Ozone flexible sensors fabricated by photolithography and laser ablation processes based on ZnO nanoparticles

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ARTICLE INFO

Article history:
Received 15 December 2013
Received in revised form 2 June 2014
Accepted 3 July 2014
Available online 14 July 2014

Keywords:
Flexible sensor
Gas sensor
Ozone sensor
ZnO nanoparticles

ABSTRACT

Ozone gas sensors on flexible substrate with Ti/Pt interdigitated electrodes have been fabricated by standard photolithography and femtosecond laser ablation processes under the same conditions. ZnO nanoparticles deposited by drop coating method have been used as sensitive thin film material with 280 nm thickness due to their excellent characteristics on gas detection. The physical properties obtained by both processes have been studied and their critical effects on the gas sensitive response are discussed. It was found that although both samples present small dimensional variations, the samples fabricated by laser ablation shows a bigger sensitive response to ozone at 200 °C. However, both samples have been used as ozone gas sensor and present excellent sensing characteristics, giving good stability, fast response/recovery and excellent range of detection from 5 ppb to 300 ppb.

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1. Introduction

In recent years a growing interest has been dedicated to the development and the fabrication of technology on flexible substrates. Some of the advantages targeting these substrates are thickness, low cost power system, stretchability, weightless, easy and low cost production, and the effective production for long scale applications [1–3]. Combination of the following characteristics allow an important range of applications to improve the electronic field as include photocells, radio frequency identification tags, pressure-sensitive materials, gas sensors, etc. [4–7]

The flexible substrates for gas sensors have been widely used owing to their remarkable advantages on the fabrication and the applications over conventional ceramic or silicon materials. In this field, a wide variety of organic and inorganic materials have been studied as sensitive materials. The commonly sensitive materials used for gas sensing applications are the semiconductor metal oxides such as ZnO, WO3, ITO, SnO2, TiO2, ZnS, etc. They are low cost, stable, high sensitive, need low maintenance and they are able to detect large number of environmental hazardous gases including oxidizing gasses (NO2, NO, N2O, CO2, O3) and reducing gases (H2S, CO, NH3, CH4, SO2) [8–13]. However, this kind of materials requires high temperatures above 350 °C in order to react with the exposure gases [14] and gives fast response and recovery time, while the maximum operating temperature of many of flexible materials is under 200 °C, representing one of the most important challenges in the flexible electronic field [1].

Several materials have been implemented as flexible substrate such as polyimide film materials, PET, PEN, PMMA (Polymethylmethacrylate), PDMS (polydimethylsiloxane), parylene, glossy paper and Kapton [2,14–19], but only few of them hold up temperatures higher than 200 °C. In this work, the flexible substrate selected is Kapton for its excellent thermal stability, solvent resistance, low cost, electronic and mechanical properties and high work temperature (+400 °C).

Selection of a suitable fabrication process is critical for the path device production. Several factors must be considered such as expenses, purity, reliability, reproducibility and specially, the procedure ought to be compatible with the substrate and sensitive material properties. Various processes have been used to compare performance and efficiency, particularly printing process, photolithography and laser treatments [20–24]. Fabrication devices on flexible substrates can allow a decrease of the production cost and time due to a reduction of infrastructure needed, a decrease of processing steps and temperatures permitting an effective production for large scale applications.

A lot of techniques can be applied to deposit the sensitive material as thin film, including sol–gel process, spray pyrolysis, photo chemical deposition, molecular bean epitaxy, chemical...
vapor deposition, spin coating, inkjet printing, sputtering, drop coating process, etc. [25–29]. Comparing to other deposition techniques, drop coating process has the advantages of low cost, low substrate temperature deposition, and a very simple process.

This work aims to compare flexible ozone sensors fabricated by photolithography process and by laser ablation process. ZnO nanoparticle solution has been selected as sensible material due to its chemical sensitivity to different absorbed gases, high chemical stability, non-toxicity and low cost. We present only the sensor response towards ozone as one of the six principal pollutants considered harmful to the public health and the environment [30]. According with the international standards in the area of health, the average of ozone concentration should be less than 75 ppb [30,31].

