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Ozone Sensors Working at Room Temperature Using Zinc Oxide Nanocrystals Annealed at Low Temperature †

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Abstract: We focus on ozone (O_3) detection at ambient temperature by Zinc Oxide (ZnO) nanoparticles (NPs) deposited on Si/SiO_2 by spin coating from colloidal solutions as sensitive layers for air quality monitoring. We establish that at room temperature using continuous Ultra-Violet (UV) light irradiation enhances the sensing responses. Three annealing temperatures of ZnO films were performed to compare the sensing properties. These sensors present repeatable responses towards O_3 with fast responses for concentrations as low as 35 ppb with processes compatible with most of flexible substrates.

Keywords: ozone gas; room-temperature; UV-photoactivated; ZnO nanoparticles; environment

1. Introduction

Chemical gas sensors are applied in many areas, such as agriculture, medical diagnosis and detection of environmental pollutants [1–3]. The naturally present ozone (O_3) in the atmosphere is harmful even at low concentrations (<200 ppb). It leads to health problems such as inflammation or respiratory tract [4]. It well known that Metal Oxide Semiconductor (MOX) sensors require high operating temperature (>200 °C) to accelerate molecule chemical reactivity in the adsorption and desorption process. We aimed to fabricate MOX sensors on flexible substrate to fit shapes on smart object for O_3 monitoring. However, most of flexible substrates do not resist to temperature higher than 120 °C. As far as we know, no study reports O_3 MOX sensors using Zinc Oxide (ZnO) nanoparticles (NPs) with annealing temperature lower than 150 °C. Furthermore, to detect low O_3 concentrations at room-operating temperature, we replaced heating excitation by continuous Ultra-Violet (UV) Light-Emitting Diode (LED) for UV illumination (λ = 390 nm). Indeed, photogenerated carriers improve the layer conductivity [5].

2. Materials and Methods

Our gas sensor consists of Ti/Pt interdigitated electrodes (5 and 100 nm, respectively) deposited on Si/SiO_2 by magnetron sputtering. To optimize the sensitive layer performances, three solutions based on ZnO NPs with or without ethanolamine (EA) were deposited during 30 s at either 1500 or

2000 rpm/min. Thus, we prepared five different sensitive layers with resulting layer thicknesses measured by a Veeco Dektak 6M stylus profiler (Veeco, USA) (see Table 1).

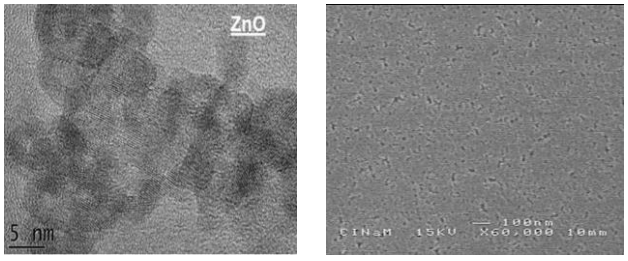
Table 1. Five sensitive layers with resulting thickness based on ZnO NPs in solutions at 10 or 30 mg/mL in isopropanol, with or without EA.

S1	S2	S3	S4	S5
30 mg/mL	30 mg/mL	10 mg/mL	10 mg/mL	30 mg/mL
without EA	with EA	with EA	with EA	with EA
0%	0.2%	0.2%	0.2%	0.2%
2000 rpm/min	2000 rpm/min	2000 rpm/min	1500 rpm/min	1500 rpm/min
100 ± 10 nm	90 ± 10 nm	80 ± 10 nm	180 ± 15 nm	205 ± 15 nm

Previous studies have shown that 0.2% volume of EA, a short-chain surfactant, gives aggregate-free solution [6,7]. ZnO NPs were deposited by spin coating on rigid substrates to compare the sensing performances for three post-annealing temperatures: 80 °C, 150 °C and 300 °C during 30 min, respectively. With a boiling point of 82.6 °C for isopropanol, solvent molecules were completely evaporated for drying temperature reaching 150 °C. The EA surfactant molecules stayed adsorbed on the surface of NPs at least up to the boiling point at 170 °C. 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, USA). Dry air was used as both the reference and the carrier gas, maintaining a constant total flow of 500 standard cubic centimeters per minute (SCCM) via mass flow controllers. Oxidizing oxygen using a UV pen-ray lamp, resulting in a generation of O_3 output level from 35 to 165 ppb.

