Aluminum-doped Zinc Oxide Nanocrystals for NO_2 Detection at Low Temperature

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Abstract — **In this work, we focus on nitrogen dioxide (NO_2) detection at temperature up to 100°C in order to be compatible with most of flexible substrates. Such low temperatures require dedicated materials, as Zinc Oxide (ZnO), a widely used material for its sensing properties. Functionalization or doping is a growing research activity to improve sensor sensibility at lower gas concentrations and lower working temperatures. Aluminum-doped Zinc Oxide (Al-ZnO) has been shown as a possible way for NO_2 detection. Moreover, nanocrystals improve the gas detection due to their high surface/volume ratio. Therefore in this work, Al-ZnO nanocrystals have been deposited by drop coating from colloidal solution as sensitive layer for air quality monitoring. The platform consists of Ti/Pt interdigitated electrodes on Si/SiO_2 substrate. Herein, a brief description of the process steps will be provided. Gas sensing properties have been investigated in dark and under ultraviolet illumination at various heating excitation from room temperature around 25°C up to 100°C. These sensors present repeatable responses toward (NO_2) with fast responses for low gas concentrations as low as 0.2 ppm.**

Keywords-Gas sensor; NO_2 sensor; light excitation; Al-ZnO nanocrystals, Ultraviolet illumination.

I. INTRODUCTION

Nitrogen dioxide comes from vehicles, power plants, industrial emissions and off-road sources, such as construction, lawn and gardening equipment. It is one of the most dangerous air pollutants. It plays a major role in the formation of ozone and acid rain. Continued or frequent exposure to NO_2 concentrations higher than 150 ppb may cause incidence of acute respiratory. These concentrations are detectable by ZnO, a widely used material for its sensing properties [1]. Aluminum-doped Zinc Oxide (Al-ZnO) has been shown as a possible way for NO_2 detection as low as 20 ppm [2]. Moreover, Pr. Morante's team has reported that illuminating metal oxide gas sensors with ultraviolet (UV) light improve SnO_2 nanowires performances to NO_2 detection [3]. In this work, NO_2 detections have been made under UV illumination by Al-ZnO nanocrystals deposited on interdigitated electrodes fabricated on Si/SiO_2 substrate using photolithography. In Section II, the Al-ZnO solution process will be described and the results will be discussed in Section III.

II. DESCRIPTION OF APPROACH AND TECHNIQUES

This description is composed of two parts, one is the sensing film fabrication; the other is the measurement system set-up.

A. Al-ZnO solution

The Al-ZnO nanocrystals were obtained by a surfactant-free chemical synthesis approach using zinc acetate and aluminum isopropylate as precursors with potassium hydroxide [4]. Fig. 1 shows a typical Transmission Electron Microscopy (TEM) image of the Al-ZnO nanocrystals, evidencing their size (diameter about 10 nm) and homogeneous size and shape dispersions.

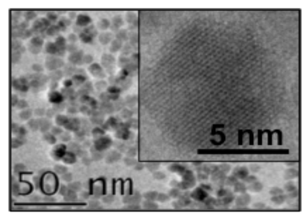

Figure 1. TEM image of AZO nanocrystals drop-casted on a TEM grid.

The Aluminum doping level of 0.8 at. % was controlled by the metal precursors ratio, and determined by inductively coupled plasma mass spectrometry (ICP-MS) analyses. The Al-ZnO nanocrystals were dispersed in isopropanol as solvent using ethanolamine as short-chain surfactant to obtain aggregate-free solution. Al-ZnO nanocrystals drop casting allows the formation of thin films with improved conductivity compared to ZnO nanocrystals reference, both with and without low temperature annealing.

B. Gas sensors

Our gas sensor consists of Ti/Pt interdigitated electrodes for gas detection. Temperature is controlled underneath up to 100°C to improve the gas detection. The metal electrodes Ti/Pt were deposited on Si/SiO_2 by magnetron sputtering with thicknesses of 5 nm and 100 nm, respectively. In this work, Al-ZnO nanocrystals were deposited by drop coating. They were used as sensitive material with a thickness of 200 nm measured by a Dektak 6M stylus profiler. The Al-ZnO films obtained were annealed for 30 min at 150°C for removing solvents and improving their quality and stability. The aim was to study the possible use, in a future work, on

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flexible substrates which do not allow temperature process higher than 150°C. In order to find the best operating conditions, the gas detections were carried out in a closed chamber by measuring the resistance through the sensitive material using UV light (λ = 325 nm) and temperature excitations (up to 100°C) under 30 s exposures to NO_2. We used a power supply to control the operating temperature, a SourceMeter Keithley 2450 for the data acquisition and one UV Light-Emitting Diode (LED) for UV illumination situated at 10 mm from the sensing material to obtained more photogenerated charge carriers.

