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NO_2 Gas Sensing at Room Temperature under Ultra-Violet Light of ZnO Nanocrystals

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Abstract: Nitrogen dioxide (NO_2) is a major component of the outdoor air pollution. Microsensors are interesting devices to check and to monitor this toxic oxidizing gas. Recent advances in flexible electronics, a complementary technology to the conventional rigid silicon technology, have motivated research efforts. Flexible substrates enable new applications such as wearable sensors, electronics on skin/organs as well as a possible reducing cost during the fabrication process. However, flexible substrates required low working temperature to avoid thermal degradation. This work aims to prove the possibility to use zinc oxide nanocrystals (ZnO NCs) post-annealed at low temperature as a sensitive material to detect NO_2 at low working temperature. Thus, our study has been performed on rigid substrates to check first the sensitive layer behaviour depending on the temperature. Then, to be able to reduce the working temperature, a continuous Ultra-Violet illumination has been used. We propose a NO_2 detection at room temperature by ZnO NCs deposited on rigid substrates by spin coating from colloidal solutions as sensitive layers for air quality monitoring.

Keywords: Gas Sensor, Nitrogen dioxide, Room-temperature, UV activation, ZnO nanocrystal, Environmental monitoring.

1. Introduction

Nitrogen Oxides NO_x (NO_x = NO + NO_2) are mainly produced by petrol or diesel burning engines and coil/oil furnaces [1]. NO is a poisonous, odorless, colorless gas. Once it is mixed with air, it quickly combines forming nitrogen dioxide (NO_2). NO_2 is a highly reactive chemical compound found in short-lived atmospheric trace gases with both anthropogenic and natural sources [2].

NO_2 is one of the most air pollutant kinds of NO_x species from the human health point of view. NO_2 is highly toxic, reddish brown gas with a very pungent odor [3]. It disturbs atmospheric oxidation rates [4], and participates to surface ozone production [5]. Therefore, the need for air quality checking is increasing and the development of NO_x sensitive microsensors enabling a mesh area monitoring is really attractive. The different organisms request detection under 3 ppm to protect human health [6]. Moreover, to improved comfort to users, more and more applications are developed with flexible electronics. It is an emerging technology, which complement rigid ones enabling new applications such

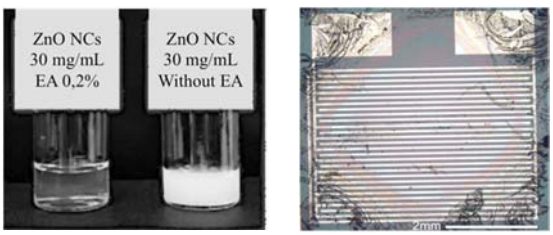
as flexible displays, printed radio frequency identification tags on packaging, sensors on skin [7-9]. These devices are expected to be lightweight, conformable, compatible with textiles, tissues, and organs [10-11]. To develop micro gas sensors on flexible substrate, the Metal OXide gas sensors (MOX) are propitious due to their high sensitivity at a low cost process. Among MOX, Zinc Oxide (ZnO) based materials have shown outstanding electrical, chemical and sensory characteristics [12]. We aimed to fabricate MOX sensors on flexible substrate to fit shapes on a smart object for NO_2 monitoring. However, most of flexible substrates do not resist to temperature higher than 120°C. Previous studies have shown detection under ozone gas as low as 35 ppb [13] and depending on filter nature, O_3 can be totally trapped while NO_2 can pass over a specific concentration range [14]. In this study, our main purpose was to point out that, using continuous Ultra-Violet (UV) light on the ZnO nanocrystals (NCs), the sensing responses at room temperature are also enhanced for NO_2 detection. In Section 2, our methodology will be summarized with the sensor fabrication and the experimental set up. Then, the results will be discussed in Section 3. We conclude the paper in Section 4.

2. Methodology

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

2.1. Device Structures

Our gas sensor consists of Ti/Pt interdigitated electrodes (5 and 100 nm, respectively) deposited on Si/SiO_2 substrates by magnetron sputtering. Fig. 1(a) shows two solutions based on ZnO NCs with a diameter of about 5 nm in isopropanol at 30 mg/mL: one named S1 without ethanolamine (EA) with a milky white aspect indicating the presence of agglomerates and the second one named S2 with EA (0.2 vol.%) with a transparent aspect [15].



(a) (b)

Fig. 1. (a) Pictures of solutions based on ZnO NCs in isopropanol at 30 mg/mL with or without 0.2 vol.% of EA. (b) Sample image with ZnO NCs with EA after a post annealing at 80 °C.