The photolithography is one of the most common and reliable fabrication processes on Si substrates with a very high resolution. In this work, the process has been successfully applied on flexible substrate presenting very good results with resolution up to 20 nm. Because of the well-known study of the photolithography, the reliability in the sensor fabrication field, and the good results obtained, the samples fabricated by this method have been taken as references to be compared over the samples fabricated by laser ablation.

For the laser ablation process, a resolution of 60 μm has been obtained based on the optical configuration and with adapted experimental conditions. The film laser ablation has been accomplished with a stress-assisted film ejection process that does not involve any thermal consequence for the substrate. This process presents important advantages such as reduction in fabrication cost and time, elimination of chemical process and lower temperatures during the photolithography. It is a main alternative to chemical and high cost processes. It is demonstrated, in the work described below, that both samples (fabricated by photolithography and by laser ablation with the same parameters) give excellent responses over different ozone concentrations using commercial ZnO nanoparticles as sensitive thin film at 200 °C as operating temperature.

2. Experimental

2.1. Design and materials

The flexible sensors consist in interdigitated electrodes for gas detection and a heater device in an area less than 4000 μm × 2500 μm. The micro sensors were designed with a gap of 60 μm between the electrodes and an electrode area of 2200 μm × 900 μm. The flexible substrate material is Kapton polyimide film with 75 μm thickness which is low cost and works from −269 to +400 °C. The layout design of the sensor is presented in Fig. 1.

For reasons of temperature stability, the interdigitated electrodes and the heater device are made of titanium and platinum with thickness of 5 nm and 100 nm respectively. The titanium thin film is used only to improve the platinum adhesion on the substrate. The flexible substrate material is Kapton with 75 μm thickness. Thickness equals to 50 μm has also been tested, and although the substrate is more flexible, it presented detachment of the electrodes. As mentioned previously, Kapton substrate has been selected because of its characteristic as excellent thermal stability, solvent resistance, shrinkage, low cost, electronics and mechanical properties and high work temperature (+400 °C). The flexible platforms were validated by thermal simulation using finite elements and computational tools.

The parameters used for the thermal simulation were defined according to the properties obtained by experimental electrical calibration at 25 °C. It was found average values for the platinum thin film: electrical conductivity $\sigma = 3.01 \times 10^6$ S/m, an electrical resistivity $\rho = 3.33 \times 10^{-7}$ Ω/m and a thermal conductivity $\lambda = 21.94$ W/m/K. Fig. 2 shows the applied mesh design and the results of the micro heater thermal simulation presenting a homogeneous temperature on the substrate surface under 300 °C.

It can be seen in Fig. 3, degree variation less than 10 °C in section X and less than 6 °C in section Y around the active layer area.

From these results, we can validate the design platform and guaranteeing a good heat distribution around the active layer area. According with our sensor geometry, the heater device around the interdigitated electrodes for gas detection is simple and functional that allows working with a homogeneous temperature during the sensing process.

2.2. Methodology and fabrication

The substrates were first treated by oxygen plasma to remove impurities and to improve the Ti film and Pt film adhesion. Titanium and platinum films have been deposited by RF Magnetron Sputtering with thickness of 5 nm and 100 nm, respectively. The circuit patterns were then made by two different technologies: Standard photolithography process [15,20], and laser ablation process [24]. The flow chart of the samples fabrication process can be described in Fig. 4.

The laser source used in this work is a femtosecond-diode-pumped ytterbium amplified laser with an operating wavelength of 1030 nm, 5 nm spectral bandwidth and pulse duration of 350 ± 20 fs. The beam is focused on the sample after passing through a set of galvo-mirrors and f-theta-lens. As the energy is deposited in the material at ultra-short time scale and the process is not affected by heat diffusion effect, the substrates do not presented any kind of damage.

