Zinc oxide optical and chemical sensors fabricated by inkjet printing and drop casting

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ABSTRACT

Nanoparticle solutions can be tailor-made to sense different wavelengths of light or the presense of various chemicals, and are promising for next generation sensors. But these "inks" are incompatible with traditional manufacturing techniques, so consistent fabrication remains a challenge. Drop casting and inkjet printing are promising techniques for large scale, cost effective fabrication of nanoparticle sensors. To explore these processes, zinc oxide (ZnO) coatings were drop cast and printed onto pre-patterened substrates to form photo-resistive and chemo-resistive devices. The devices were tested for sensitivity to ultraviolet (UV) light and H_2, N_2, and NH_3 gasses. The drop cast devices were found to be sensitive to all four stimuli and appeared to show chemical selectivity. The inkjet devices were found to be sensitive to UV light and showed good uniformity over 1 cm^2 devices. The inkjet devices were less chemically sensitive than the drop cast devices due to device design. Some critical characteristics for improved performance are identified and discussed.

Keywords: zinc oxide, inkjet printing, gas sensor, UV sensor

1 INTRODUCTION

The unique optical, electrical, and mechanical properites of zinc oxide (ZnO) nanostructures show great promise for a variety of applications, including next generation ultraviolet (UV) photodetectors [1], chemical sensors [2] and pressure sensors [3]. Zinc oxide has a direct bandgap (3.4 eV), high electron mobility, and environmental stability. When fabricated as a nanostructure, such as a quantum dot or nanoparticle, the large surface to volume ratio and large active area improve optical absorption and chemical sensitivity. Nanoparticles of ZnO can also be placed in solution, enabling simple fabrication methods such as drop casting and inkjet printing. Drop casting and inkjet printing offer a number of advantages over traditional thin film fabrication of bulk ZnO, such as low cost, high volume manufacturing [4], monolithic integration with CMOS devices, creation of unique device shapes, the ability to deposit on various substrates (e.g. silicon, quartz, plastic), and the ability to create multi-functional devices by depositing different materials side by side. In this paper we investigate drop casting and inkjet printing as low cost, versatile, and repeatable fabrication processes for optical and chemical sensing devices.

2 EXPERIMENTAL

In this study, we investigated the optical and chemical response of resistive sensors made by either drop casting or inkjet printing ZnO coatings [5]. For the drop cast devices, 50 nm thick Au electrodes were evaporated onto an oxidized Si chip, graphene flakes were transferred onto the Au electrodes, then ZnO nanoparticles were drop cast upon the electrodes (**Fig. 1(a)**). The graphene interlayer was used to promote charge transfer between the ZnO and Au electrodes. Bond pads were created on the chip using In metal, and Au wires were soldered to an 8 pin prototype chip carrier. For the inkjet printed devices, 1 um thick interdigitated Au electrodes of various lengths were patterned onto a thermally oxidized Si wafer using standard photolithography and patterning processes (**Fig. 1(b)**). ZnO coatings were prepared by inkjet printing a zinc acetate precursor directly onto the electrodes using a Sonoplot printer and then annealing the chip to form ZnO. The chips were then placed into a standard quadflat package for testing. For both types of devices, the photoresponse was determined by measuring the current change while biasing the devices to 5 V in a two-point configuration and illuminating the drop cast and printed devices with 340 nm UV light at 10 μW and 100 mW, respectively. Chemical testing was conducted with the same biasing conditions but with the device placed in a vacuum chamber. H_2, N_2, and NH_3 were then bled into the chamber to various pressures.

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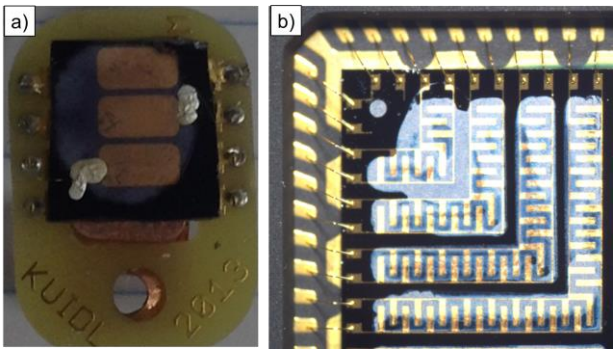

Figure 1: Images of drop cast ZnO devices (a) and inkjet printed ZnO devices (b).

