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Nozzle-less Ultrasonic Spray Deposition for Flexible Ammonia and Ozone Gas Sensors

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Abstract: In the last years printing and flexible electronic is transforming the way we used electronic devices. Among these, special interest is given to the development of gas sensors for industrial and environmental applications. Nozzle-less ultrasonic spray deposition is a simple and precise technique, which offers good homogeneity and high quality of the sensitive thin film. In addition, it represents a potential fabrication process for flexible electronic with low cost production and low waste of material. In this paper, nanoparticles of zinc oxide were deposited by nozzle-less ultrasonic spray deposition on flexible substrate. The sensing properties towards reducing and oxidizing gases in function of the operational temperature are reported. The flexible platform consists in titanium/platinum interdigitated electrodes and a micro-heater device, both fabricated by lift-off and photolithography. The operating temperature of the sensor is also challenging in term of power consumption. It is allowing the reaction with the exposure gases. Most of the semiconducting metal oxide materials used for gas sensing applications require high temperatures above 250 °C. Flexible gas sensors fabricated in this work present good responses towards ammonia and ozone at 300 °C and 200 °C respectively, with fast response and recovery time in a wide range of gas concentration. *Copyright © 2016 IFSA Publishing, S. L.*

Keywords: Flexible gas sensor, Nozzle-less ultrasonic spray deposition, Ammonia sensor, Ozone sensor, Zinc oxide sensitive material.

1. Introduction

Flexible electronic is an interesting technology for no planar objects of our daily life. The commercial opportunities are growing by years and new sensor generation is emerging in various applications. Therefore, the research and development of new fabrication techniques for flexible sensors are taking a lot of attention.

In the last years, the elevated pollution and their negatives effects on health have caused the demand of new flexible sensors in the field of environmental monitoring, disease diagnostic, personal safety, chemical and industrial processes, and toxic and pollutant detection for human health [1]. These needs have been increased the research and development of new manufacturing processes with low cost and easy fabrication on flexible substrates.

Selection of a suitable fabrication process is critical for the device production. Important factors must be considered such as expenses, purity, reliability, reproducibility, and especially the procedure ought to be compatible with the substrate and the sensitive material properties.

Nozzle-less ultrasonic spray deposition is a good candidate to fabricate thin film at low cost in a large area and low waste of material [2, 3].This simple deposit methodology not only offers good film homogeneity and good control of parameters, but also is easy to integrate into industrial processes [4 – 6].

Gas sensor on flexible substrate based on zinc oxide (ZnO) as sensible material represents an interesting option due to its low cost, portability, reliable response, and excellent characteristics in the gas detection. The electrical resistance of metal oxide materials changes upon exposure to the target gases.

In this work, the interdigitated electrodes and the micro – heater device were fabricated using photolithography process as we described it in previous work [7]. Then, ZnO nanoparticle films were deposited by nozzle-less ultrasonic spray deposition on Kapton HN substrate [8]. It is well known that for metal oxide semiconductors the gas detection depends on the temperature range. The gas sensing properties of the ZnO nanowires were investigated as function of the operational temperature and different ammonia and ozone concentrations.

2. Materials and Methods

2.1. Flexible Gas Sensor Fabrication

The flexible gas sensor consists of a 75 µm thin Kapton polyimide foil, with titanium/platinum (Ti/Pt) interdigitated electrodes for gas detection, and integrated micro-heater device to control the sensitive film temperature. Fig. 1 presents the electrodes fabricated by photolithography and lift – off process on Kapton HN substrate.

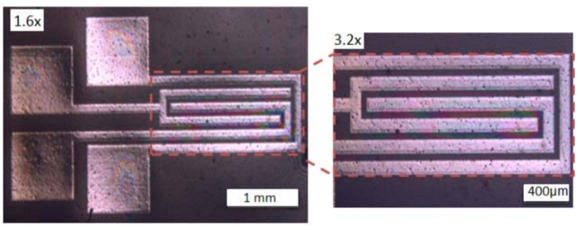

Fig. 1. Interdigitated electrodes fabricated by photolithography and lift-off process on Kapton HN flexible substrate (zoom 1.6X and 3.2X).

