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Ammonia sensing properties of ZnO nanoparticles on flexible substrate

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Abstract—**We report the ammonia gas sensing properties of ZnO nanoparticles on flexible substrates. The flexible platform contains Ti/Pt interdigitated electrodes for gas detection and a micro heater device. The Ti/Pt film has been deposited by Magnetron Sputtering with thickness of 5nm and 100 nm respectively. The circuit patterning has been fabricated by standard photolithography and femtosecond laser ablation processes. ZnO thin film has been deposited by drop coating process with a thickness of 275 nm and the gas sensing properties towards ammonia have been studied. The physical properties obtained by both processes have been observed and theirs effects on the gas sensitivity have been discussed. Despite there are small variations in the physical characteristics between the samples fabricated by different patterning processes, both devices present high sensitivity and reproducibility to different ammonia concentrations from 5 ppm to 100 ppm at 300 °C.**

Keywords-Ammonia; flexible substrate; zinc oxide; gas sensor; Kapton.

I. INTRODUCTION

Flexible electronic is playing an important role in the daily life and industrial applications. Consequently, a new generation of flexible sensor is emerging and the market is increasing year by year. Motivated by the environmental and industrial pollution and their effects on human health, the progress of gas sensors to monitor toxic and hazards gases is quickly advancing.

Flexible substrates allow obtaining low cost, portable and lightweight gas sensors with an easy and inexpensive fabrication process. A widely variety of organic and inorganic materials have been studies as sensitive film to be used on flexible substrates. Among these, ZnO metal oxide as sensitive material has been found as one of the most promising candidates for detecting toxic and hazard gases due to his low cost, high sensitivity, and high chemical stability [1].

The most common flexible substrates used in flexible electronic are PET and PEN, however these materials do not support temperatures above 200 °C, while the metal oxide require higher temperatures (around 350 °C) to react with the exposure gases [2, 3]. Therefore, in this work polyimide Kapton has been used as flexible substrate because of its excellent thermal stability, solvent resistance and high work temperature until 400 °C.

The fabrication process for the circuit path production is one of the critical factors to obtain high quality devices. Various aspects should be considered to select the most appropriate, such as expenses, reliability, reproducibility, resolution, and especially the procedure must meet the flexible substrate and sensitive material requirements.

Photolithography is one of the most common and reliable fabrication processes on rigid substrates, and in this work, it has been successfully applied on flexible substrate with a resolution up to 20 µm. On the other hand, femtosecond laser ablation process presents advantages such as reduction in fabrication time, elimination of chemical process during the path fabrication, and the process does not involve any thermal consequence for the substrate [4]. The process has been applied on flexible substrates with a resolution of 60 µm based on the optical configuration and adapted to experimental conditions.

In the present paper, we report and compare the development of flexible gas sensors fabricated by photolithography and laser ablation processes. ZnO thin film has been used as sensitive material towards ammonia as a common toxic gas and high health hazard. Ammonia is corrosive to skin, eyes and lugs; and it causes comma, blindness and even death at high levels of concentration. The Occupational Safety and health Administration (OSHA) recommend an exposure less than 50 ppm [5].

II. EXPERIMENTAL PROCEDURE

A. Desing and Materials

The flexible platform is composed of a polyimide Kapton substrate with thickness of 75 µm, Ti/Pt interdigitated electrodes for gas detection and a micro heater device. The sensor has an area less than 4000 µm x 2500 µm and a gap between electrodes of 60 µm. The top schematic design and the dimensions are illustrated in Fig. 1.

The interdigitated electrodes and the micro – heater device are made of titanium and platinum with thickness of 5 nm and 100 nm respectively. Platinum offers good stability at high temperatures and the titanium film is used to improve the adhesion of the platinum film on the substrate. Kapton substrate presents characteristics as low cost, and good mechanical and electrical properties in a wide range of temperatures (from -69 °C to +400 °C).

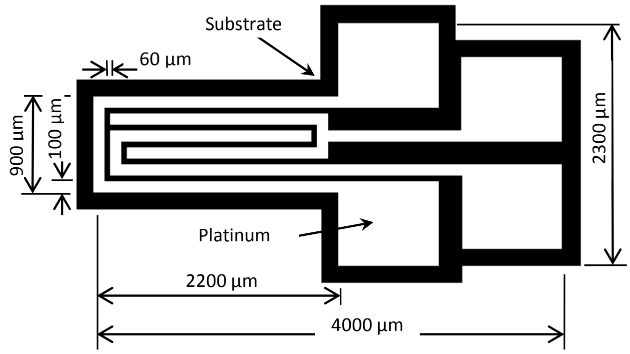

Fig. 1 Layout design of the flexible sensor.

