Ultra-Violet Assisted ZnO Nanocrystals for NO_2 Sensing at Room Temperature

Sandrine Bernardini [1], Mohamed Hameda Benchekroun [1], Khalifa Aguir [1]
Aix Marseille Univ, Univ Toulon, CNRS, IM2NP, Marseille, France
e-mail: sandrine.bernardini@im2np.fr
e-mail: hameda.benchekroun1993@gmail.com
e-mail: khalifa.aguir@im2np.fr

Meriem Gaceur [2], Olivier Margeat [2], Jörg Ackermann [2], Christine Videlot-Ackermann [2]
Aix Marseille Univ, CNRS UMR 7325, CINaM, Marseille, France
e-mail: gaceur@gmail.com
e-mail: olivier.margeat@univ-amu.fr
e-mail: ackermann@cinam.univ-mrs.fr
e-mail: videlot@cinam.univ-mrs.fr

***Abstract*—In this paper, we focus on nitrogen dioxide detection at room temperature to avoid thermal degradation on flexible substrates. We propose nitrogen dioxide detection at room temperature by zinc oxide nanocrystals deposited on rigid substrate by spin coating from colloidal solution as sensitive layer for air quality monitoring. We investigated gas sensing properties at low post-annealed temperature and under continuous Ultra-Violet illumination for working at room temperature with a process compatible with flexible substrates.**

Keywords-Nitrogen dioxide; Room-temperature; UV-photoactivated; ZnO nanocrystal; environment.

I. INTRODUCTION

Nitrogen Oxides (NO) are produced by petrol or diesel burning engines and coil/oil furnaces. NO is a poisonous, odourless, colourless gas. Once it is mixed with air, it quickly combines forming nitrogen dioxides (NO_2), which is highly toxic, reddish brown gas with a very pungent odour. NO_2 is a major component of the outdoor air pollution. The need for air quality monitoring demands the development of NOx sensitive sensors under 3 ppm [1]. 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 [2]. 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 [3] and depending on filter nature, O_3 can be totally trapped while NO_2 can pass over a specific concentration range [4]. 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.

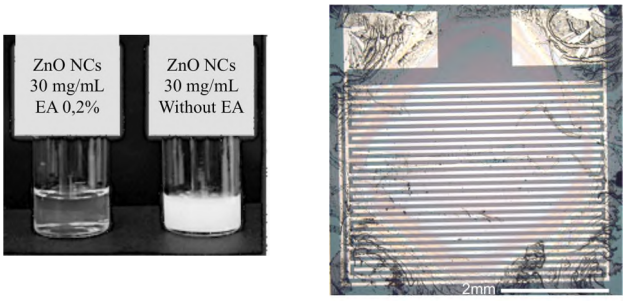
In Section II, the sensor fabrication will be detailed and the results will be discussed in Section III. We conclude the paper in Section IV.

II. DECRIPTION 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. Gas sensors

Our gas sensor consists of Ti/Pt interdigitated electrodes (5 and 100 nm, respectively) deposited on Si/SiO_2 by magnetron sputtering. Figure 1(a) shows two solutions based on ZnO NCs with a diameter of about 5 nm: one named S1 without EthanolAmine (EA) with a milky white aspect indicating the presence of agglomerates [4] and the second one named S2 with EA with a transparent aspect. These solutions (S1 and S2) were deposited by spin coating on rigid substrates during 30s at 2000 rpm/min. Figure 1(b) presents an optical images of a sensor based on ZnO NCs at 30 mg/mL with 0.2 vol.% of EA.



(a) (b)

Figure 1. (a) Optical images 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 NC 30 mg/mL with EA after a post annealing at 80°C.

Previous studies have shown that 0.2% volume of EA, a short-chain surfactant, gives aggregate-free solutions [5]. 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 nanocrystals to form sensing thin films is 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 done for 30 min.

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B. Setup

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.). 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. 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 = 325 nm) at room temperature. We used a Light-Emitting Diode (LED) for UV illumination situated at 10 mm from the sensing material to obtain more photo generated charge carriers.

III. RESULTS AND DISCUSSIONS

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 before and after being exposed to NO_2:

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

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

Figure 2 presents sensor responses of thin film obtained with solution S2 and post annealed at 300°C to test working temperatures up to 275°C. 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.

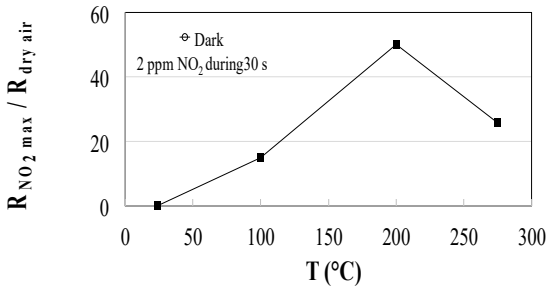

Figure 2. Sensor responses based on S2 solution and post anneald at 300°C versus working temperatures under 2 ppm of NO_2 in dark.

This result indicates no resistance variation at room temperature in dark and an optimum working temperature 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 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 [3][6]. To be able to work at room temperature, a continuous UV illumination is needed. Figure 3 shows the sensors responses for four concentrations under continuous UV light at 25°C.

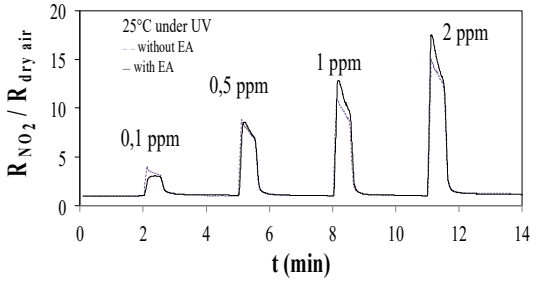

Figure 3. Sensor responses at 25°C of ZnO Ncs thin films, with or without EA, post annealed at 80°C versus NO_2 concentrations under UV light and dry air flow (RH = 0%).

The sensors behaviors were in the same order of magnitude.

IV. CONCLUSION AND FUTURE WORK

This work reported an ambient temperature way to detect NO_2 molecules by sensors based on ZnO NCs thin films. 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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