The electrode area is 2200 µm × 900 µm. DuPont^{TM} Kapton HN was selected because it is an all-polyimide film with an excellent balance of properties over a wide range of temperatures up to 400 °C: low cost, excellent thermal stability, solvent resistance and flexibility. As first step for the flexible gas sensors fabrication, Kapton HN substrate was initially cleaned with acetone, ethanol and deionized water. Then, the flexible substrate was treated by oxygen plasma to clean and improve the surface properties. The metal films Ti/Pt were deposited by radio frequency magnetron sputtering with thickness of 5 nm and 100 nm, respectively.

2.2. Validation of the Micro-heater Platform

Thermal simulation using finite element analysis has been done in order to validate the platform. It was found a homogeneous temperature around the sensitive area as shows in Fig. 2. We can also observe the linear behavior of the power and the Ti/Pt temperature sensor from the electrical calibration of the micro-heater device.

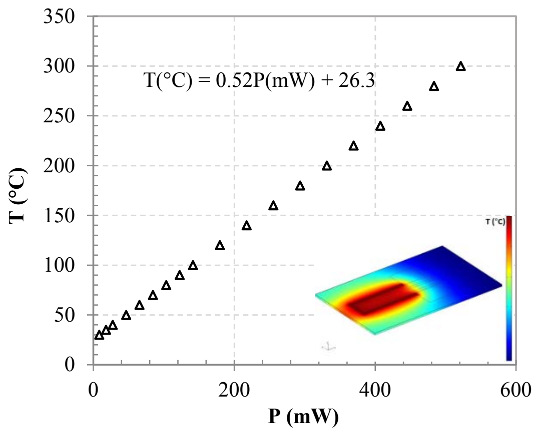

Fig. 2. Calibration of the micro-heater device showing the relation between the power and the Ti/Pt temperature sensor.

This figure presents an efficient control of the temperature by the Ti/Pt micro- heater device. It is improving the surface reactions and the detection of gases using metal oxide as sensitive material.

2.3. Nozzle-less Ultrasonic Spray Deposition

Nozzle-less ultrasonic spray deposition is a potential technique to fabricate thin films at lower cost in large areas with low waste material.

Several organic and inorganic materials have been investigated as sensitive thin films. Among these, zinc oxide is highly attractive for gas sensing applications due to its low-cost, non-toxicity, high sensitivity over many gases and availability for preparation by many reliable processes [9-11].

In this work, ZnO nanoparticles have been used as sensitive material. We used ink solution from

Genes'Ink company (ZnO_5F_{12}). Thin films with thickness of 100 nm were deposited by nozzle-less ultrasonic spray deposition on Kapton HN polyimide substrate. Afterwards an annealing has been done during 3 hours at 300 °C under environmental conditions. This annealing improves the quality and stability of the ZnO nanoparticle films.

The deposition was carried-out with a programmable nozzle-less spray machine Prism BT Benchotp X-Y-Z Coating System from Ultrasonic System, Inc. (USI manufacturer). It gives a thinner and more precise coating than conventional spray systems, film coaters, roll coaters and jetting technology. In Addition, the system delivers thin films with good thickness homogeneity. The precision is around of ± 4 % on an A4 sheet of Kapton HN.

This nozzle-less ultrasonic spray deposition is a simple technique ideal for thin and uniform applications of several sensitive materials with low viscosity. The operational principle consists of an ultrasonic transducer with a spray forming tip, an ultrasonic generator, an external liquid applicator, a precision liquid delivery system, and air directors. The spraying takes place by the vibration of a titanium transducer and a rectangular tip. The particular ultrasonic frequency is selected based upon the material to be sprayed and the coating application requirements. The amplitude of vibration of the spray-forming tip is also set with the ultrasonic generator. The coating patter is flat, uniform and rectilinear due to the rectangular tip used on our samples [8, 12].

In Fig. 3, we can observe one of our flexible gas sensor fabricated on Kapton HN substrate by photolithography process.

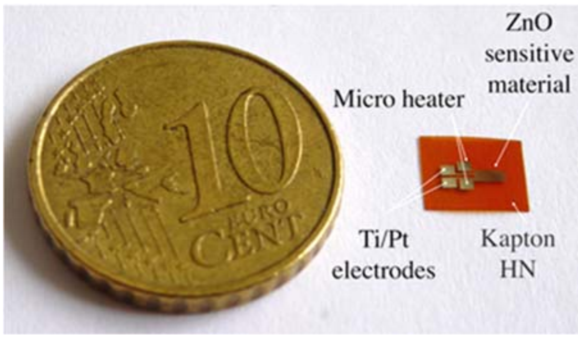

Fig. 3. Sensor fabricated on Kapton HN substrate by photolithography process and ZnO thin film deposited by nozzle-less ultrasonic spray.