3. Results and Discussion

By High-Resolution Transmission Electron Microscope (HR-TEM) JEOL 3010, ZnO NPs, ZnO NPs drop casted from a diluted solution on a mesh-coated carbon film (Figure 1a), presented a homogeneous size (diameter about 5 nm) and shape dispersions [6,7]. By scanning electron microscope (SEM) a JEOL JSM 6320F, analysis of spin-coated ZnO thin films highlights the formation of uniform and densely packed agglomerates (Figure 1b).



(**a**) (**b**)

Figure 1. (**a**) TEM image of ZnO nanospheres at 30 mg/mL with 0.2% ethanolamine and (**b**) SEM image of a spin-coated ZnO thin film as S2 and post-annealed at 80 °C.

Figure 2 presents O_3 detection with sensitive layer without and with EA for 30 mg/mL of ZnO nanocrystals annealed at 80 °C. For comparable thickness (~100 nm) and same concentration (30 mg/mL) of ZnO, the sensor responses with EA are slightly lower than the one without EA due to grafting and isolating EA properties [7].

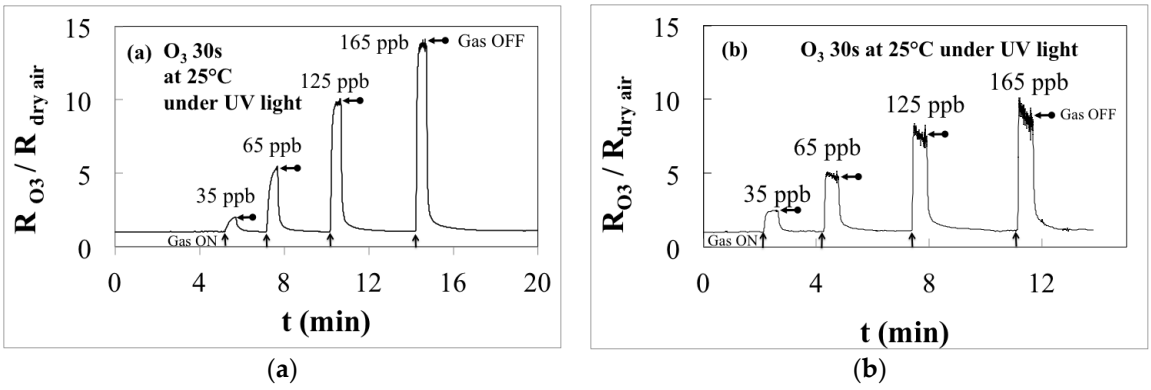


Figure 2. Normalized responses at 25 °C for O_3 sensors based on ZnO at 30 mg/mL (post-annealed at 80 °C) under UV light (**a**) without EA (S1) and (**b**) with EA (S2).

Figure 3 exhibits higher amplitude response for S5 and good repeatability for low O_3 concentrations without sensor saturation.

