etch the ZnO film by varying degrees, resulting in an enhancement of the resistance switching for extended etching times.**

I. Introduction

ZnO is well known for a myriad of applications ranging from ecofriendly cosmetic sunscreens [1] to solar cells [2], FETs [3], LEDs [4], UV photodetectors [5], and low cost and stable gas and bio sensors [6] to name a few. Its wide band gap (~3.37 eV) and large exciton binding energy (60 meV) makes it susceptible to electromagnetic radiation in the UV range (~368 nm). In a recent paper it has been reported that a flexible thin film of ZnO nanoparticles can undergo significant changes in resistivity when exposed to ethanol gas and illuminated by monochromatic UV radiation (wavelength 370nm) [7]. Some research has also indicated that ZnO can be used as an ethanol sensor in dark conditions, but only at elevated temperature. Several models have tried to explain the change in electrical resistance of ZnO in these conditions, with a particular emphasis on the role of ZnO nanostructures [8]. The most acceptable model so far proposes that the resistance change is an artifact of the absorbance of oxygen molecules onto the ZnO surface [9]. ZnO exhibits the properties of an n-type semiconductor, whose origin is still under considerable debate [10], so the adsorption of oxygen molecules in this case may trap free conduction band (CB) electrons on the ZnO surface, thus reducing the mobility of electrons and increasing the resistance of the sample. If ethanol vapor is introduced it knocks out surface oxygen molecules resulting in the release of trapped electrons into the conduction band and yielding an increase in conductivity. However, because of the large adsorption energy of the oxygen ions (-0.35 eV), the surface adsorbed O_2^- is thermally stable and can be difficult to remove from the ZnO surface at room temperature [11]. Thus effective ethanol sensing using metal oxides occurs at significantly higher temperatures (~ 250°C) than room temperature [12]. Here we report a remarkable effect of visible light on ethanol-adsorbed ZnO thin films, which results in an order of magnitude drop of resistance contrary to some of the earlier hypothesis and models. Moreover, a significant time delay in the transition between the high resistance and low resistance states on the order of minutes is described, which indicates a complex mode of electron transport in the thin film. Finally, the effect of ZnO surface properties and adsorbed molecules on the transition process is investigated by plasma etching and by varying the frequency of incident light.

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II. Procedure

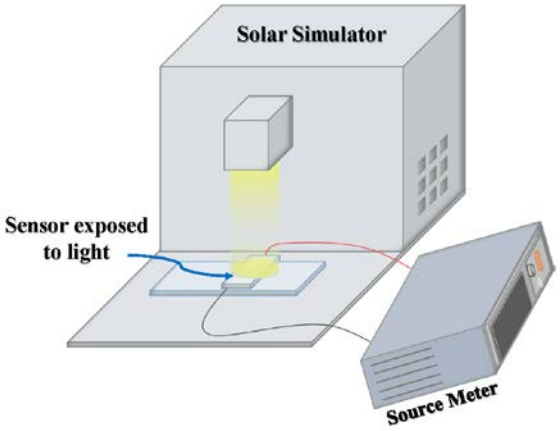

Figure 1: Apparatus for measuring the photo-resistive property of ethanol adsorbed ZnO thin films consisting of a solar simulator and source meter.

A. ZnO Thin Film Preparation

Sensors were fabricated by depositing an 8mm wide strip of zinc oxide powder (Sigma Aldrich) from a suspension in acetic acid (1% v/v) and ethanol (67% v/v) in water on a glass substrate using the doctor's blade method. The substrate coated with the ZnO film was then annealed in air by ramping the temperature from room temperature to 500°C over 7 minutes. Thickness of the ZnO thin films were measured by a laser displacement meter (Keyence, LK-H022). The average thickness of the resulting film was 0.7mm. Thin copper leads were connected to each end of the zinc oxide strip with a minimal amount of silver epoxy glue manufactured by Atom Adhesives (electrical resistivity 0.0001 Ω·cm). To determine the effect of surface modification, some devices were subjected to microwave plasma etching. This process is summarized in Fig. 2.

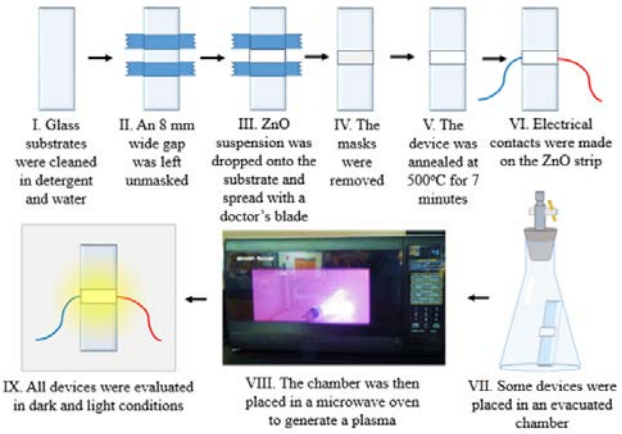

Figure 2: A six-step fabrication process was used for making the ZnO films. An optional plasma etching process is shown in steps VII and VIII.