3. Results and Discussion

The gas sensing properties were carried-out in a closed chamber by measuring the resistance through the sensitive thin film at a monitoring temperature. A power supply was used to control the temperature, and the data acquisition was done with a source meter Keithley 6430.

In order to find the optimum operational conditions, five samples were tested at different temperatures from room temperature to 350 °C under the target gases. The exposure time was 1 minute. The main response parameters investigated are the resistance variation under gas, the response time and the recovery time. As oxidizing gas, when ozone is absorbed on the ZnO surface the O atoms of oxidative gas molecules extract the electrons from the ZnO nanostructure. Consequently, the depletion layer becomes thicker due to the decreasing of the carrier of concentration, producing a resistance increase as shown in Fig. 4a. As a reducing gas, when ammonia is absorbed on the surface of ZnO, the reductive gas molecules react with the absorbed O_2^-, O^- or O^{2-} ions and release the electrons back to the ZnO nanoparticles. Thus, the resistance decreases as presented in Fig. 4b.

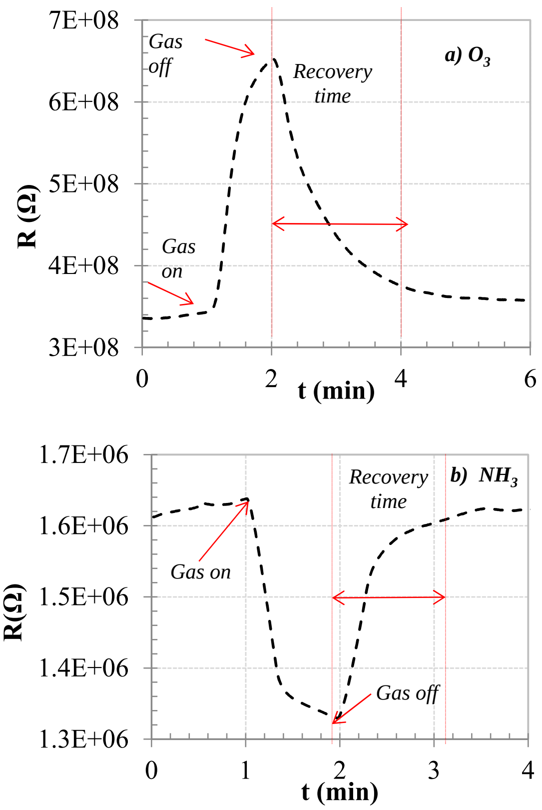

Fig. 4. Response and recovery time of the sensor deposited by nozzle-less ultrasonic spray under: a) 500 ppb O_3 at 200 °C and b) 50 ppm NH_3 at 300 °C.

As illustrated in Fig. 4, it was found a fast response less than 30 s for both gases and a recovery time around 2 minutes for an ozone exposure of 500 ppb at 200 °C (Fig. 4a), and around 1 minute for an ammonia concentration of 50 ppm at 300 °C (Fig. 4b). The fast recovery time highlights that it can be used several times in a short period. The response time is defined as the time taken by a sensor to achieve 90 % of the total signal change when the sensor is exposed to a target gas [10, 13]. The recovery time is the time interval over the sensor resistance reduces to 10% of the saturation value when the sensor is exposed to full scale of concentration and then placed in the dry air [14]. We monitored the resistance variation of the sensor fabricated by nozzle-less ultrasonic spray deposition when the gas is brought on the sensor.

The best compromise between the response and the recovery times of the sensor were obtained with ozone at 200 °C and ammonia at 300 °C.

The repeatability of the ozone response was studied at 200 °C with a concentration of 500 ppb with a target time of 1 minute. Fig. 5 presents the normalized response of the sensor where R is the sensor resistance under the target gas, and R_0 the sensor resistance under dry air.