B. *Thermal simulation and Electrical calibration*

Fig. 2 illustrates the thermal simulation by finite element used to validate the platform. The thermal simulation parameters were defined according to the properties obtained by experimental electrical calibration at 25 °C in order to obtain the closest device behavior. The thermal simulation validates the platform presenting a homogenous temperature around the sensitive area.

For the device fabrication, the substrates were first treated by oxygen plasma to clean and improve the surface properties, and then a Ti/Pt thin film with thickness of 5 nm and 100 nm were deposited by magnetron sputtering. Finally, the circuit patterning were fabricated by photolithography and femtosecond laser ablation processes.

The laser ablation process uses a femtosecond-diode-pumped ytterbium amplifier laser with an operating wavelength of 1030 nm, a spectral bandwidth of 5 nm, and pulse duration of 350 fs ± 20 fs. The beam is focused in the sample after passing through a set of galvo-mirrors and f-theta-lens. Owing the energy is deposited in the flexible substrate at ultra-short time scale and the process is not affected by heat diffusion effects, the substrate does not present damage [6].

The comparative values of the final dimensions obtained after the fabrication by photolithography and laser ablation processes are presented in Table. 1.

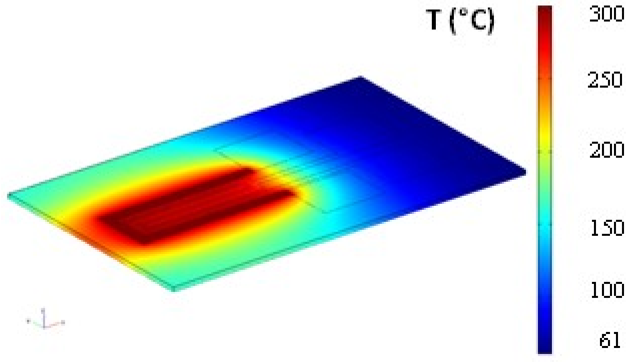

Fig. 2 Thermal simulation of the flexible platform.

Table 1. Dimensional characteristic comparison of the samples fabricated by photolithography and laser ablation.

Characteristic	**Photolithography**	**Laser ablation**
Thickness *(th)*	100nm	100nm
Path length *(L)*	100µm	90µm
Heater device length *(l)*	5.91mm	5.36mm
Pt film transversal section *(S_f)*	10pm²	9pm²
Electrode transversal section (S_e)	1.87µm²	1.98µm²

We can observe that there are small length variations for the transversal section and the heater device. These dimension differences can be reduced by refining the laser ablation parameters to improve the resolution process.

The electrical behavior of the Ti/Pt electrodes was characterized and the linear response of the temperature versus the source power for the micro - heater devices for both processes is similar as presented in Fig. 3.

The experimental electrical parameters of the samples were obtained using (1), which define the electrical resistivity as a function of the temperature.

$$R = \rho \cdot L/S \tag{1}$$

Where ρ is the electrical resistivity, R the path resistance, L the path length and S the path transversal cross - section.

The final electrical parameters of the samples fabricated by photolithography and laser ablation processes are compared in Table. 2 at 25 °C.

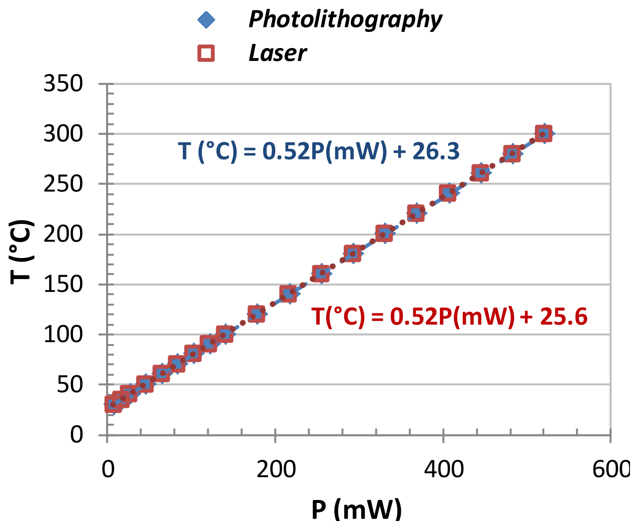

Fig. 3 Relation between the power and temperature, for both photolithography and laser processes.

Table 2. Electrical parameter comparison of the samples fabricated by photolithography and laser ablation.

