Structural and dimensional control in micromachined integrated solid state gas sensors

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Abstract

The application of electron microscopy for quality control in the fabrication of solid state integrated tin oxide gas sensors is described. Among the parameters that influence the performance and mechanical stability of these devices are the thickness, grain size, porosity and point defect oxygen vacancy distribution of the active SnO2 layer and the intrinsic stresses and interfacial adhesion in the support layers. The sputtered SnO2 films were highly crystalline with a columnar growth structure and equiaxed grains of mean diameter of 10 nm. HREM studies revealed evidence of CSP defects, which act as traps for free carriers and can therefore be expected to influence the conductivity of the oxide layer. Increasing the thickness of the film from 300 to 600 nm lead to an increase in the sensitivity to low concentrations of NO2 (~1 ppm) by up to a factor of two. Sensitivity is also affected by surface roughness and film porosity, which increase the effective area on which gas molecules can be adsorbed. ©2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Solid state technology may be employed to fabricate integrated tin oxide gas sensors consisting of several individual microsensor elements on a single silicon chip. The advantages of applying micromachined fabrication technology in the manufacture of sensor devices include reduced costs, small dimensions, low power consumption and the possibility of designing compact sensor arrays [1]. Furthermore, the use of silicon micromachining techniques allows thermally isolated structures to be fabricated, in order to minimize the heat dissipation from the sensor elements. However, in common with the manufacturing of other microelectronic devices, appropriate quality control procedures are necessary to ensure reproducibility and reliability. Electron microscopy is useful for this task and is also a suitable technique for investigating the effect of the technological processes on the microstructure of the SnO2 film, which acts as the gas-sensing layer. The most important parameters of interest are the grain diameter, growth structure, porosity and surface roughness of the oxide layer and the mechanical stresses present in the underlying layers. An additional factor that strongly affects the reliability of the device is the quality of the inter-layer adhesion, which is influenced by the choice of the membrane material.

2. Device fabrication

An integrated sensor with an array of eight microsensor elements was designed using finite element analysis, to achieve reduced power consumption, and constructed using microelectronic fabrication technology [1]. The sensor array is illustrated in Fig. 1: the sensing elements are deposited on thermally isolated membranes of two different sizes and with two different heater patterns. The active
Fig. 1. The solid state integrated microsensor array: sensors 1 and 3 have large area membranes and meander heater patterns; sensors 2 and 4 have large area membranes and loop heater patterns; sensors 6, 7 and 9 have small area membranes and meander heater patterns; sensor 8 has a small area membrane and a loop heater pattern.

The area of each microsensor element was 500 \times 500 \, \mu m and the finished chip was mounted on a standard TO-8 package. From the finite element thermal simulations [2], the minimum practical dimensions of the Si$_3$N$_4$ dielectric membrane that acts as the support for the microsensor were determined to be 900 \times 900 \, \mu m. Membranes of both this size and a slightly larger one of 1100 \times 1100 \, \mu m were used in the present chip. Si$_3$N$_4$ was chosen in preference over SiO$_2$ as the membrane material, despite the lower thermal conductivity of the latter, because it allows thinner membranes to be employed and therefore lower power consumption to be achieved.

Each microsensor consists of the gas-sensing layer, Pt/Cr electrodes, an insulating layer and a polysilicon heater [3–5]. The principal technological processing steps involved in fabrication are as follows: (1) deposition of the membrane layer (Si$_3$N$_4$); (2) deposition and patterning of the polysilicon heater; (3) deposition of an SiO$_2$ insulating layer; (4) contact opening; (5) deposition and patterning of the electrodes; (6) patterning of the rear side etching mask; (7) deposition and patterning of the sensing layer; (8) rear side silicon etching; (9) packaging. The main processing steps are outlined schematically in Fig. 2. A more detailed description of the various processing steps can be found in a previous publication [6].

The devices were fabricated on 300-\mu m thick p-type (100) Si substrates. A 200- or 300-nm thick layer of LPCVD Si$_3$N$_4$, implanted with boron to reduce its inherent internal stress, was used as the membrane material. The resistance heater consisted of a 480-nm layer of POCl$_3$-doped polysilicon of resistivity 20 $\Omega$ cm, with either a meander or loop pattern, that also acted as the temperature sensor. A 500-nm layer of amorphous SiO$_2$ was used to provide the electrical insulation between the resistance heater and the gas-sensing layer. The Cr/Pt electrodes were of 350-nm thickness, with interdigitated layouts, deposited by sputtering. These are found to give better reliability than pure Pt and are resistant to oxidation up to the maximum operating temperature of 350°C. The SnO$_2$ films of 300-, 400- or 600-nm thickness, were grown by reactive r.f. sputtering at room temperature, from an SnO$_2$ target, under a 10%:90% oxygen–argon atmosphere at a total pressure of 0.5 Pa. After lift-off processing, the completed devices were subjected to a final annealing at 500°C for 4 h in air. Subsequently, bulk silicon micromachining was carried out from the rear side using KOH at a temperature of 70°C.