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

In Table 1, we can notice an important variation on the sample dimensions obtained by both processes: the electrode length, the cross section and the heater device length. In this case, the dimensions presented in the samples fabricated by laser ablation are the farthest comparing with the ones of design; these dimension

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Photolithography</th>
<th>Laser ablation</th>
</tr>
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<tbody>
<tr>
<td>Thickness Ti/Pt (th)</td>
<td>100 nm</td>
<td>100 nm</td>
</tr>
<tr>
<td>Electrode length (L)</td>
<td>100 μm</td>
<td>90 μm</td>
</tr>
<tr>
<td>Heater device length (l)</td>
<td>5.91 mm</td>
<td>5.36 mm</td>
</tr>
<tr>
<td>Pt film cross section ($S_1$)</td>
<td>10 pm$^2$</td>
<td>9 pm$^2$</td>
</tr>
<tr>
<td>Electrode cross section ($S_o$)</td>
<td>1.87 μm$^2$</td>
<td>1.98 μm$^2$</td>
</tr>
</tbody>
</table>
differences can be reduced by using better laser ablation parameters to improve the resolution process.

Because of the sensors contain a heater device, it is important to experimentally calibrate it in order to correlate the applied voltage to the device temperature. The relation between the path heater temperature in function of its electrical resistance is given by Eq. (1) [32].

$$R = R_0 (1 + \alpha (T - T_0))$$  \hspace{1cm} (1)

where $R_0 =$ resistance at $T_0$ temperature, $\alpha =$ material characteristic function, $\alpha = 1$ for $T = T_0$, and $T =$ absolute temperature.

The samples were placed in a thermostatic chamber in order to measure the Pt path resistance for a temperature range from 20°C to 100°C. The results show in Fig. 5 linear behaviors between the resistance and the temperature of the circuit patterns by both processes. This behavior is in accordance with the literature.

Using the linear regression factor $R(T)$ obtained, the electrical voltage applied on the heater device is determined in function of the desired temperature. The temperature is selected by applying a voltage across the Pt paths of the micro heater. From the relation between resistance and temperature, it is possible to find the linear relation giving power versus temperature (Fig. 6) for both processes.

The experimental measurements have been done using a sourcemeter KEITHLEY 6430, a programmable power supply IPS-405 and HPVEE software.

As mentioned above, the experimental information obtained by the electrical and thermal calibration allowed us to know the platinum thin film parameters that were used in the thermal simulation.

**Fig. 2.** Design simulation: (a) mesh design and (b) thermal simulation.

**Fig. 3.** Degree variation in the geometry sections: (a) geometry sections, (b) plotting section X, (c) plotting section Y.
Fig. 4. Flow chart of photolithography and laser ablation processes.

Fig. 5. Linear behavior resistance versus temperature, photolithography and laser samples.

Fig. 6. Relation between the power and temperature, for both photolithography and laser processes.
In order to find the platinum thin film parameter, we used the Wiedermann–Franz equation (Eq. (2)) defined by the relationship between the thermal conductivity and the electrical conductivity. The thermal conductivity as a function of the temperature was determined by Eq. (3).

\[
\frac{1}{\sigma} = \frac{\pi^2}{3} \cdot \left( \frac{K_0}{T} \right)^2 \cdot T = \angle T
\]

\[
R(T) = \rho(T) \cdot \frac{L}{S}
\]

where \( R \) = resistance of the path, \( \rho \) = electrical resistivity, \( L \) = length of the path, \( S \) = cross section of the path, \( \sigma \) = electrical conductivity, \( \lambda \) = thermal conductivity, \( \angle \) = Lorentz number = \((\pi^2 - K^2)/(3 - 2^2)) = 2.45 \times 10^{-8} \text{ W K}^{-1} \).

Using these equations, parameters shown in Table 2 were calculated at 25 °C and 50 °C, for a platinum thin film with thickness of 200 nm.

Comparing the properties acquired after the electrical characterization, it is clear that the different sample dimensions obtained by the photolithography and laser ablation (Table 1) represent a critical factor for the final properties of the sensors, regarding directly in the sample resistance values and the parameters involved to it by Eqs. (1) and (2). In this work, as mentioned previously, the samples fabricated by classical photolithography process have been taken as references due to this is a well-known and reliable process in the sensor fabrication field.