III. Results and Discussion

The gas sensor fabricated with Al-ZnO nanoparticles as sensitive material and deposited by drop coating on Si/SiO_2 substrate is presented in Fig. 2.

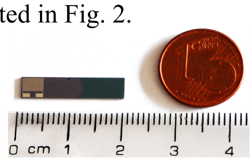

Figure 2. Sensor fabricated on Si/SiO_2 substrate.

Gas response of a gas sensor is defined by (1) as the ratio of the resistance change on the surface of the gas sensor before and after being exposed to NO_2:

$$R= R_a/R_{NO2} \quad (1)$$

where R_a is the sensor resistance through dry airflow and R_{NO2} the sensor resistance in presence of NO_2.

Detection was possible in dark at 25°C, but without coming back to the baseline (not shown here). From 75°C, the resistance returns to its reference value obtained through dry airflow. In dark, our best operating temperature has been determined at 100°C. Fig. 3 shows responses in dark for 0.2 ppm to 2 ppm of NO_2 at 100°C.

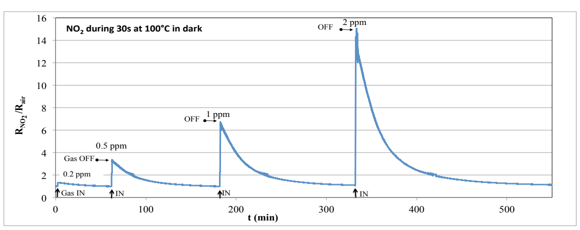

Figure 3. Sensor responses at 100°C in dark for 0.2 ppm to 2 ppm NO_2.

Oxygen vacancies on metal-oxide surfaces function as n-type donors increasing the conductivity of oxide. When Al-ZnO gets exposed to NO_2 (a typical oxidizing gas), an increase in resistance occurs due to oxygen ion adsorption from NO_2 on the surface by trapping of electrons. Under UV illumination, the interaction between NO_2 and oxide is greatly enhanced with the abundant photogenerated free electron. Similarly, UV illumination facilitates desorption of oxygen anions into neutral gaseous oxygen by providing photogenerated holes during the recovering period. Under continuous UV illumination, it was possible to detect low NO_2 concentrations at room temperature and return to the sensor resistance in dry air after stopping the gas injection. However, Fig. 4 shows that, at 25°C under UV, about 45 minutes are needed to return to the baseline.

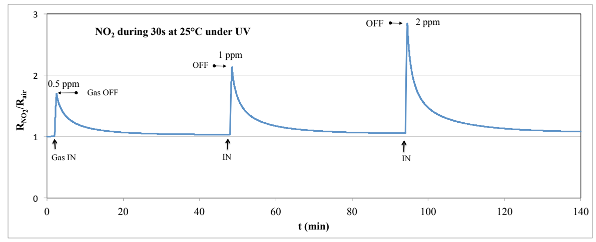

Figure 4. Sensor responses at 25°C under UV for 0.5 ppm to 2 ppm NO_2.

By increasing the temperature up to 100°C, the response amplitude is multiplied by 10 at least and the time to return to the baseline is divided by 8. Fig. 5 illustrates sensor responses at 100°C under UV light illumination for 0.2 ppm to 2 ppm of NO_2.

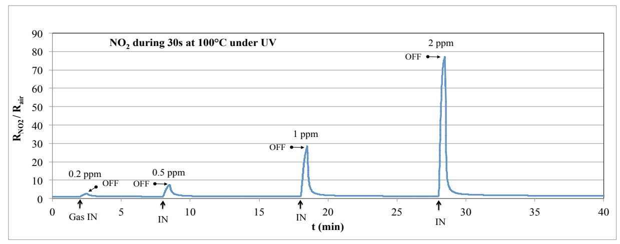

Figure 5. Sensor responses at 100°C under UV light for 0.2 to 2 ppm NO_2.

IV. Conclusion

This paper reports nitrogen dioxide (NO_2) detection at temperature up to 100°C. Room temperature NO_2 detection have been achieved by sensors on rigid substrate and improved with one UV LED illumination. The gas measurements in our experiments under UV showed good responses with fast response / return times towards NO_2 even at 0.2 ppm. The photogenerated charge carriers (electrons and holes) present important benefits for working at low temperatures. UV light illumination results in an increase in the response signal, enhanced sensing reversibility, and an enhanced recovery rate. It is open a new way to use Al-ZnO nanocrystals as sensitive layer for gas sensor devices on flexible substrates.

Acknowledgment

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