The optical and electronic properties of the ZnO films were determined using a solar simulator at 1 Sun intensity (Abet Technologies, model 10500) and a Keithley SourceMeter (SMU 2450). A constant voltage of +20 V was applied across the film as resistance or current was measured as a function of time or incident light frequency.

III. RESULTS

A. Current response in dark and illuminated conditions

Initially, the resistance of the film was measured in darkness for ~200s. The sensor was then illuminated to record the time-dependent current response curve in Fig. 3. Approximately 600s were required for the current to saturate, indicating a significant delay in the movement of the charge carriers under constant voltage. When the light was turned off, current did not return to its initial value instantaneously, but instead a delayed transition was observed again pointing towards a similar damping of charge carriers as seen in the illuminated transition regime.

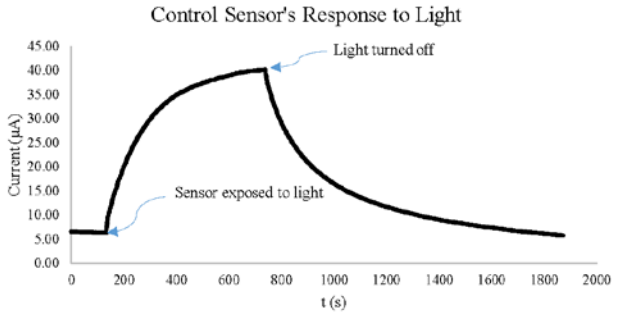

Figure 3: Current response of ethanol adsorbed ZnO thin films in dark and illuminated conditions.

To investigate the time-dependent nature of these transition regimes, the following equation was used for the current decay after the device was removed from the light:

$$I_0 - I_{dark} = I_0 e^{-\frac{t}{\tau}} \quad (1)$$

where I_0 is the saturation current under the illuminated conditions and τ is the time constant of decay.

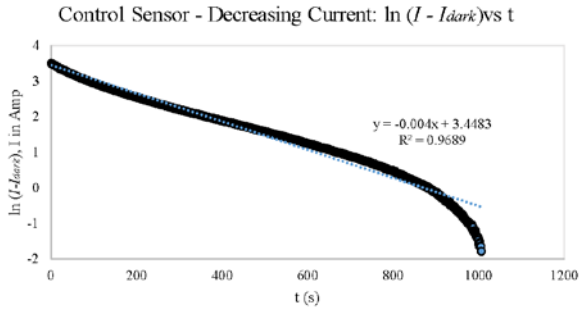

Figure 4: A plot of ln (I - I_{dark}) vs time was used to calculate the time constant from the current decay curve.

To calculate τ we have plotted ln (I - I_{dark}) vs time in Fig. 4. τ comes out as the inverse of the slope of the fitted straight line, and in our case had a value of ~250 seconds.

B. Effect of surface modification on resistance switching

Devices were etched with a microwave-induced nitrogen plasma to determine if the resistance switching phenomena described above were the result of ZnO surface properties. Microwave plasma was generated in the following way [13]: a ZnO coated glass device was placed in a vacuum flask which was then evacuated to a pressure less than 6 Torr and placed in a conventional microwave oven. The microwave was run until a deep purple plasma was clearly visible through the microwave window. Devices were exposed to this plasma for 4, 8, and 12 s. Results in Fig. 5. show that as the etching time is increased, the current saturation value for the device increases. This effect of plasma etching indicates that the resistance switching is indeed dependent on the surface properties of the ZnO.

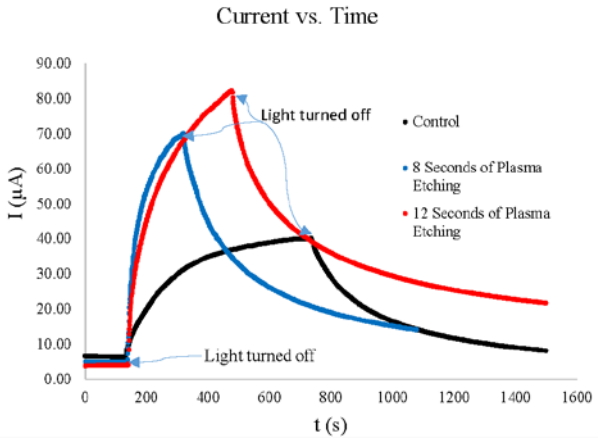

Figure 5: Current response of ethanol adsorbed plasma etched ZnO thin films in dark and illuminated conditions.

The impact of plasma etching on the surface properties of the ZnO was verified by drop analysis and can be seen in Fig. 6. A 2 μL drop of deionized water was placed on a ZnO film before and after etching. In some tests, the hydrophilicity of the ZnO film was shown to increase with plasma etching as the water droplet instantly dispersed over the etched surface but beaded on the non-etched surface.