3 RESULTS

3.1 Drop Cast Samples

The devices produced by drop casting showed a strong response to UV illumination of 10 μW. **Fig. 2** shows the dynamic response of one device as a UV light is turned on and off. The dark current was on the order of 10 μA and the response current exceeded 120 μA. The rise and fall times are both ~20 seconds.

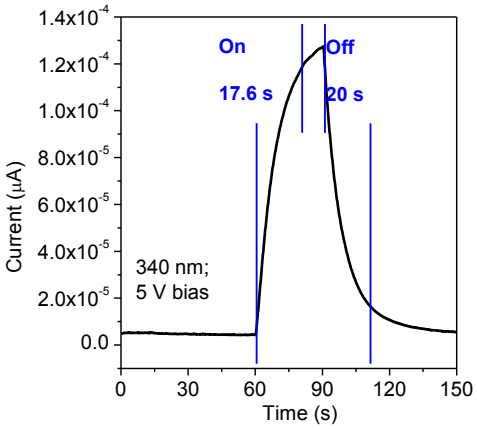

Figure 2: Dynamic response to UV exposure of drop cast ZnO device.

Additional chemical testing was performed on three separate drop cast devices, including measuring their responses to H_2, N_2, (**Fig. 3**) and NH_3 (**Fig. 4** and **Fig. 5**). The response to gasses was not as significant as the response to UV and occured on much longer time scales. Furthermore, we note a large sample-to-sample variation in electrical characteristics, and we attribute this to a difficult to control fabrication process. However, the responses to different chemical species was distinct in magnitude, as shown by **Fig. 3.** These data were collected from the same sample and show clearly distinct responses; the current increaseed by 0.7% for H_2 up to 50 Torr but only 0.3% for N_2 up to 400 Torr. The response to NH_3, shown in **Fig. 4**, is further evidence of selectivity, with the current increasing by 28% up to 20 mTorr. However sample-to-sample variation may account for the difference in scale between **Fig. 4** and **Fig. 5**.

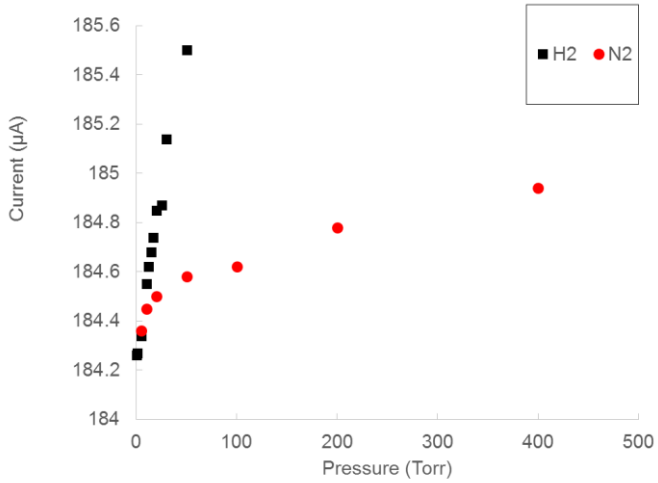

Figure 3: Current versus pressure for drop cast ZnO devices exposed to H_2 (squares) and N_2 (circles).

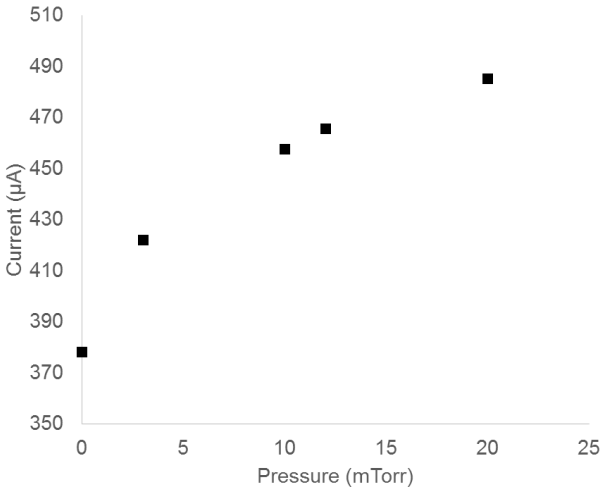

Figure 4: Current versus pressure response for drop cast ZnO devices exposed to NH_3.

