

UV-Assisted Alcohol Sensing With Zinc Oxide-Functionalized Gallium Nitride Nanowires

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Abstract—Alcohol sensors using gallium nitride (GaN) nanowires (NWs) functionalized with zinc oxide (ZnO) nanoparticles have been demonstrated. These sensors operate at room temperature, are fully recoverable, and demonstrate a response and recovery time on the order of 100 s. The sensing is assisted by UV light within the 215–400-nm band and with the intensity of 375 nW/cm² measured at 365 nm. The ability to functionalize an inactive NW surface, with analyte-specific active metal–oxide nanoparticles, makes this sensor technique suitable for fabricating multianalyte sensor arrays.

Index Terms—Chemical sensors, nanoparticles, nanoscale devices, photoconductivity, semiconductor nanostructures.

I. INTRODUCTION

NANOWIRE (NW) and other nanostructure-based devices are widely used for sensing applications because of large surface area, miniature size, low power consumption, and nanomoles-per-mole (ppb) sensitivity [1]. In a chemiresistor-type NW sensor, the sensitivity and selectivity depend on the interaction of different chemical analytes with the NW surface. Constrained by the surface properties of the NW material, most NW sensors can detect only specific type of analytes. In order to make a nanosensor array for a wide range of analytes, there is a need to tune the device sensitivity and selectivity toward different chemicals.

We have used GaN NWs with relatively inactive surface properties (i.e., with no chemiresistive sensitivity to different classes of organic vapors) and functionalized them with analyte-dependent active metal–oxides. Photoconductive metal–oxide–semiconductors are attractive as a functionalizing material due to their active surface properties and possible

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UV-assisted sensing operation as explained later. In this letter, we show the selective sensing of alcohols with GaN NW devices functionalized with ZnO nanoparticles. In our earlier work, we have shown selective sensing of benzene-containing molecules using hybrid GaN NW/TiO₂ nanoparticle sensor [2] and selective sensing of alcohols using GaN NW/SnO₂ nanoparticle sensor [3].

Unlike most metal–oxide–based sensors that operate at high temperatures, the photoconductive GaN NW/ZnO nanoparticle hybrid sensor enables UV-light-assisted sensing at room temperature. It has been shown that UV light for photoconductive materials may have a similar effect on the device sensing characteristics as does the elevated temperature for traditional oxide sensors [4]. However, temperature-assisted sensing requires an integrated heater for the device. Additionally, light-assisted sensing allows sensitivity modulation as demonstrated in [5].

II. EXPERIMENT

A. Fabrication

Si-doped *c*-axis n-type GaN NWs were grown using catalyst-free molecular beam epitaxy on Si (111) substrate as described in [6]. The NW diameter and length are in the ranges of 250–350 nm and 21–23 μm, respectively.

The GaN NWs were detached from the substrate by sonication in isopropanol and dielectrophoretically aligned across the prepatterned electrodes. The electrodes were fabricated using photolithography followed by deposition of a metal stack of Ti (40 nm)/Al (420 nm)/Ti (40 nm). Thick bottom electrodes ensure the free suspension of the NWs. For the formation of ohmic contacts to the NW ends, the top metal contacts were fabricated using a metal stack of Ti (70 nm)/Al (70 nm)/Ti (40 nm)/Au (40 nm) as described in [7]. Rapid thermal anneal (RTA) was performed at 700 °C for 30 s in argon atmosphere to promote the formation of ohmic contacts and to reduce the stress in the thick bottom electrodes. Finally, the ZnO nanoparticles were sputter deposited on the NW device with an RF power of 300 W in 60 standard cubic centimeters per minute (sccm) of oxygen and 40 sccm of argon gas flow at room temperature. Deposition time of 160 s was found to be optimal for the formation of uncoalesced oxide nanoparticles.