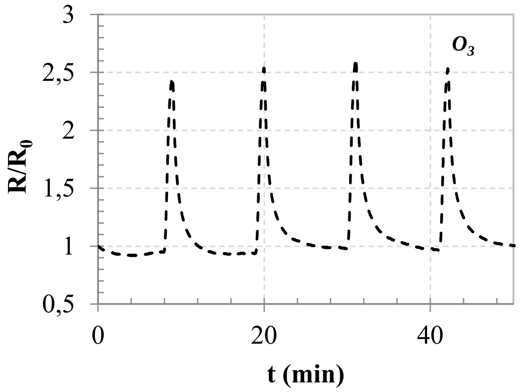

Fig. 5. Normalized response of the ozone sensor based on ZnO nanoparticles deposited by nozzle-less spray under 500 ppb O_3 at 200 °C.

The ozone sensing properties show a normalized response around of R/R_0= 2.5 with a stable base line and small variations between each gas exposure. A repeatability test of the samples using ammonia concentration of 50 ppm at 300 °C is presented in Fig. 6.

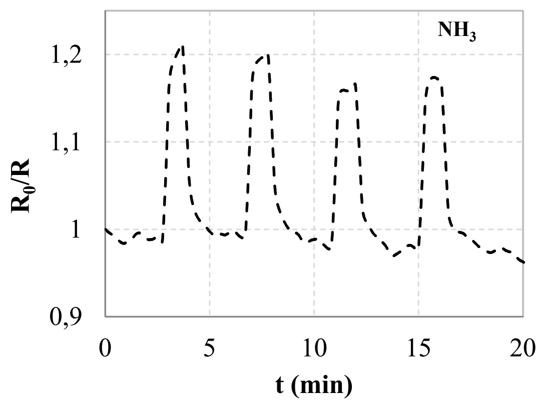

Fig. 6. Normalized response of the ammonia gas sensor based on ZnO nanoparticles deposited by nozzle-less spray under 50 ppm NH_3 at 300 °C

Keeping the same time between each gas exposure, some instability in the base line appears during the repeatability response of ammonia. During the experiments with ammonia, it was observed that the ZnO based sensor is more sensitive to small changes of temperature, thus the instability in the base line could be attributed to this behavior and to the surface reactions.

Although the continuous repeatability of the ammonia gas exposure presents small variations on the base line, it was found a normalized response around of R_0/R=1.2 with a concentration of 50 ppm with small variations between each measurement. The good repeatability of both gas detections point out that after several test, the sensor is free of pollution and the sensitive material does not present saturation under large gas concentration, around 500 ppb and 50 ppm for ozone and ammonia, respectively. As observed in Fig. 5, the target time of 1 minute did not allow reaching the response peak saturation during the O_3 exposure; in the other hand, this targeting time of ammonia exposure is enough to reach the response peak saturation (Fig. 6). However, for both gases this exposure time is enough to always obtain fast response for all concentrations as well as the recovery times to the baseline.

The sensing performances of the flexible sensor over different concentrations of ammonia and ozone are presented in Fig. 7.

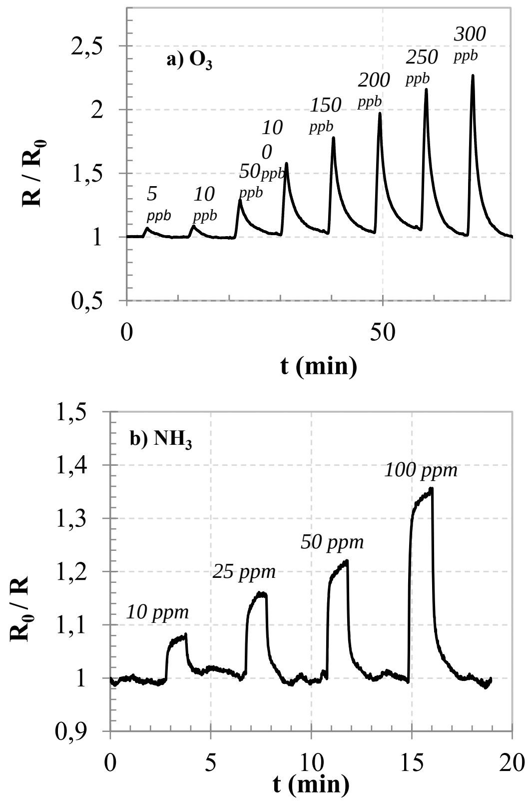

Fig. 7. Response of the flexible gas sensor based on ZnO nanoparticles deposited by nozzle-less spray over different gas concentrations: a) O_3 from 5 ppb to 300 ppb at 200 °C, and b) NH_3 from 10 ppm to 100 ppm at 300 °C.

