MICROMECHANICAL CHEMICAL SENSOR

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In the human life, there are several areas, where chemical sensors are necessary. Such are medical care and analysis, breath analyzers, food control, wine aroma analysis, ecological air analysis, alcohol tests, technological gas and atmosphere analysis etc. In recent years, interest has grown in developing of an electronic "nose", capable of detecting mixed gases and even odors.

There are several different ways to make such chemical sensors. One of them is to use chemical sensitive material to analyze the presence and the quantity of some gaseous component in the technological or surrounding atmosphere.

In the last 5 – 10 years, in Micro Electro Mechanical Systems (MEMS), one of the most frequently used materials is Tin Oxide (SnO_2). This is semiconductor metal-oxide material, which change its surface and near surface conductivity, depending on the type and the quantity of the gaseous components of the atmosphere. It could be used for detecting very small quantities (ppm range) of such gases like CO, H_2, NO, NO_2, H_2S, CH_4, C_2H_5OH etc.

There are different technological ways for creation of SnO_2 layers. They could be made using Thin Film Technologies (Vacuum Evaporation, Sputtering in Vacuum), Chemical Vapor Deposition, Thick Film Technologies (Screen Printing), Sol–Gel Process etc.

Depending on the working temperature and the kind of impurities, these structures have different sensitivity and selectivity to different gases. Except gas–sensing layer, in the structure have to be included also a heating element and a temperature sensing element, like microhotplate (MHP).

INTRODUCTION

Chemical sensors usually consist of a sensitive layer or coating and a transducer [3], [4]. Upon interaction with a chemical species (absorption, chemical reaction, charge transfer, etc.), the physicochemical properties of the coating, such as its mass, volume, optical properties, resistance etc. reversibly change. In the sensitive layer, these changes are detected by transducer and transformed into an electrical signal, such as frequency, current or voltage, which is then read out and subjected to further data treatment and processing.

Various inorganic and organic materials can be coated onto different transducers [3]–[5] and serve as chemically sensitive layers. Typical inorganic materials include electron-conducting oxides like tin dioxide (SnO_2) for monitoring reducing gases such as hydrogen, carbon monoxide, and nitrogen oxides. Ion-conducting oxides like zirconium dioxide (ZrO_2) are applied to determine oxygen, but also nitrogen oxide and ammonia. Organic layers, mostly consisting of conducting or nonconducting polymers such as polysiloxanes, polyurethanes or polyaniline, are used for monitoring hydrocarbons, halogenated compounds, and other kinds of toxic volatile organics [3]–[5]. The different sensitive materials and their operation conditions, such as elevated temperature, impose certain requirements on the transducer design. Specific chemically sensitive materials will hence be mentioned in the context of the corresponding transducer structures in the following sections.

A variety of transducers, based on different physical principles have been devised. Following the suggestion of Janata, chemical sensors can be classified into four principal categories, according to their transduction principles [4], [5]:

1) chemomechanical or mass-sensitive sensors (e.g., mass changes upon absorption);

2) thermal sensors (e.g., temperature changes through chemical interaction);

3) optical sensors (e.g., changes of light intensity by absorption);

4) electrochemical sensors (e.g., changes of potential or resistance through charge transfer).

CHEMOMECHANICAL or MASS-SENSITIVE SENSORS

Chemomechanical sensors are in the simplest case, e.g. gravimetric sensors responding to the mass of species accumulated in a sensing layer [4]. Some of the sensor devices additionally respond to changes in a variety of other mechanical properties of solid or fluid media in contact with their surface, such as polymer elastic module, liquid density, and viscosity [4].

Mass changes can be monitored by either deflecting a micromechanical structure due to stress changes or mass-loading (static measurements), by frequency changes of a resonating structure, or a traveling acoustic wave upon mass loading.

Cantilevers: A mass-sensitive cantilever usually is a layered structure (Fig.1) composed of, e.g. silicon, silicon oxide/nitride, and, eventually, metallization [1], [2]. The cantilever base is firmly attached to a silicon support (chip). The free-standing cantilever end is coated with a sensitive layer.