B. Characterization

The microstructure of the devices was characterized using a scanning electron microscope (SEM) and X-ray diffraction (XRD). Due to the small size of the nanoparticles, the XRD signal from ZnO was not detected. Thus, the analysis was

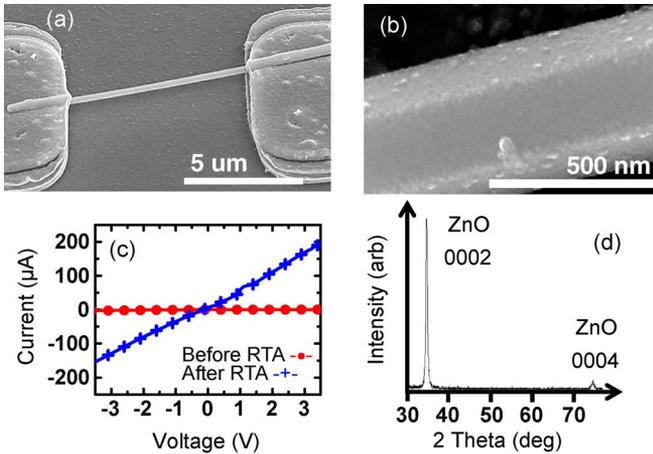


Fig. 1. (a) SEM image of the NW bridge structure. (b) ZnO nanoparticles on the facets of GaN NW. (c) I - V characteristics of the device before and after RTA. (d) XRD Ω - 2Θ scan of a 300-nm-thick ZnO film.

performed on a 300-nm-thick ZnO film sputter deposited on Si (111) substrate with the assumption that the ZnO crystallinity is similar for nanoparticles and for thin films deposited at the identical conditions. Current-voltage characteristics of the devices were also measured to determine the nature of the NW-metal contacts.

C. Sensor Measurement Setup

For the gas sensing measurements, a device was placed inside the stainless steel chamber with an inlet and an outlet for the analyte vapors. The chamber, with a volume of 0.73 cm³, has a quartz window on the top to facilitate exposure of the device to UV light. The wavelength of the light bulb was confined to the range of 215–400 nm; the intensity recorded at 365 nm was 3.75 nW/cm². The sensor baseline was established at a constant flow of 40 sccm of breathing air under illumination. For sensing experiments, 40 sccm of the mixture of the breathing air and analyte vapor was passed through the chamber. All sensing measurements were performed in the presence of UV light and 5-V dc voltage bias applied across the device terminals. Negligible or no chemiresistive response was observed for all the chemicals in the absence of the illumination.

III. RESULTS

A. Structural and Electrical Properties

Fig. 1(a) shows a SEM image of a device with a single GaN NW suspended across the metal electrodes. Fig. 1(b) shows the ZnO nanoparticles on the facets of a GaN NW. The current-voltage characteristics of the device measured before and after RTA are shown in Fig. 1(c). As shown in Fig. 1(d), XRD reveals that the sputter-deposited ZnO is crystalline and highly (0002) textured.

B. Sensor Response to Air and Nitrogen

Fig. 2(a) shows the device response to the different flow rates of breathing air. As seen from the figure, device conductance

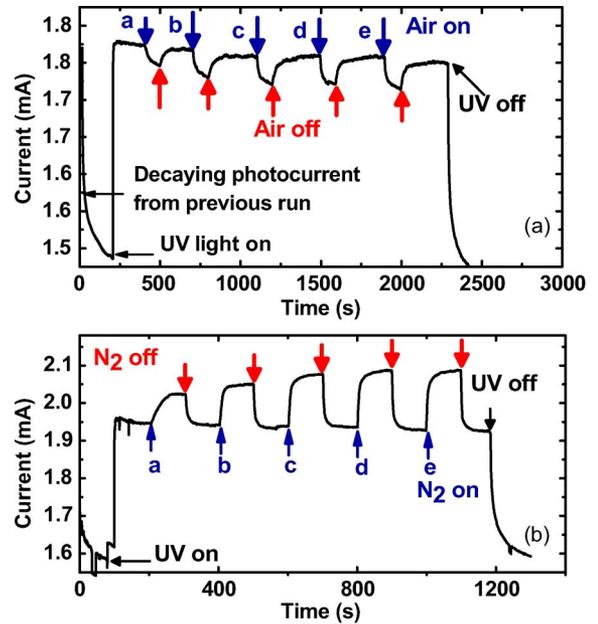


Fig. 2. Device response to different flow rates of (a) breathing air and (b) nitrogen gas. The flow rates of the gas are denoted as $a = 20$ sccm, $b = 40$ sccm, $c = 60$ sccm, $d = 80$ sccm, and $e = 100$ sccm.