Fig. 7 presents good normalized responses and wide range of detection towards ozone (Fig. 7a), and ammonia (Fig. 7b).

Ozone is one of the six principal pollutants considered harmful to the public health and the environment. According with the international standards in the area of health, the average concentration of ozone exposure should be less than 75 ppb [15]. Likewise, ammonia is a common toxic gas considered a high health hazard because it is corrosive to skin, eyes and lungs. The maximum recommended exposure is up to 50 ppm from The Occupational Safety and Health Administration (OSHA) [16]. As illustrated in Fig. 7, the detection ranges obtained for both gases, from 5 ppb to 300 ppb to ozone, and from 10 ppm to 100 ppm for ammonia stand out that the flexible gas sensor fabricated is capable of sensing gas concentrations into the range of detection recommended from the international and occupational standards. It was found good gas sensing properties with fast response time, recovery time around of 2 minutes, and very wide range of detection for both gases.

The sensor based on ZnO thin film as sensitive material and deposited by nozzle-less ultrasonic spray technique on flexible substrate has presented very good performance towards an oxidizing (O_3) and a reducing (NH_3) gas with lower operating temperature (200 °C for ozone and 300 °C ammonia) compared to the metal oxide based sensors in the literature [17 - 20]. Furthermore, it does not require an external stimulus or dopant for fast response and fast recovery time [21].

Many studies have proved that the sensing properties of metal oxide materials depend on different factors such as morphology, sensing temperature and thickness of the thin film. As further study, the good control of parameters obtained by ultrasonic spray deposition technique will allow us to optimize the thickness of the thin film in order to enhance the gas sensing properties.

Thus, nozzle-less ultrasonic spray technique could be a key to reach some benefits such as: flexibility, environmental credential, transparency, reliability, and enhance of the sensor performances, that the emerging flexible sensing technologies are demanding.

4. Conclusions

A flexible platform was fabricated by photolithography patterning for gas sensor applications. During the fabrication it was observed neither substrate damage nor irregularities in the Ti/Pt film pattern.

ZnO nanoparticles were used as sensitive material and were deposited by nozzle-less ultrasonic spray deposition with a thin film thickness of 100 nm at environmental conditions. Then, it was annealed by 3 hours at 300 °C to improve the quality and stability of the metal oxide sensitive material.

The deposited technique has shown important characteristics such as good thin film distribution and good control of parameters. The gas measurements presented good responses with fast response/recovery time around of 2 minute towards ozone and ammonia. The wide range of detection and the low operational temperatures found for both gases indicate that the flexible sensor device is suitable to operate according to the recommended international standards.

The gas sensing properties on flexible Kapton HN substrate and the use of nozzle-less ultrasonic spray deposition highlight the promising opportunity in the flexible electronic field to fabricate quality devices with fast and low cost production which can be used in different applications in the field of environmental, health and industrial processes.

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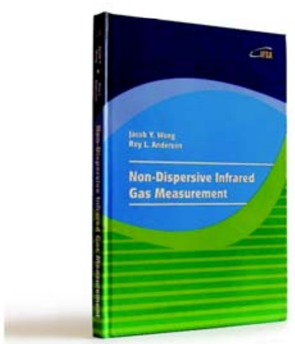
Jacob Y. Wong, Roy L. Anderson

Non-Dispersive Infrared Gas Measurement



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Written by experts in the field, the *Non-Dispersive Infrared Gas Measurement* begins with a brief survey of various gas measurement techniques and continues with fundamental aspects and cutting-edge progress in NDIR gas sensors in their historical development.

- It addresses various fields, including:
- Interactive and non-interactive gas sensors
- Non-dispersive infrared gas sensors' components
- Single- and Double beam designs
- Historical background and today's of NDIR gas measurements

Providing sufficient background information and details, the book Non-Dispersive Infrared Gas Measurement is an excellent resource for advanced level undergraduate and graduate students as well as researchers, instrumentation engineers, applied physicists, chemists, material scientists in gas, chemical, biological, and medical sensors to have a comprehensive understanding of the development of non-dispersive infrared gas sensors and the trends for the future investigation.

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