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

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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.

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, WO_3, ITO, SnO_2, TiO_2, 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 g gases (NO_2, NO, N_2O, CO_2, O_3) and reducing gases (H_2S, CO, NH_3, CH_4, SO_2) [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

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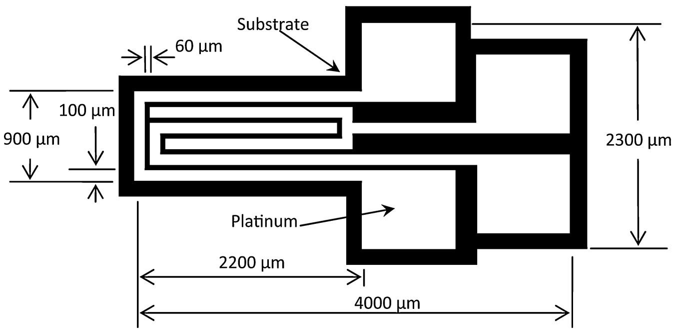

Fig. 1. Layout design of the flexible sensor.

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 μm. 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 path fabrication. 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.

Table 1
Characteristics comparison for the electrodes fabricated by photolithography and laser ablation.

Characteristic	Photolithography	Laser ablation
Thickness Ti/Pt (*th*)	100 nm	100 nm
Electrode length (*L*)	100 μm	90 μm
Heater device lenght (*l*)	5.91 mm	5.36 mm
Pt film cross section (S_f)	10 pm^2	9 pm^2
Electrode cross section (S_e)	1.87 μm^2	1.98 μm^2

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 $\sigma = 3.01E+06$ S/m, an electrical resistivity $\rho = 3.33E{-}07\ \Omega$ 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 homogenous 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 interdigited 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