Concerning mechanical strains, a simple deformation test of Kapton flexible substrate with thickness of 75 μm was done. The flexible substrates were placed in circular surfaces with two different diameters (\( d = 1.2 \text{ cm} \) and \( d = 0.5 \text{ cm} \)) in order to observe the electrical resistance behavior of the metal film under mechanical contraction and mechanical expansion on the electrodes. Different supply voltages were applied on the micro-heater device fabricated by photolithography and its electrical resistance variation was monitored at room temperature. Then, the obtained curves were compared (Fig. 7).

In Fig. 7, we can notice that the electrical resistances of the micro-heater path do not present an important variation compared with the flat surface neither in expansion nor contraction using a circular surface with diameter equal to 1.2 cm, indicating that either the micro-heater device calibration or the gas sensing measurement will not suffer any modification under small mechanical deformations.

However when the samples are placed in circular surface with a smaller diameter (\( d = 0.5 \text{ cm} \)), the curves obtained when the electrodes are expanded present an increment of electrical resistance around 20 Ω. In the case of the mechanical contraction with the smaller diameter the measurements could not be acquired because the electrodes had been cracked.

2.3. Sensitive material ZnO

The flexible substrates fabricated were cleaned ultrasonically in acetone and ethanol, then ZnO nanoparticle commercial ink (from Genes’ink) was deposited by drop coating and dried at room temperature. A thickness of 280 nm was measured in situ by a surface profilometer (Dektak – 6M). Finally, an annealing at 300 °C for 3 h under environmental conditions was done in order to improve the film density, the grain growth, the quality and the stability of the sensitive material.

The final sensors fabricated by photolithography and laser ablation are illustrated in Fig. 8. The small defects showed on the edge path (Fig. 8b) are caused by the splatter of laser irradiation, but these do not affect the gas responses.

Since the temperature is a critical parameter for the ZnO material sensitivity, the material sensing properties were studied by measuring the resistance response towards ozone in order to find the optimum conditions.

According with the dimensional properties of the sensor that were mentioned above, the electrode cross section is bigger by 117 mm² in the samples fabricated by laser ablation. This is giving a little increase of the surface of the ZnO sensitive film deposited.

2.4. Gas sensor experiments

The gas sensing properties were carrying out in a closed chamber using a programmable power supply to control the sample temperature; an ozone calibration source InDevR ZR Model 306 was used to produce and obtain the different oxidizing gas concentrations. The sensor responses represented by the resistance variations caused by the gas exposure in function of time, are performed by a Keithley 6430 source meter. The response monitoring is done by HPVEE software.

The ozone calibration source InDevR scrubs ozone from ambient air and produces any mixing ratio of ozone in the range 1–1000 ppb. The ozone production is done by UV photolysis of O2 at 185 nm. The ozone source makes use of a low pressure mercury lamp to photolysis oxygen and produce ozone. The vacuum UV lines are absorbed by O3 to produce oxygen atoms. The oxygen atoms attach to O2 to form O3. Absorption of one photon of light by O3 results in the formation of two ozone molecules. The ozone concentration produced in a flowing air stream depends on the photolysis lamp intensity, the oxygen concentration (determined by pressure and temperature), and the residence time in the photolysis cell (determined by volumetric flow and cell volume).

The ozone mixing ratio is controlled to be independent of ambient temperature, pressure and humidity. An important advantage of the device is that provides a known ozone concentration in ambient air containing the same level of humidity as the air sample to be measured. The Ozone source is factory calibrated against a NIST-traceable ozone standards.

The samples were tested at different temperatures from room temperature to 300 °C with different target times of the gas concentrations.

In this work, the normalized sensor response is calculated using the relation \( R_{gas}/R_{air} \), where \( R_{air} \) and \( R_{gas} \) are the sensor resistance in presence of dry air and the target gas (ozone) respectively (Fig. 9).