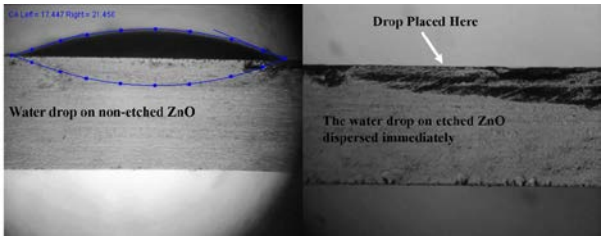

Figure 6: In this test, a 2 μL water droplet beaded on the surface of the non-etched ZnO device (left) but dispersed across the surface of the etched device (right).

In Fig 7. it is seen from FTIR analysis that plasma etching also resulted in the loss of the OH stretching band centered at ~3500 cm^{-1}, indicating that the plasma treatment changes the surface chemistry of the ZnO film by removing adsorbed alcohol and/or water molecules.

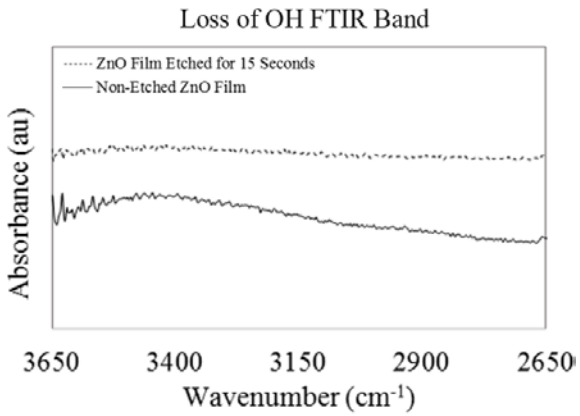

Figure 7: Loss of the OH stretching band at ~3500 cm^{-1} due to plasma etching.

C. Wavelength dependence of the photo-response

In Fig. 8 the photo-response of ethanol-adsorbed ZnO films placed under different lighting conditions is shown. Four different Wratten filters were used in this experiment: red, yellow, green and blue. Unfiltered white light from the solar simulator was used first, and then a UV filter was used to block the UV component from the white light before it passed through the Wratten filters. Thus, while the response with respect to colors were purely from visible light, a significant drop in the saturated resistance values in comparison to dark resistance value was still observed in all cases. It should be noted that red, yellow, and green filters all yielded a photo-response of similar magnitude, while blue and solar spectrum light illumination generated a larger drop in resistance. These trends held true for all time lengths of plasma etching treatment, indicating that the photo-response of these devices can be tuned simply by varying the frequency of incident light or the extent of surface modification.

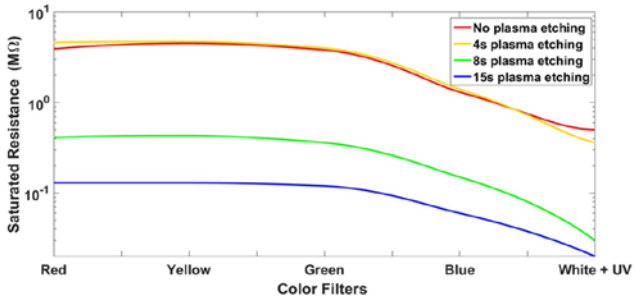

Figure 8: Minimum resistance values for ZnO films with variable plasma etching and incident light frequency

IV. Conclusion

A significant electrical response of ZnO films to visible light was observed at room temperature. The response was manifested as an order of magnitude change in resistance under a constant voltage. There was a significant time delay on the order of several minutes in the transition between high and low resistance states. An inverse transition of similar delay was observed when the sensor was removed from the light. We hypothesize that, based on the impact of plasma-based surface modification shown by drop analysis and FTIR experiments, electronegative molecules adsorbed on the surface of the ZnO layer withdraw CB electrons resulting in the high resistivity of ZnO in dark conditions. We propose that when light with sufficiently high energy is incident on the ZnO film, the surface-bound electronegative molecules are desorbed, releasing electrons back into the ZnO CB in the process. This hypothesis is reinforced by the use of incident light of different frequencies on the ZnO surface wherein low energy red, green, and yellow light resulted in only a small change in resistance, whereas high energy blue and solar spectrum light yielded a large drop in resistance. We propose that the time delay observed in the transition region is the result of the returning electrons interacting with the free electron flow in the same way that ionized impurities scatter and damp the flow of electrons under a constant potential difference. Once the electrons reach a terminal velocity, a saturation current is obtained in the illuminated conditions. When the light is turned off, ambient oxygen readsorbs to the ZnO surface, again trapping electrons from the CB. This causes electron-electron scattering and damping in the charge carrier flow causing delay in the current decay process as described earlier. This delay characteristic can be useful in memory devices in the future.

Appendix

Abbreviations and Acronyms

FET: Field Effect Transistor

LED: Light Emitting Diode

UV: Ultra Violet

CB: Conduction Band

Ω: Ohm

eV: Electron Volt

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