Sputtered and screen-printed metal oxide-based integrated microsensor arrays for the quantitative analysis of gas mixtures

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Received 16 September 2003; received in revised form 20 January 2004; accepted 10 February 2004
Available online 28 March 2004

Abstract

Either by screen-printing or sputtering, sensitive layers of tin oxide were deposited on silicon micromachined substrates (four-element integrated microarrays). The procedures allow the deposition of sensing layers before membranes have been etched, which leads to gas micro-sensors with an excellent fabrication yield. The response of the different microarrays to ethanol, acetone and ammonia vapours and their binary mixtures was studied. The influence of ambient humidity was also investigated. By using an integrated array of four integrated microsensors operated at two different temperatures and a fuzzy ARTMAP neural network, it was possible to simultaneously identify and quantify the different species (success rate was 100%). These results confirm the viability of the techniques introduced to obtain micromachined sensors suitable for battery-powered gas/vapour monitors.

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Keywords: Tin oxide; r.f. sputtering; Screen-printing; Integrated microarray; Micro-hotplate; Quantitative gas analysis

1. Introduction

Semiconductor oxides such as SnO₂ or WO₃ are commonly used as sensing materials in metal oxide gas sensors. These devices are typically operated at elevated temperatures (above 300 °C), to activate the reactions that are responsible for the sensor response. One important drawback of these devices is that they are responsive to a wide spectrum of reducing and oxidising gases. Different methods to enhance the selectivity of metal oxide gas sensors have been introduced. The most widespread strategy consists of using an array of different metal oxide sensors with partially overlapping sensitivities and a pattern recognition engine to analyse the response patterns from the sensor array. This is based on the fact that a sensor array can provide a specific and unique response pattern for different individual chemical species or mixture of species [1–3].

In the last years, microsystem technology has been applied to develop substrates for integrated gas sensor arrays. The use of microsystem technology and, particularly, of conventional silicon micromachining offers all the advantages that typically characterise integrated circuits such as low cost, small size and low power consumption. The sensitive layer of micromachined metal oxide gas sensors is deposited onto a thin dielectric membrane of low thermal conductivity which provides good thermal insulation between the substrate and the gas-sensitive heated area on the membrane. In this way, the power consumption is kept low (typical values obtained lay in the range between 30 and 150 mW for normal operating conditions [4–9]). An important issue in the fabrication of integrated arrays of micromachined gas sensors is the method used to deposit the active films onto the sensor membranes. Different methods have been envisaged for the deposition of either thin or thick metal oxide films. These include physical and chemical vapour deposition for the formation of thin films [10] and drop-coating [11], pulverisation [12], spin coating [13,14] and screen-printing [15] to obtain thick-films. Physical or chemical vapour deposition lead to compact films (i.e. with low surface to volume ratio), which results in a reduced sensitivity. The drop-coating method still remains a manual process with inherent reproducibility problems. In the methods leading to thick-films reported above, the active film is deposited after the membrane has been etched, which may result in a significant number of membranes damaged after film deposition.

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is unacceptable in the fabrication of integrated arrays of micro-machined gas sensors, because the damaging of a single membrane would invalidate the whole device.

Recently, we described a deposition method based on screen-printing to obtain active layers before the membranes had been etched, which resulted in integrated microarrays with very high fabrication yield [16]. In this work we further extend this approach to film deposition by r.f. magnetron sputtering. The usefulness of both active-film deposition methods (screen printing and r.f. sputtering) in terms of fabrication yield, sensor performance and compatibility with conventional microelectronic technology is demonstrated.

A comparison between the two deposition methods is made through the analysis of vapours and vapour mixtures using four-element integrated microarrays.

2. Integrated micro-sensor arrays

The integrated micro-hotplates arrays with arrays of four microsensors were fabricated on double-side polished p-type (100) Si substrates 300 μm thick [17,18]. The structure of the device basically consists of a gas sensing layer, the electrodes, insulating layers and a polysilicon heater. The technological process needed to fabricate the sensors had the following steps. (1) Deposition of the membrane layer. Membranes consisted of a 0.3 μm thick SiNx layer grown by LPCVD. Each chip had four membranes, the size of which was 900 μm × 900 μm. (2) Deposition and patterning of a POCl3-doped polysilicon heating meander of 6 Ω/sq. The temperature coefficient of resistivity (TCR) was 6.79 × 10⁻³ C⁻¹. The heater is used as a temperature sensor. (3) Deposition of a 0.8 μm thick SiO2 layer to insulate the heater from the electrodes and the sensing film. (4) Opening of contacts for the heater bonding pads to be accessible. (5) Deposition of either parallel or interdigitated 0.2 μm thick Pt electrodes, patterned by lift-off. The electrode area was 400 μm × 400 μm with an inter-electrode distance of 50 μm. Each integrated microarray has two sensors with parallel electrodes and two sensors with interdigitated ones. (6) Patterning of the backside etch mask. (7) Deposition of the sensing layer onto the electrode area. (8) Backside silicon etching with KOH to create the thermally-insulated membranes. (9) Wire bonding and packaging.