Fig. 5 shows the dynamic response of a third sample exposed to 10 Torr (left) and 20 Torr (right) of NH_3. The response increased with increasing pressure, but the rise and fall times were similar at approximately 5 minutes.

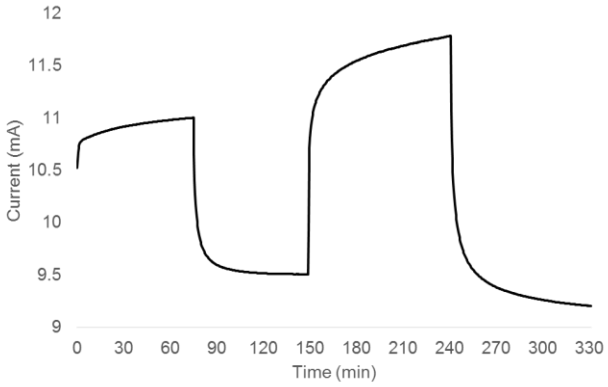

Figure 5: Dynamic response of the drop cast ZnO device to 10 Torr (first peak) and 20 Torr (second peak) of NH_3.

From these data, we speculate that H_2 sensing is dominated by charge carrier generation and transfer as H_2 molecules absorb and disassociate to –OH on the ZnO surface. We further speculate that the response to N_2 is dominated by the piezoelectricity of ZnO, where the material compresses under pressure, reducing its resistance. The response to NH_3 may therefore be a combination of the two mechanisms. Further experiments are planned to explore this speculation.

3.2 Inkjet Printed Samples

Two devices produced by inkjet printing were tested for their response to UV light under similar conditions as the drop cast devices, but at higher UV power. Each device has three active quadrants with four different resistor lengths each. The printing was done one quadrant at a time. The dark and response currents were measured for each device, and the corresponding data was normalized to the size of the device, averaged over the quadrant, and presented in **Table 1**. We note again a large sample-to-sample variation evident in the dark current and attribute the difference to a difficult to control fabrication process. Despite this, the response current for all devices was ~1 mA/cm^2, and the on/off ratios were adequate for sensing applications.

Table 1: Electrical measurement data for printed ZnO devices exposed to UV light.

Sample/ Quadrant	Dark Current (A/cm^2)	On Current (A/cm^2)	On/Off ratio
1/1	1.94E-05	6.54E-04	3.3E+01
1/2	6.18E-06	6.82E-04	1.1E+02
1/3	3.05E-05	9.20E-04	4.7E+01
2/1	7.76E-08	9.22E-04	1.2E+04
2/2	1.86E-07	1.33E-03	1.0E+04
2/3	2.92E-07	1.04E-03	4.0E+03

The dynamic response of two of the inkjet devices to 100 mW UV is shown in **Fig. 6**. The rise time of both devices was approximately 60 seconds, similar to the drop cast devices. However, the fall time was dramatically longer, on the order of minutes, and was truncated from **Fig. 6**. **Fig. 7** shows the dynamic response of one of the inkjet devices exposed to 50 Torr and 100 Torr of NH_3. Similar to the UV response, it had longer rise and fall times compared to the drop cast samples, and also required higher gas pressures to observe a measurable response.

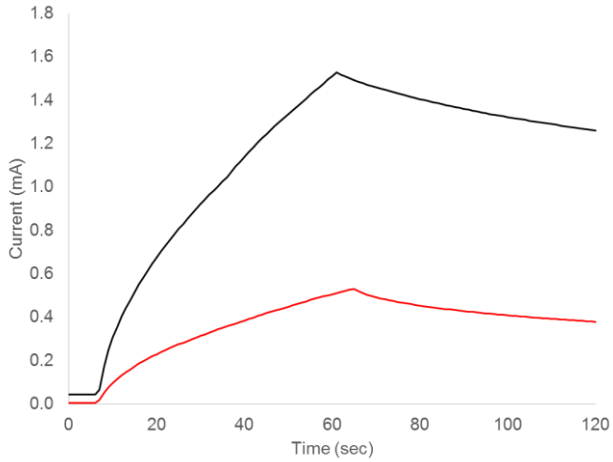

Figure 6: Dynamic response of inkjet printed ZnO devices to UV light.