These solutions (S1 and S2) were deposited by spin coating on substrates during 30 s at 2000 rpm/min. Fig. 1(b) presents an optical images of a thin film sensor based on ZnO NCs dispersed in isopropanol with of EA as short-chain surfactant. Previous studies have shown that 0.2 % volume of EA gives aggregate-free solutions [16]. After mixing ZnO NCs with 0.2 vol.% of EA in isopropanol, the EA molecules spontaneously graft on the surface of ZnO NCs and enhance the particles solubility. The small sized NCs to form sensing thin films are beneficial for the surface-area-to-volume ratio to adsorb gas molecules. To be compatible with a flexible substrate, a low post-annealing temperature (80°C) was realized for 30 min before gas sensing measurements.

2.2. Experimental Setup

A 0.1 V DC voltage was applied to the sample while the electrical resistance was monitored using a Keithley Model 2450 SourceMeter Source Measure Unit (SMU) Instrument (Keithley, U.S.A.). It is well known that humidity interferes with ZnO nanoparticles and increases the layer conductivity. Indeed, the adsorption of water molecules on the ZnO surface led to a decrease in electrical resistance. At high temperature, it is easy to evaporate water molecules on the ZnO surface. However, at low temperature, they will stay at the sensitive layer surface and they will disturb the gas detection. To avoid these water molecules some filters have been used in the experimental set up to focus only on NO_2 detection without humidity. Dry air was used as both the reference and the carrier gas (it means no humidity RH = 0 %). A constant total flow was maintained at 500 Standard Cubic Centimeters per Minute (SCCM) via mass flow controllers to reach the NO_2 concentration in a short time (less than 30 s). In order to find the best operating conditions, the gas detections were carried out in a closed chamber under 30 s exposures to NO_2 by measuring the resistance through the sensitive material in dark and temperature excitations (up to 300°C) or using UV light (λ = 390 nm) at room temperature. We used a Light-Emitting Diode (LED - UV5TZ-390-30) fixed at 10 mm from the sensing material as continuous UV illumination to obtain more photogenerated charge carriers. The samples were illuminated during 30 minutes under dry air before the first measurement to reach a stable resistance value.

3. Result and Discussion

We prepared two different sensitive layers with resulting layer thicknesses measured by a contact profilometer Dektak XTS (Bruker, Germany) equipped with a stylus of 2 μm radius. The sensitive layer without EA deposited by spin coating is around 80 nm thick. The sensitive layer with EA realized by

spin-coating at the same speed (2000 rpm/min during 30 s) is around 50 nm. The gas response is defined in (1) as the ratio of the resistance change on the surface of the gas sensor after and before being exposed to NO_2:

$$R = R_{NO_2} / R_{dry\ air}, \quad (1)$$

where R_{NO_2} is the sensor resistance in presence of NO_2 and $R_{dry\ air}$ is the sensor resistance through dry airflow.

2.1. Temperature-dependent NO_2 Sensing Properties of ZnO Nanoparticles in Dark

As a n-type semiconductor material when ZnO is exposed to air, oxygen atoms will be adsorbed on the surface of ZnO and capture electrons from its conduction band to form oxygen ion species. A depletion layer is formed in ZnO, which causes the resistance increase. NO_2 is an oxidizing gas. Therefore, it will capture electrons, increasing the sensor's resistance. After completing the sensing response process, the sensing element can be regenerated by exposing it to dry air again, as oxygen will be adsorbed on the surface to form oxygen ions again. Generally, metal oxide based gas sensors operate at high temperatures (200-400 °C) to facilitate the chemical reaction to produce the sensor response. The gas molecules interact with the surface via Van Der Waals force. To remove these molecules, heating the substrate can provide some activation energy. To investigate the ZnO NCs sensing properties in dark, a temperature dependence study has been done. Fig. 2 presents sensor responses of thin film obtained with solution S2. The sensors were exposed 30 s to 2 ppm of NO_2 in dark for four working temperatures: 25 °C, 100 °C, 200 °C and 275 °C. Prior gas sensing measurements, the deposited thin film was post-annealed to 300 °C.

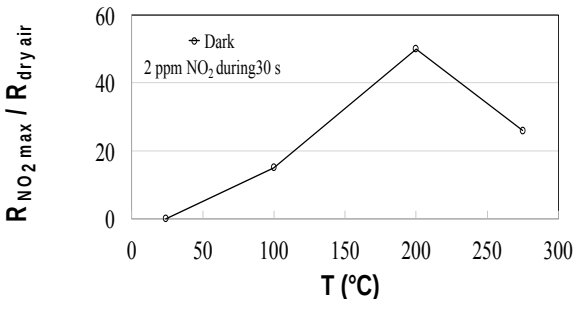


Fig. 2. Sensor responses based on S2 solution and post annealed at 300°C versus working temperatures under 2 ppm of NO_2 in dark.