The deposition of the active films was either by screen-printing or by r.f. magnetron sputtering. The deposition details are as mentioned below.

The screen-printed sensing layer consisted of a 5 μm thick SnO2 commercially available nanopowder, with grain size near 18 nm (Aldrich 549657). A printable paste with excellent viscosity was prepared by using an organic vehicle based on terpineol, ethylcellulose, texaphor and rilanit. The paste was printed onto the semi-processed wafers by using a high precision screen-printing machine that allows one-side mask alignment. Wafers were subsequently dried for 15 min at 125 °C for the organic vehicle to be completely removed, and then fired for 1 h in a belt furnace at a single level of temperature, equal to 600 °C.

The sputtering was done on semi-processed wafers using a metallic Sn target at ambient temperature. Pressure was set to 5 × 10⁻³ mbar, and gas flow was set to O2 = 6 sccm, Ar = 6 sccm. After deposition, wafers were annealed in air for 2 h at 400 °C.

Sputtered or screen-printed wafers were then ready for backside etching, dicing and packaging (see Fig. 1). The screen-printing or the sputtering were made before backside silicon etching and packaging. This procedure avoids damaging the sensor membranes and thus leads to an excellent yield (>95%).

3. Experimental

The morphology and composition of the screen-printed sensing layers was investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The specimens were coated previously with a thin (around 20 nm) gold layer, which was sputtered on top of the samples to avoid charging effects. Specimens were observed at accelerating voltages ≤20 kV using a JSM 6400 field emission scanning electron microscope. The sputtered samples were studied by atomic force microscopy (AFM) and EDX. The AFM was accomplished in a D3 100 from Digital Instruments, using a triangular shaped (0.06 N/m) Si3N4 cantilever tip in contact mode.

The sensitivity of the sensors to vapours of acetone, ethanol, ammonia and their binary mixtures diluted in air was studied. Repeatable concentrations of these vapours were delivered to the 10 ml test chamber at a fixed flow rate of 100 ml/min. Humidity was kept constant at 20% R.H. (measured at 30 ± 1 °C) during all the measurement process.
The sensors were operated at three different temperatures between 110 and 480 °C. Before the measurements were started, the sensors were kept at the maximum temperature for 8 h. The operating temperature of the microsensors was set by applying a current to their polysilicon heating resistor. The measurement process was as follows: Data acquisition started 40 s before the volatiles were injected into the sensor chamber (initially clean air flowed through the chamber, so the baseline sensor resistance could be recorded). An automatic static headspace sampling system injected a sample of the volatiles in the air flow (see Fig. 2). The sensors detected the volatiles, which produced a sharp decrease in their resistance, and soon after their resistance increased towards the baseline value (after the volatiles had crossed the sensor chamber, the sensors were in the presence of clean air again). Every measurement took 10 min to complete. The sensitivity of eight microsensors was studied (i.e. four screen-printed tin oxide sensors and four r.f. sputtered tin oxide sensors). Table 1 summarises the different measurements performed. Each measurement was replicated five times. The concentrations of the single gases and gas mixtures shown in Table 1 were estimated by injecting the samples delivered by the headspace autosampler into a calibrated GC–MS system (Shimadzu, Inc.). Finally, the response of the sensors to different levels of moisture (varying between 10 and 70% R.H. at 30 °C) in air was also investigated. For this purpose, a computer driven system was used to inject a continuous flow of humidified air into the sensor chamber.

### 4. Morphology, composition and gas sensitivity results

AFM, SEM and EDX were used to study the morphology and composition of the films. For the screen-printed films, grain size was below 40 nm. Grains form agglomerates which create a porous layer. For the sputtered films, grain size was around 80 nm. SEM and AFM showed that the sputtered films were more compact than the screen-printed ones (see Fig. 3). EDX analysis showed that the grains and the bottom of the voids contained tin (the EDX equipment is not suitable for detecting the presence of oxygen).

The sensitivity to different concentrations of ethanol, acetone and ammonia vapours (single gases and binary mixtures) was studied at different operating temperatures. The sensor response was calculated as the ratio \( R_a / R_g \), where \( R_a \) is the resistance of the sensor in the presence of clean air (20% R.H., 30 °C) and \( R_g \) is the sensor resistance in the presence of a diluted volatile. Fig. 4 summarises the results of the sensitivity study. Operating temperatures were 110, 200 and 380 °C for interdigitated electrodes and 150, 250 and 480 °C for parallel ones. Differences in operating temperatures are due to the fact that membranes with parallel and interdigitated electrodes had different values of the heating polysilicon resistors (i.e. 600 and 700 Ω for interdigitated and parallel electrodes, respectively) and the same heating current was injected to these resistors. The power consumption of the membranes operated at 480 °C was around 80 mW.
Devices with interdigitated electrodes have higher sensitivities at lower operating temperatures than those with parallel electrodes. The sputtered sensors showed more repeatability than the screen printed sensors: for each vapour or mixture and concentration measured, the ratio between standard deviation of the response and its mean (over five replicate measurements) was below $4.6 \times 10^{-2}$ and $1.1 \times 10^{-1}$ for the sputtered and screen printed sensors, respectively. The lower this ratio is, the better the repeatability.