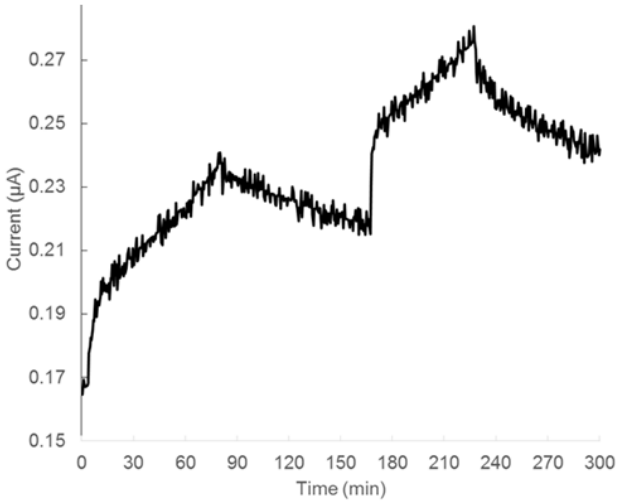

Figure 7: Dynamic response of inkjet printed ZnO devices to 50 torr (first peak) and 100 torr (second peak) of NH_3..

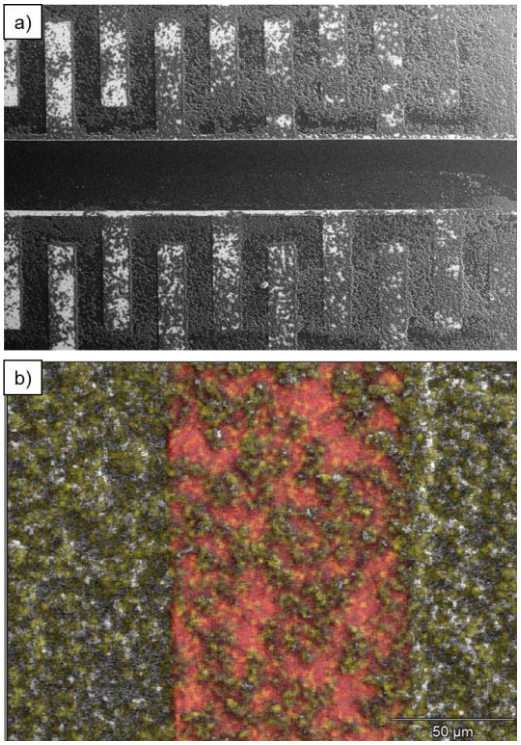

Figure 8: SEM (a) and EDS (b) of inkjet printed devices showing location of Au (red) and Zn (yellow).

Scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS) was used to study the surface morphology of the inkjet printed devices. The SEM image (**Fig. 8(a)**) shows inconsistent surface coverage of the ZnO on the Au. A higher magnification EDS map (**Fig. 8(b)**) of one of the more densely covered elecrodes again shows sparse coverage. We speculate that this poor coverage contributes to the diminished sensitivity of the inkjet devices compared to the drop cast devices, and future experiments will explore this relationship.

The preliminary results presented here show that inkjet printing is a fabrication method that could yield more uniform and repeatable optical and chemical sensor devices. Furthermore, process improvements, such as printing multiple layers on top of each other, rapid thermal annealing or ozone treatments, might improve surface morphology and coverage, leading to higher performance devices.

4 CONCLUSIONS

ZnO sensors were fabricated using two methods, drop casting onto graphene coated Au electrodes and injket printing directly onto Au electrodes. The drop cast devices responded strongly to 340 nm UV light with rise and fall times of approximately 20 seconds. Additionally, the devices were found to be sensitive to H_2, N_2, and NH_3 gasses. The inkjet printed devices were also sensitive to UV light with a reponse current density of ~1 mA/cm^2. While the inkjet devices had rise times similar to the drop cast devices, their fall times were remarkably longer. Furthermore, they were not found to be very sensitive to NH_3, though a small response was detected. We attribute the difference in performance to device design and processing conditions, particularly with the graphene interlayer used on the drop cast devices and the poor surface coverage observed in the injket printed devices. Injket printing is a viable method of mass producing ZnO based UV sensors on a variety of substrates, but further work is necessary to understand the requirements for chemical sensitivity.

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