3. Results and discussion

3.1. ZnO morphology and crystallographic structure

In order to characterize the morphology and the crystallographic structure of the sensing material without and with annealing, a 300 nm layer of ZnO ink was dropped on glass substrate. Electron
Table 2

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Photolithography</th>
<th>Laser ablation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Resistance</td>
<td>Ω</td>
<td>147</td>
<td>238</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>[Ω·cm]</td>
<td>2.5 × 10⁻⁰⁷</td>
<td>2.6 × 10⁻⁰⁷</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>[S/m]</td>
<td>4.0 × 10⁰⁶</td>
<td>3.9 × 10⁰⁶</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>[W/mK]</td>
<td>29.31</td>
<td>30.72</td>
</tr>
</tbody>
</table>

Microscopy specimens were prepared by crushing small amount of powder in an agate mortar and dispersing in ethanol. The suspension was then dropped on a holey carbon film supported by a copper grid.

Analyses by Transmission Electron Microscopy (TEM), Energy-dispersive X-ray spectroscopy (EDS) and X-Ray Diffraction (XRD) have been performed. Electron diffraction (ED) patterns and EDS spectra were obtained with a LaB₆ FEI Tecnai transmission electron microscope (TEM) operated at 200 kV equipped with an EDAX Si (Li) detector.

TEM images in Fig. 10 present ZnO nanospheres grains with regular shapes, high density, and diameter less than 10 nm.

The ED pattern and the EDS analysis reveals polycrystalline ZnO nanospheres with hexagonal wurtzite structure P6₃mc and cell parameters: a = b = 3.22 Å, c = 5.2 Å and beta = 120° (Fig. 11).

The EDS spectrum and the quantitative analysis of ZnO nanospheres films show the presence of oxygen and zinc. The detection of copper (Cu) comes from the sample grid.

The film structure with annealing of 3 h at 300 °C was characterized by XRD on a diffractometer Panalytical Empyrean in parallel beam setting, with monochromatic Cu Kα₁ radiation (λ = 1.5406 Å). The ZnO XRD analysis indicated that the hexagonal wurtzite structure consists of a single phase with good crystallography and measurement density of 5.66 [g/cm³]. Fig. 12 shows 6 peaks belonging to ZnO crystallography orientation (reference pattern JCPDS 03-065-0523) with preferred orientation along (101) plane.

Fig. 8. Sensors fabricated on flexible substrate by: (a) photolithography and (b) laser process.

![Fig. 8](image)

Fig. 9. Ozone sensor response at 200 °C and concentration of 100 ppb.

In order to find the sample grain size, we used the Scherrer relation:

\[ D = \frac{k\lambda}{B \cos \theta} \]  

where \( \lambda \) is the wavelength of X-ray diffraction \( (\lambda = 1.54 \text{ Å}) \), \( \theta \) is the Bragg angle, \( k \) is a dimension constant which is related to the shape and distribution of crystallites \( (k \approx 0.94) \), and the \( B \) value was calculated using the procedure of the full width at half maximum (FWHM).

The average grain size calculated using Eq. (4) was found of 23 nm. Comparing with the grain size obtained from the sample without annealing, it is observed that the grain size increases with the annealing temperature, this is a typical behavior founded in the literature [33].

3.2. Working temperature

Fig. 13 illustrates the sensor response dependency with the temperature using an ozone concentration of 500 ppb, which the best gas sensing reaction is presented around 200 °C.

The critical influence of the temperature on the sensitivity arises due to several reasons. First, the charge of oxygen species adsorbed at the oxide surface depends on the temperature. At low temperature, the low response can be expected because the gas molecules do not have enough thermal energy to react with the surface absorbed oxygen species. The response increase around 200 °C can be attributed to the fact that the thermal energy obtained is high enough to overcome the activation energy barrier to the reaction and a significant increase in electron concentration resulted from the sensing reaction [34]. Secondly, since the oxidation reaction is an active process, its rate increases with temperature. Finally, the temperature dependence of the three processes occurring on the ZnO film surface: the adsorption, the desorption and the activity of the O ions. If the temperature increases, the ions activity increases as well, promoting the material sensitivity. However, the response decreases when the temperature is over the optimum temperature. This behavior occurs because in this stage the desorption activity is the main process while the activity of ions still increasing [35].
Fig. 10. TEM pictures of undoped ZnO films produced by drop coating on glass substrate with grain diameter less than 10 nm.