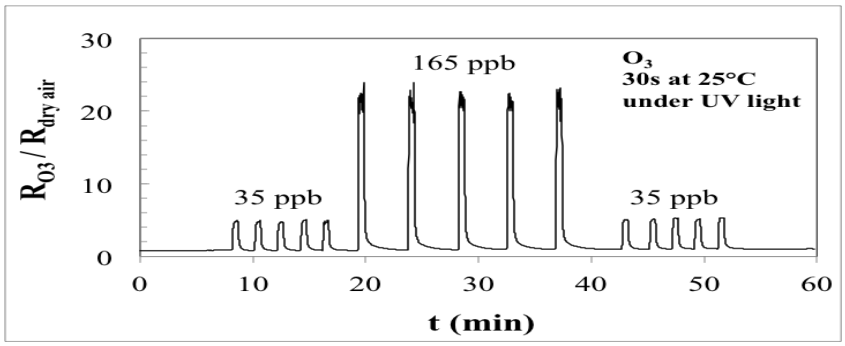


Figure 3. Repeatability of a 200 nm thick sensor with a sensitive layer based on ZnO at 30 mg/mL with EA (S5) and post-annealed at 80 °C, working at 25 °C under continuous UV illumination for 35 ppb and 165 ppb of O_3.

Figure 4 demonstrates that sensitive layers gave already good O_3 detection at 25 °C even with a low post-annealing temperature (80 °C) which is compatible with most of flexible substrates.

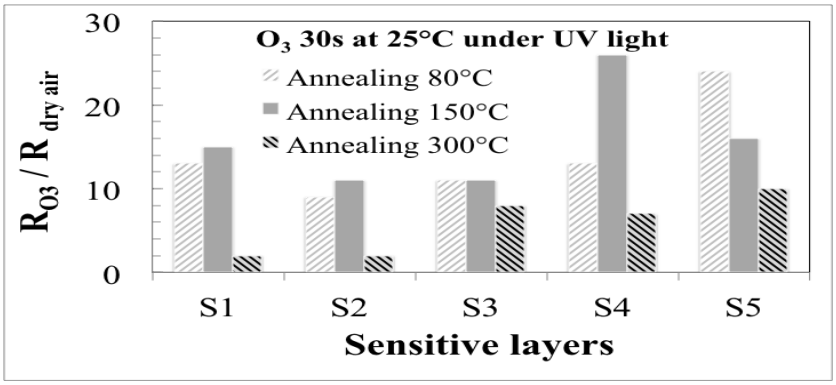


Figure 4. Sensor responses for 165 ppm of O_3 at 25 °C under UV light for three post-annealing temperatures.

To compare the O_3 detection at room temperature and high classical temperature detection (275 °C), measurements have been realized on S4 post-annealed at 300 °C. No detection was possible in dark at room temperature due to the high layer resistivity. Figure 5 revealed that the amplitude is higher at 275 °C in dark and under UV light than at room temperature. However, these temperatures cannot be used on all flexible substrates.

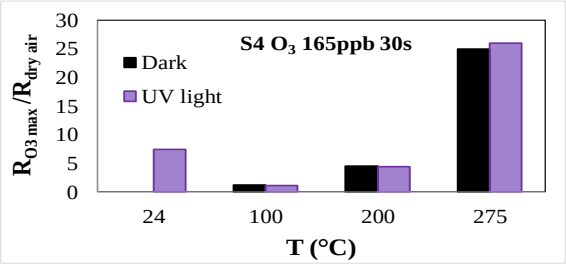


Figure 5. O_3 sensor responses of S4 (post-annealed at 300 °C) for working temperatures from 25 to 275 °C without and with UV light.

Based on our studies on Kapton substrate showing NO_2 detection in dark at lower temperature than for O_3 detection by ZnO NPs [8], we are now focusing our attention on NO_2 detection by these samples in the same conditions with UV light and/or temperature excitations.

4. Conclusions

This work reported an ambient temperature way to detect ozone molecules by sensors based on thin-film ZnO NPs structures synthetized by hydrothermal process. Gas sensing measurements showed the great potential of ZnO NPs, which display a fast response, short recovery time, at room temperature under UV-light irradiation. This versatile methodology provides an alternative way to manufacture gas sensor devices, operating at room temperatures, which is compatible with most of flexible substrates. Electrical resistance measurements at room temperature under UV irradiation showed that ZnO thin films were sensitive even at low O_3 concentration (35 ppb).

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Conflicts of Interest: The authors declare no conflict of interests.

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