3. Device testing and electron microscopy

The sensitivity of the microsensors to low concentrations of NO$_2$ in artificial air was determined by measuring the change in resistance at a constant flow rate of 200 ml/min in a stainless steel test chamber. Gas concentrations were predetermined by mass-flow controllers and the exposure time to NO$_2$ was 10 min in each case. Measurements were made at 250°C, the temperature that was previously found to give the highest sensitivity to NO$_2$ [6].

Scanning and transmission electron microscopy were used to investigate the effect of processing and material variables on the mechanical stability of the layers that provide the support structure for the tin oxide film, as well as the structure of the film itself. Because of the low threshold for electron beam damage in CMOS devices, and to avoid surface charging effects, it was necessary to

Fig. 2. Main technological processing steps involved in the fabrication of an individual microsensor element: deposition of the polysilicon heater and interlevel oxide layer; deposition of the electrodes and contacts; deposition of the SnO$_2$ layer, rear side etching of the substrate.
perform scanning electron microscopy at accelerating voltages of <2 kV. The specimens were observed without coating with a metallized layer or other prior preparation using a JEOL 6400F field emission scanning electron microscope.

Cross-sectional specimens for transmission electron microscopy (TEM) were prepared by embedding the silicon substrate, sectioning with a diamond saw, mechanical grinding and low angle ion beam milling with 3–5-keV argon ions, following the procedure described by Alani and Swann [7]. Conventional transmission electron microscopy (CTEM) was performed at an accelerating voltage of 200 kV using a JEOL 200CX microscope, while high resolution transmission electron microscopy (HRTEM) was carried out using a JEOL 3010 instrument operated at 300 kV.

4. Results

High sensitivities and rapid response times have been obtained using sensor devices of this sort for the detection of NO\(_2\), CO and toluene at low concentrations in air [6,8]. Discrimination between the various gases in a mixture is improved, because with this type of device, it is possible to heat each sensor element to a different, uniform operating temperature and to achieve high operating temperatures with low power consumption. The power consumption depends on the thickness, lateral dimensions and material of the membrane (~50 MW at a temperature of 350°C for \(\text{Si}_3\text{N}_4\) [6], compared with a value of ~180 MW reported for an \(\text{SnO}_2\) microsensor of different design [3].

Test results for NO\(_2\) in artificial air using sensor elements with an \(\text{SnO}_2\) layer of 300-, 400- and 600-nm thickness, operated at 250°C, are compared in Table 1. The sensitivity \(S(R/R_0)\) increases significantly with increasing layer thickness. It has previously been demonstrated that the effect of the thickness of the \(\text{SnO}_2\) layer is more important than that of membrane size or that of the heater pattern [6]. The times to reach equilibrium and for recovery after exposure to the gas were typically ~3 min.

Fig. 3 shows a scanning electron micrograph (secondary electron image) of the \(\text{SnO}_2\) film. Surface steps, corresponding to the meander pattern of the underlying polysilicon heater, and sub-micrometre diameter porosity are visible in this layer. The width of the surface steps is approximately 8 \(\mu\)m. The surface of the tin oxide layer, shown in more detail in Fig. 4, exhibits roughness on the scale of ~1 \(\mu\)m, comparable to that observed in films deposited on polycrystalline alumina substrates under the same conditions [9]. This texture is similar in appearance to the characteristic dome structure described by Movchan and Demchishin [10] for vacuum-evaporated ZrO\(_2\) and Al\(_2\)O\(_3\) condensed on substrates at homologous temperatures below 0.22–0.26.

