Selective GAS sensor based on screen-printed ZNO nanorods
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1) Context / Study motivation

Screen-printing processes offer many advantages in precise control of thickness and chemical composition of films, totally compatible with MEMS technology, and low-cost for large-scale production. This technique is widely used in the field of gas sensors since many years [1,2] but mostly used to elaborate thick films for heating resistance than sensing element based on semiconducting oxides.

Metal oxide thin film sensors have been widely used for gas sensing applications thanks to their sensitivity toward a large variety of gases [3], but they suffer from a lack of selectivity.

One method to overcome this problem consists in using a temperature modulation of the sensor, by changing the power consumption [4,5]. This kind of profile allows fast chemical reaction changes, and consequently fast gas sensitivities changes while maintaining the integrity of the material.

This work demonstrates the feasibility of well controlled films of a ZnO nanostructured sensing material deposited by screen printing technique on microhotplate and the sensing performances by using specific profile associated to the temperature and bias current modulation.

2) Description of sensor technology

The tested devices have been developed on an optimized microhotplate that can work at high temperature and low power consumption (500°C, 55mW). The platform consists of a silicon bulk on which a thermally resistive bilayer SiO2/SiNx membrane was grown. Afterwards, Ti/Pt metallization was realized by lift-off to define heating resistor and the sensing resistor. SiO2 passivation layer was previously sputtered in order to electrically isolate the two electrodes. Finally, the rear side of the bulk was etched to release the membrane in order to increase the thermal resistance and then to limit thermal dissipation (Figure 1).

ZnO nanorods sensitive material was prepared by an organometallic approach [6]. ZnO ink was prepared with organic vehicle and thin films were deposited using an automatic DEK horizon screen-printing machine through a polyester mask. After deposition, the films were left 24h at room temperature and then annealed under ambient air at 500°C during 2 h.

Chips were then diced one by one using a diamond blade dicing method and packaged in TO-5 can, and then aluminum wires were wire-bonded between Pt metal pad on the microhotplate and the TO-5 pad in for electrical connections.

The response $S$ (%) toward different gases is defined by the following equation (1):

$$S(\%) = \left( \frac{R_{gas} - R_{air}}{R_{air}} \right) \times 100$$  \hspace{1cm} (1)

3) Results / Conclusions / Perspectives

Screen printed ZnO nanorods thin films were analyzed using a classic SEM S4800 (Figure 2). After annealing at 500°C the morphology of the nanorods still remains the same; 200nm in length and 10nm in width.

According to previous study [5], Figure 3 shows the profile that allows good reproducibility, fast stabilization and best sensing performances. This profile includes power (temperature) and bias current changes. This profile generates a huge amount of information, thus only 3 gases at 1 concentration (CO [300ppm], NH3 [5ppm] and NO2 [0.2ppm]), 2 temperatures from the profile (500 and 200°C) and 2 bias current (1 and 10µA) will be considered.

The variation of the bias current leads to several phenomena. On the Figure 4, at 1µA (hatched surface), decrease the temperature increases the response to CO. The opposite is observed at 10µA. At 500°C (red surface) and whatever the bias current applied, there is no influence observed for NH3 and NO2 detection. However, at 200°C (blue surface) the response to NO2 is ten times increased with a higher current and an inversion of the signal occurs for NH3 at 10µA.

The principal component analysis (PCA) algorithm is a popular technique for reducing the dimensionality of data [7]. Thus, PCA was performed using sensor responses for ZnO nanorods to each gas. Figure 5 displays a visual appraisal of the discrimination of each gas.

In conclusion, thin films of ZnO nanorods have been synthetized by an organometallic route and deposited by screen printing method onto the microsystems. Since the sensor temperature is not permanently at high operating temperature, sensor defects caused by diffusion and chemical reactions are less likely, the sensor lifetime may possibly be increased. Moreover, thanks to electrical control, the obtained sensor displays an enhanced selectivity toward CO, NH3 and NO2 gases. Furthermore, this work highlights the potential application of a low cost sensor array based on several metal oxide sensors in discriminating toxic and pollutants gases leading to an effective way to achieve high selectivity.
Pt metallization  Sensing layer

Figure 1: Top view (left) and cross section (right) of the micromachined device

Figure 2. SEM image of screen printed ZnO nanorod

Figure 3. Power consumption and bias current profiles applied to the sensor

Figure 4. Normalized responses of screen printed ZnO nanorods towards 3 gases with 2 bias currents applied

Figure 5. Principal Component Analysis

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