Parameters			**Photolithography**	**Laser ablation**
Temperature	*T*	°C	25	25
Resistance	*R*	Ω	147	238
Electrical resistivity	p	[Ω·m]	2.5×10^{-07}	4.0×10^{-07}
Electrical conductivity	σ	[S/m]	4.0×10^{06}	2.5×10^{06}
Thermal conductivity	λ	[W/m·K]	29.31	18.24

The value comparison demonstrates clearly that the different dimensions given in Table 1 represent a critical factor for the final sensor properties, regarding directly in the resistance values of the samples and the parameters involved to it.

The fabricated flexible substrates were cleaned ultrasonically in acetone and ethanol and then a commercial ZnO ink (Genes'Ink) was deposited by drop coating with a thickness of 275 nm. In order to improve the quality and the stability of the sensitive material without damaging the substrate, an annealing of 300 °C for three hours under environmental conditions was done. The final flexible sensors fabricated by both processes are illustrated in Fig. 4.

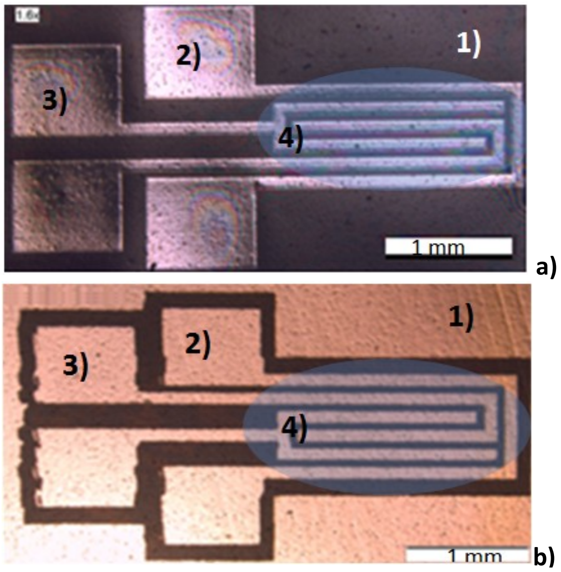

Fig. 4 Sensors fabricated on flexible substrate by: a) Photolithography process and b) Laser ablation process. Where 1) Flexible substrate, 2) Micro – heater device, 3) Interdigitated electrodes, 4) ZnO sensitive material.

III. RESULTS AND DISCUSSION

To observe their sensing properties toward ammonia and the response/recovery time, the samples were target by one minute with a concentration of 50 ppm at 300 °C as operational temperature (Fig. 5). The normalized responses were calculated using the relation R_0/R, where R_0 is the resistance measured in dry air and R is the sample resistance under ammonia.

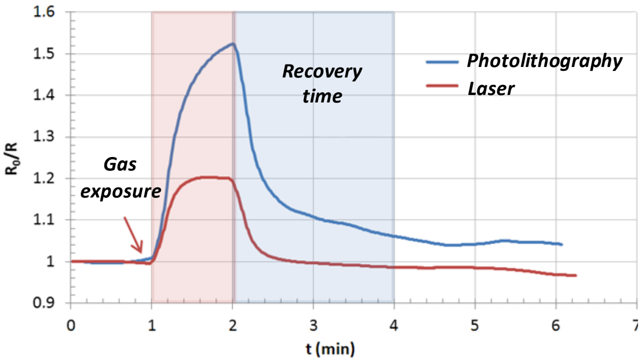

Fig. 5 Normalized responses of the sensor fabricated by photolithography laser ablation processes with 50 ppm NH_3 at 300 °C.

The measurements were carried out in a closed chamber using a programmable power supply to control the sample temperatures, and a source meter Keithley 6430.

Both samples present good responses towards ammonia. It was found a recovery time around 2 minutes for the sample fabricated by photolithography and less than 1 minute for the one fabricated by laser ablation. It is also observed that higher normalized response represents an increase of the recovery time.

Although there is a small instability in the base line at 300 °C, the gas sensors responses in Fig. 6 presented good reproducibility and a normalized response over 50 ppm of ammonia equals to $R_0/R = 1.51 \pm 0.02$ for the samples fabricated by photolithography, and to $R_0/R = 1.21 \pm 0.01$ for the samples fabricated by laser ablation.