Fig. 11. Analysis of ZnO nanospheres films produced by drop coating on glass substrate: (a) electron diffraction (ED) pattern and (b) EDS spectrum.

3.3. Target time

The target time was determined by measuring the ozone response of 100 ppb with different exposure times. 1 min is representing the minimum time needed to obtain a reliable ozone response, and 4.5 min is representing the time to obtain the maximum response of the sensor until the response reached its flat.

Fig. 14 shows the sensor responses obtained at 200 °C using an ozone concentration of 100 ppb and different target times. Although the response obtained by exposed the sensor for 4.5 min presents a little increase of sensitivity comparing with the one exposed for 1 min, it also needs a longer recovery time. This indicates that the sensor reaches the maximum value of sensitivity in a short exposure time and it is not needed to compromise the sensor behavior.
Relying in the results, an operating temperature of 200 °C and a target time of 1 min are used in order to get a maximum sensor response avoiding the pollution and saturation of the sample.

3.4. Ozone sensor properties

After the optimized parameters of the sensors were found, several devices (fabricated by photolithography and laser) have been tested at 200 °C under different ozone concentrations during 1 min.

The sensor responses have been carried out consecutively at 500 ppb of ozone. For the samples fabricated by photolithography, it was found an average normalized response around \( R/R_0 = 10.7 \pm 0.3 \), while the sensors fabricated by laser ablation process presented an excellent normalized response of \( R/R_0 = 26 \pm 2.3 \), both with fast response and recovery time (Fig. 15).

Although the fabricated sensors show repeatability with relatively minor deviations over the replications around \( \pm 0.3 \) and \( \pm 2.3 \) between each gas exposure, they present very good normalized responses. This behavior indicates that the sensitive area under large concentration of ozone does show neither high pollution nor saturation after the gas exposure.

The samples are able to detect a wide range from 5 ppb to 300 ppm (Fig. 16). Comparing the values of the ozone responses...
in the repeatability tests, the increasing and decreasing exposures show a relatively small deviation, demonstrating an important response, a good reversibility, fast response and recovery. The limitations of part per million (ppb) levels extents the application for low vapor pressures analysis monitoring such as chemical warfare agents and explosives.

Although the responses obtained with both samples, by photolithography and laser ablation processes, present high normalized responses to different ozone concentrations, the one fabricated by laser ablation shows an increasing of response by more of two factors of magnitude; this result can be attributed directly to the different physical dimensions and parameters obtained in the sensor fabrication phase (fabrication process and sensitive material deposition). In this case, the sample fabricated by laser ablation presents bigger cross section of the ZnO film and bigger sensitivity even if the difference is relatively small (117 nm² of deviation between the samples).

3.5. Ozone sensing mechanism

In the presence of gases, the electrical conductivity of semiconductor film sensor changes due to two main reactions occurring on the surface. The gas response is related to the number of oxygen ions adsorbed on the film surface. If the film surface chemistry is favorable for adsorption, the response would be improved. This chemical reaction depends strongly on the operating temperature.