This result indicates no noticeable resistance variation at room temperature in dark. Then, by heating the substrate, the semiconductor conductivity increases and surface reactions facilitated. Thus, the sensor responses were measured and an optimum working temperature was obtained at 200 °C. It confirms that sensors based on ZnO NCs as most MOX sensors need a high operating temperature to enable the adsorption and the desorption process. This is also in agreement with our previous studies and this optimum is lower than for ozone detection found around 300 °C in dark [17].

2.2. NO_2 Sensing Properties of ZnO NCs at Room Temperature under UV Light

Working at high temperature could affect device lifetime and long-term stability of sensing performances. In our case, it will also limit the sensor's application on flexible substrate or in explosive environment. To be able to work at room temperature, a continuous UV illumination is needed. Fig. 3 shows the sensors responses for four concentrations under continuous UV light at 25 °C.

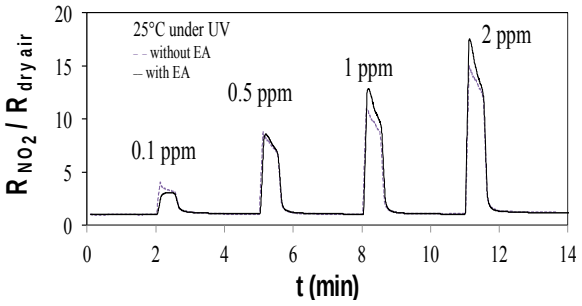


Fig. 3. Sensor responses at 25°C of ZnO NCs thin films, with or without EA, post annealed at 80°C versus NO_2 concentrations under constant UV light and dry air flow (RH = 0 %).

We observe a linear response increase with the concentrations. At each concentration, the sensors behaviors were in the same order of magnitude independently of EA. Light illumination will create excitons and enhances sensing properties. It is reported that O_2^- is formed at temperature lower than 150 °C and O^-, O^{2-} are formed at higher temperature [18–19]. At room temperature, we assume that only O_2^- will be present at the ZnO NCs surface. A depletion layer is formed at the surface that causes the resistance to increase. Reactions between the oxygen ions and the target gas molecules lead to the sensor's signal output. In 2016, Fabbri, *et al*. have confirmed this widely accepted sensing mechanism, which involves oxygen adsorption and desorption [20]. They have shown that the NO_2 sensing response by ZnO thin film on alumina was higher in N_2 than in the air but irreversible in N_2. Detections of 5 ppm NO_2 at room temperature were reported in the air with light illumination at different wavelengths. However, the final annealing at 500 °C is not compatible with

flexible substrate. It is important to remind here that in our work low NO_2 detection as low as 0.1 ppm were obtained with ZnO NCs layers post annealed only at 80 °C. Fig. 4 presents a fine response repeatability of a sensor at 25 °C under UV for 0.1 ppm of NO_2, the lowest concentration available during these experiments.

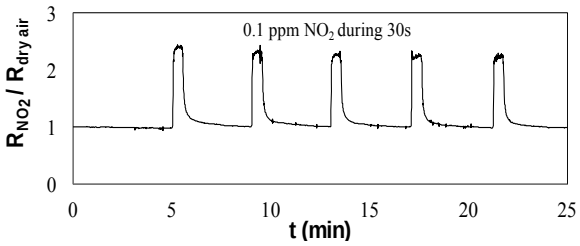


Fig. 4. Sensor response repeatability under 0.1 ppm of NO_2 at 25°C and UV illumination of ZnO NCs thin films with EA, post annealed at 80 °C.

Our study demonstrates that it possible to detect at room temperature low NO_2 concentrations as 100 ppb using UV light activation. A small amount of EA will not reduce the response but greatly improve the dispersion and thus enable reproducible deposition as spray process on flexible substrate at room temperature.

7. Conclusion

This work reports an ambient temperature way to detect NO_2. Using UV light activation, low NO_2 concentrations as 100 ppb have been detected by sensors based on ZnO NCs fabricated in solution. This kind of materials can be spray on flexible substrate. It opens a new way to develop NO_2 sensors on flexible substrate. For next studies, ZnO NCs sensors will be processed on flexible substrate and tested in presence of various gases at room temperature assisted by light activation.

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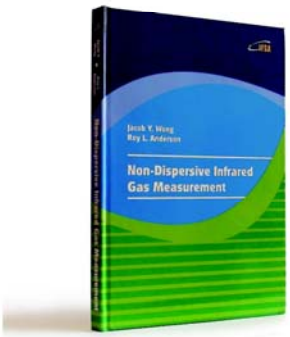
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