Fig. 5 shows a CTEM image of a cross-section through a microsensor and selected area diffraction (SAD) patterns

<table>
<thead>
<tr>
<th>NO(_2) (ppm)</th>
<th>300 nm</th>
<th>400 nm</th>
<th>600 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>78</td>
<td>110</td>
<td>180</td>
</tr>
<tr>
<td>1.0</td>
<td>151</td>
<td>205</td>
<td>310</td>
</tr>
<tr>
<td>1.5</td>
<td>197</td>
<td>275</td>
<td>330</td>
</tr>
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obtained from the tin oxide and polysilicon layers. The thickness of the SnO$_2$ layer is $\sim 300$ nm and the mean grain size is $\sim 10$ nm. A columnar growth structure is evident, but the diffraction pattern does not indicate any evidence of a pronounced preferential orientation. The mean grain diameter in the polysilicon layer is 300–500 nm, with the crystals tending to be elongated in the direction parallel to the substrate. An intermediate layer of amorphous SiO$_2$ between the polysilicon heater and the SnO$_2$ layer provides electrical insulation and a smooth interface that promotes good adhesion of the sputtered film. The Si$_3$N$_4$ membrane, which is $\sim 300$-nm thick in this microsensor, is amorphous and apparently free from internal stress. Adhesion between the polysilicon heater and the membrane is excellent.

Fig. 6 shows an HRTEM image obtained from a crystallite in the r.f. sputtered SnO$_2$ layer, revealing the presence of fine scale (011) twinning and/or crystallographic shear plane (CSP) faults. CSP can be distinguished from fine 011 twins due to the 1/2(011) displacement of the (110) lattice planes, associated with a missing plane of oxygen atoms in the cassiterite crystal structure. The films were almost perfectly crystalline; grain boundary disorder extended over a distance of typically no more than 1 nm from the interface.

5. Discussion

The sensitivity of SnO$_2$ gas sensors is strongly dependent on the grain size and surface morphology of the oxide layer, since these parameters influence the effective surface area on which gas molecules can be adsorbed [11]. Porous columnar films with ultra-fine grain sizes have higher sensitivities and lower optimum operating temperatures [12]. These sputtered films have smaller grain sizes and a higher degree of crystallinity than those deposited by spraying [13] or CVD [14,15]. AFM measurements of films deposited under similar conditions on polycrystalline alumina substrates [9] have shown that surface roughness can lead to an increase of the effective surface area of the film by a factor of $\sim 2$.

Localized non-stoichiometry due to the presence of CSP defects provides traps for free carriers that modify the
electrical conductivity of the oxide layer [16,17] and therefore may be expected to influence the gas sensitivity. CSP have been observed in SnO films deposited on NaCl monocrystalline substrates by electron beam evaporation and subsequent annealing [17]. XPS analyses [18] have indicated that the r.f. sputtered films are slightly understoichiometric.

The LPCVD Si$_3$N$_4$ membrane has a smooth surface that does not significantly affect the morphology of the interfaces between the overlying layers. Implantation of boron ions is successful in compensating the effect of intrinsic tensile stresses in the Si$_3$N$_4$ layer. Hall effect measurements have demonstrated that the carrier mobility, $\mu_H$, in sputtered SnO layers varies from $0.1-10$ cm$^2$ V$^{-1}$ s$^{-1}$, at a temperature of 200°C, depending on the type of growth structure [19]. Values of $\mu_H$ measured in SnO layers deposited under similar conditions to the present ones were $2-3$ cm$^2$ V$^{-1}$ s$^{-1}$ [20]. This range is consistent with the columnar growth structure observed by electron microscopy.

6. Conclusion

It has been demonstrated that it is possible to combine the techniques of microelectronic fabrication with thin film technology (sputter deposition) to produce low cost, compact, miniaturized sensor arrays with reproducible dimensions and structure. The sensitivity of these devices to NO$_2$ concentrations at the $\sim 1$-ppm level is dependent mainly on the thickness of the active SnO$_2$ layer. Surface roughness and film porosity may also play a significant role by increasing the effective area on which adsorption of gas molecules may occur. It is therefore important to control these microstructural and morphological features in order to ensure reproducibility of sensor response.

References


Biographies

Dr. David Rickerby obtained his PhD in Physics at the University of Cambridge in 1978. He spent 3 years as a research fellow at the Pennsylvania State University and is currently head of the electron microscopy group at JRC Ispra.

Norbert Wächter has been a senior technician in the electron microscopy group at JRC Ispra since 1985. He is responsible for developing specimen preparation techniques and equipment for electronic materials and thin films.

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Prof. Javier Gutiérrez is Director of the Laboratorio de Sensores of CSIC Madrid. His research interests include semiconductor sensor devices applied to environmental monitoring, metrology and instrumentation.

Dr. Isabel Gracia joined CNM in 1986 to work on photolithography. In 1993, she received her PhD in Physics at the Universitat Autònoma de Barcelona for work on chemical sensors, her current research field.

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