The response of the sensors to variations in the ambient moisture was also studied. It was observed that the sensor resistance decreased when the relative humidity was increased (see Fig. 5). Furthermore, when the sensors were operated at higher temperatures, the change in their resistance caused by a change in the moisture level was higher. Fig. 5 shows the ratio between the resistance of the sensors at 10% R.H. (this humidity level is taken as a reference value) and the values for different humidity levels (up to 70% R.H.). From Fig. 5, it can be derived that the devices with screen-printed active layers are more affected by changes in the moisture level than the sputtered ones. These results are in accordance with previous studies on sputtered and screen-printed tin oxide gas sensors [20]. However, the response to moisture can be considered as moderate, when compared to the sensitivities found for the different vapours studied.

5. Gas analysis using integrated microarrays

Qualitative and quantitative analysis of the vapours were performed using PCA and a fuzzy ARTMAP [21,22] neural network, respectively. These PARC methods were implemented using standard functions from MATLAB [23,24]. The interdigitated electrode sensors were operated at 380 °C and the parallel electrode sensors at 480 °C.

Prior to perform the principal component analysis, the data were mean-centred. This is a usual pre-processing method considering that all the sensors were of similar nature. Two PCA were performed, one using the responses of a four-element screen-printed microarray and the other one using the responses of a four-element sputtered microarray. For each measurement, the feature extracted from the response of each sensor within the microarray was the conductance change: $\Delta G = 1/R_s - 1/R_a$. For each microarray, the response features were gathered to form a response matrix. Each response matrix had four columns (one column per sensor within the array) and 90 rows, which corresponded to the number of measurements (three single vapors + three binary mixtures) × three different concentrations × five replicates per measurement). In either case, the first two principal components accounted for more than 90% of the variance in the mean-centred data. Fig. 6 shows the results of the PCA performed on the responses of the sputtered microarray. Measurements belonging to the same vapour (or vapour mixture) cluster together in the score plot. Furthermore, clusters are formed according to vapour concentration,
Fig. 4. Sensitivity to: (a) simple gases and (b) binary mixtures. Plots on the left column are for sputtered sensors, plots on the right column are for screen-printed sensors.
Fig. 4. (Continued).
this shows that it would be possible to identify and quantify the samples. The results of the PCA performed on the responses of the screen-printed microarray are very similar to the ones obtained for the sputtered one. However, since the screen-printed sensors are far more sensitive to ammonia vapours than to acetone or ethanol vapours, the clusters for binary mixtures containing ammonia are always very near to the clusters corresponding to ammonia vapours.

The quantitative analysis consisted in a 18-category classification (six species and binary mixtures $\times$ three concentrations). Since either the response (conductance change) of the four sputtered or the four screen-printed sensors were used, the neural networks had four input neurones and 18 output neurones. Since each measurement was replicated five times, a total of 90 measurements were available to train and validate the networks. A leave-one-out cross-validation and the bootstrap method [25] were implemented to estimate the performance of the neural networks. With the leave-one-out, the networks were trained 90 times using 89 measurements and tested against the measurement left out. The performance of a network was estimated as the average over the 90 tests. To implement the bootstrap method, 50 training sets were formed by selecting 90 measurements at random with replacement from the data matrix. For each training set, its corresponding test set was formed by those measurements not found in the training set. The performance of the fuzzy ARTMAP method was defined as the average performance over the 50 tests. The results for the leave-one-out cross-validation were as follows: when the responses of the four screen-printed sensors were input to the network an 89% success rate in vapour identification and 82.3% in quantification were reached. On the other hand, when the responses of the four r.f.
sputtered sensors were input to the network, 100% success rates in vapour recognition and concentration estimation were reached. The results of the bootstrap method used to estimate the performance in the simultaneous recognition and quantification of vapours are summarised in Table 2. These results are very similar to the performances estimated using the leave-one-out approach.

6. Conclusions

We have reported on two methods (r.f. sputtering and adapted screen-printing) to deposit sensing films onto integrated microarrays. The films are deposited before the membranes of the integrated micro-hotplates are etched. This avoids damaging the membranes during film deposition, which results in a high fabrication yield. The different single vapors and vapor mixtures measured could be discriminated and quantified with high success rates using an integrated microarray of four sensors operated at two different temperatures. These results confirm the viability of the fabrication techniques introduced in this study. Thus, resistive gas sensors based on different metal oxides, screen-printed or sputtered on micro-hotplates show a very attractive potential for hand-held gas/vapour monitors.

Acknowledgements

This work was funded in part by the Spanish Commission for Science and Technology (CICYT) under Grant no. TIC2000-1598-C02.

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