In n-type semiconductors, the majority charge carriers are electrons and when they are exposed to a reducing gas an increase of conductivity occurs. In the case of ozone as oxidizing gas, the reaction takes place directly with the oxide surface. After the gas is absorbed on the ZnO surface, the O atoms of oxidative gas molecules extract the electrons from the ZnO nanostucture; consequently the depletion layer becomes thicker due to the decreasing of the carrier concentration. Thus, the ZnO layer resistance is increased after exposure to ozone. The sensor response can be explained by the following reaction:

\[ \text{O}_3 + e^- \rightarrow \text{O}_2 + \text{O}^{ads} \]

While several experimental techniques and materials have been proposed to ozone detection [36–41], just few works with flexible substrates have been presented [15]. Kiriakidis et al. [15] presented an ozone sensor on PET substrate fabricated by magnetron sputtering and used InO₃ as sensitive material which works at room temperature showing fast response, but the assistance of UV light were applied. The devices produced in this work fabricated by photolithography and laser ablation using drop coating, do not required the exposure of an external source of light; moreover both needed shorter target times (1 min), shorter response (few seconds) and shorter recovery times (around 1 min) compared with other reported sensors fabricated on rigid substrates (2 min [20], 4 min [36] and few minutes [37]).

Furthermore, numerous experimental investigations of metal oxide materials to ozone gas detection showed a working temperatures range above 350 °C [36–41] which cannot be tolerated by most of flexible substrates. The ozone detector obtained using the drop coating process reaches the maximum response with an operating temperature of 200 °C, acquiring an excellent behavior without compromising the substrate.

Although the difference in the sensor responses with two different processes of fabrication (photolithography and laser ablation) is above two factors of magnitude, both samples show good potential for ozone monitoring, exhibiting good sensitivity, low operating temperature (200 °C), a wide range of detection (from 5 to 300 ppb) and a fast response and recovery with a target of 1 min. Additionally, the response variations between samples performed from both techniques are consequences of the dimensional differences of the path and the shape of the sensitive material; characteristics that can be controlled in further experiments as using better laser ablation parameters and improving the deposited method.

The sensing properties were also studied towards NH₃, CO and NO₂. The sensor presented a good normalized response over 50 ppm of ammonia concentration at 300 °C of \( R_0/R = 1.51 \pm 0.02 \) for the samples fabricated by photolithography and \( R_0/R = 1.21 \pm 0.01 \) for the samples fabricated by laser ablation. However, not significant responses were observed towards CO and NO₂ at operational temperatures from 25 °C to 350 °C. Temperatures over 350 °C were not studied because of the allowed operating temperatures of the flexible substrate.

4. Conclusions

Commercial ZnO nanoparticles were deposited by drop coating on flexible platforms fabricated by two different processes, classical photolithography and laser ablation processes. The detection analysis revealed that both devices represent promising ozone sensors.

The flexible substrate was designed and validated by thermal simulation presenting a homogenous temperature around the sensitive area. Comparing the properties acquired after the electrical characterizations, it is clear that the different dimensions of the samples obtained by the photolithography and laser ablation represent a critical factor for the final sensor properties. These properties regard directly in their resistance values and the parameters involved to them as the thermal and electrical conductivity.

ZnO structural properties have been reported, it was found polycrystalline film with hexagonal wurtzite structure and good crystallography. It was observed that the grain size increases with the annealing temperature: less than 10 nm for the sample without annealing and around 23 nm for the samples with annealing 3 h at 300 °C.

Although the different physical characteristics of the samples fabricated using the same substrate, at the same time and by two different methods are not high, the sensor responses increase for the one obtained by laser ablation process. These results expose the critical relation between the initial parameters (electrode path dimensions, sensitive film distribution and thickness, operating temperature, etc.) and the final properties of the sensor.

All samples present a wide ozone detection range from 5 ppb to 300 ppb using a relatively low operating temperature (200 °C), with very good and fast response and recovery time, an excellent response at different ozone concentrations without presence of high pollution on the sensitive film and not requirement of external stimulus for response and recovery.

These simple and efficient fabrication methods demonstrate the wide prospective of utilizing these processes and materials as ozone gas sensors on flexible substrates for a variety of applications, especially those requiring low processing cost, low temperature, high reliability, good efficiency and environmentally friendly.

Acknowledgments

The first author would like to acknowledge the research grant of CONACyT-MX (214895/310187). In the same manner the authors would like to acknowledge to A. Combes for his technical support in this work.

References

sensors, temperature

time

gas

printing


Information on: http://www.epa.gov/air/criteria.html


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