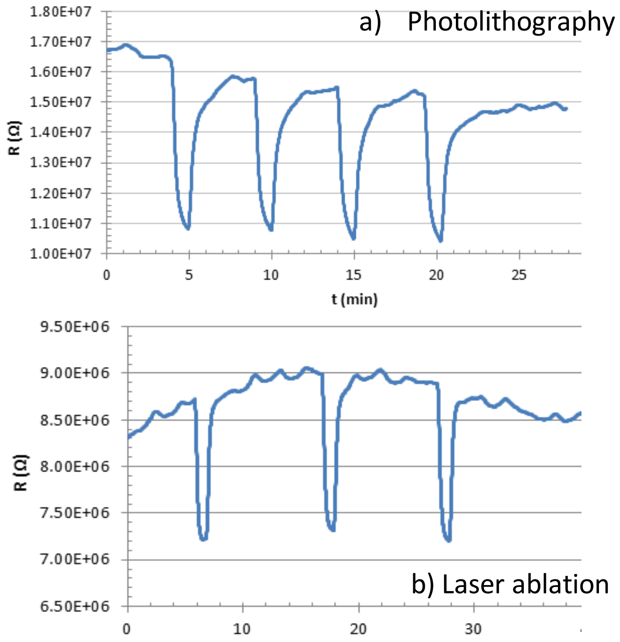

Fig. 6 Ammonia response of the sensor with 50 ppm NH_3 at 300 °C: a) Fabricated by photolithography process, b) Fabricated by laser ablation process.

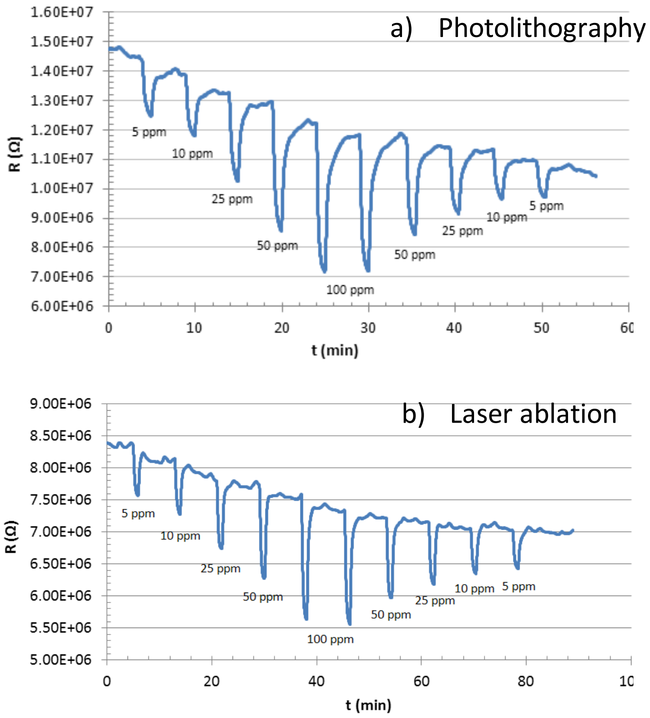

Fig. 7 Sensor response deposited by drop coating with thickness of 275 nm and fabricated by photolithography process as function of NH_3 concentrations at 300 °C.

An important range of detection from 5 ppm to 100 ppm is illustrated in Fig. 7. The measurements were done by increasing and decreasing gas concentrations in order to observe the free pollution after high ammonia concentration.

The gas exposures using several increasing and decreasing ammonia concentrations have presented good reproducibility with small variations, and fast response and recovery time. This behavior indicates that the ZnO sensible thin film does not shows either pollution or saturation after the high concentrations.

Even though the samples obtained by different fabrication processes have presented good sensing properties towards ammonia, it easily observed that the physical dimension variations caused by the different patterning process and the ZnO thin film deposition represent critical factors for the final sensors behavior.

Ammonia sensors have been widely investigated [7 - 9], however only some of them have been fabricated on flexible substrates [10]. The devices presented in this work, has presented good sensing properties towards ammonia with faster response and recovery time over a wide range of concentrations.

IV. CONCLUSION

Flexible ammonia sensors based on ZnO nanoparticles have been fabricated by two methods: photolithography and laser ablation processes. The flexible platforms were validated by thermal simulation presenting a homogenous temperature around the sensible area.

ZnO thin film with thickness of 275 nm was deposited by drop coating and the gas sensing properties were carried out at 300 °C for several ammonia concentrations. Despite of the small variations between the electrode dimensions, it was found good responses, good repeatability and a wide range of detection from 5 ppm to 100 ppm at 300 °C without presence of pollution in the sensible film.

The obtained sensor responses using two different patterning processes indicate the critical influences between the initial fabrication parameters and the final sensor properties. However, both patterning fabrication processes have been successfully applied on flexible substrates, demonstrating their wide applications on flexible gas sensors and flexible electronic in general.

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