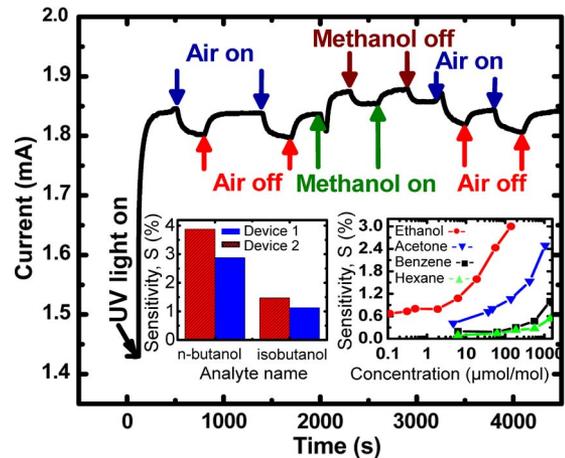


Fig. 3. Device response to 500- μ mol/mol (ppm) of methanol. (Bottom left) Inset shows the sensitivity of two devices toward 500 μ mol/mol (ppm) of each isomer of butanol. (Bottom right) Inset shows the response to ethanol, acetone, benzene, and hexane. Sensitivity S is given by $(I_g - I_a) \times 100 / I_a$, where I_g is the device current in the presence of an analyte in breathing air and I_a is the current in pure breathing air, both measured 300 s after the flow is turned on. Percentage standard deviation of the device sensitivity is 3.2% based on the five data points collected over the period of 3 days in response to the breathing air.

decreases upon exposure to the breathing air, and the decrease is proportional to the flow rate. Opposite behavior, i.e., an increase in conductivity, is observed when the device is exposed to nitrogen gas as seen in Fig. 2(b).

C. Sensor Response to Alcohols and Other Analytes

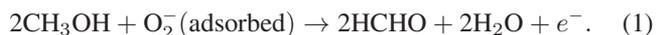
When exposed to alcohol vapors (methanol, ethanol, n -propanol, isopropanol, n -butanol, and isobutanol), the devices show an increase in conductivity with maximum sensitivity toward methanol. Fig. 3 shows the device response to 500- μ mol/mol (ppm) methanol vapor in breathing air.

For the isomers of an alcohol, the sensitivity decreases with branching in the carbon chain. Hence, as shown in Fig. 3 (inset, bottom left), the sensitivity toward isobutanol is less than that toward *n*-butanol. As shown in Fig. 3 (inset, bottom right), the devices show a negligible response to possible interfering chemicals such as benzene and hexane, whereas the sensitivity toward 100 $\mu\text{mol/mol}$ (ppm) of ethanol is similar to the sensitivity toward 1000 $\mu\text{mol/mol}$ (ppm) of acetone. Ethanol vapor concentration down to 100 nmol/mol (ppb) has been successfully detected, and the detection of even lower concentrations is only limited by our measurement setup.

IV. DISCUSSION

The response mechanism of the GaN NW/metal–oxide nanoparticle hybrid sensor has been discussed in detail in [3]. The conductivity model of GaN NW comprises of a conducting channel surrounded by a surface depletion region, where modulation in the width of the depletion region induces a change in the conductivity of the NW. Similarly, ZnO nanoparticles have a surface depletion layer, which enhances upon exposure to air due to electron capture by surface-adsorbed oxygen. When UV light is turned on, the photogenerated holes in ZnO assist in removing the adsorbed oxygen, thus releasing the electrons captured by surface oxygen back into ZnO. We speculate that the photoinduced excess of electrons in the ZnO nanoparticles promotes photogenerated charge separation in the GaN NW, resulting in increased conductivity. Conversely, there is a reduction in the number of free electrons in the ZnO nanoparticles when exposed to air, leading to a reduced conductivity. As seen in Fig. 1(a), this effect increases with increasing flow rate of air due to enhanced coverage of the device surface with adsorbed oxygen.

The device response to alcohols is explained from the following generic reaction occurring on the surface of ZnO:



As observed from Fig. 3, the exposure to alcohol vapors leads to increased device conductivity due to the removal of adsorbed oxygen. In the case of exposure to N_2 , although there is no

surface reaction, N_2 assists in desorption of the oxygen, thus restoring the conductivity as shown in Fig. 2(b).

V. CONCLUSION

We have fabricated hybrid GaN NW/ZnO nanoparticle devices for UV-assisted alcohol sensing at room temperature. These devices are a suitable candidate for making nanosensor arrays because of their tunable selectivity, ability to detect the ppb level of analytes, and fast response and recovery time.

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