Another method of classification is according to the electronic components [3]–[5]. There are chemoresistors, chemocapacitors and chemotransistors.

Chemoresistors (Conductometry): Chemoresistors rely on changes in the electric conductivity of a film or bulk material upon interaction with an analyte. Chemoresistors are usually made as a metal.1/sensitive layer/metal.2 configuration.

The resistivity/conductance measurement is done either via a Wheatstone bridge by recording the current at an applied voltage in a DC mode or in a low-amplitude, low-frequency AC mode to avoid electrode polarization. The contact resistance should be much lower than the sample resistance and should be minimized, so that the bulk contribution dominates the overall conductance.

There are two major classes of chemoresistors:

1) high-temperature chemoresistors (200^{o}C–600^{o}C) with semiconductor metal oxide coatings,

2) low-temperature chemoresistors (room temperature) with polymeric and organic sensitive coatings.

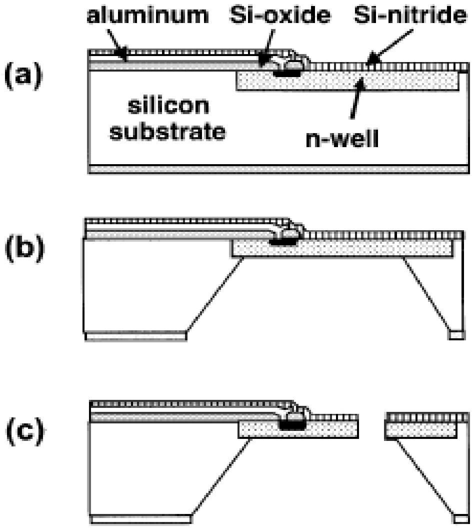

Fig. 1. Micromachining steps necessary to fabricate an integrated CMOS resonant cantilever with on-chip circuitry. (a) Chip after completion of the CMOS process, patterning of the silicon nitride mask. The micromachining steps include (b) anisotropic silicon etching from the back side of the wafer to release an n-well membrane and (c) front-side reactive ion etching to release the cantilever.

The sensitive materials used with high-temperature chemoresistors include wide-bandgap semiconducting oxides such as tin dioxide, gallium oxide, indium oxide, or zinc oxide, all of which can only be operated as sensing materials at high temperature (>200°C) [4], [5]. In general, gaseous electron donors (hydrogen) or acceptors (nitrogen oxide) adsorb on the metal oxides and form surface states, which, only at high temperature, can exchange electrons with the semiconductor. An acceptor molecule will extract electrons from the semiconductor and thus decrease its conductivity. The reaction between gases and oxide surface depends on the sensor temperature, the gas involved, and the sensor material [4], [5].

Consequently, the device requirements for a microfabricated high-temperature chemoresistor include a thermally well isolated stage such as a suspended membrane, which allows for keeping the sensing materials at high temperature without heating the bulk chip (power consumption), an integrated heater, electrodes, and a temperature sensor.

Semiconductor metal oxide sensors usually are not very selective, but respond to almost any analyte (carbon monoxide, nitrogen oxide, hydrogen, hydrocarbons). One method to modify the selectivity pattern includes surface doping of the metal oxide with catalytic metals such as platinum, palladium, gold, and iridium.

DEVICE DESIGN AND FABRICATION

Tin oxide films were extensively used in gas sensors applications. It is sensitive to specific gas at high temperatures (~300°C). To achieve such high operating temperature, a microstructure called microhotplate (MHP) was developed. The thermally isolated hotplate was fabricated using surface silicon micromachining technique.

The top view and the cross-section of the device are shown in Fig.2 and 3. Finite element thermal analysis using ANSYS suggested that 1.5 to 2µm air-gap provides effective thermal isolation for the micro-hotplate (Fig. 6 and Fig. 7)

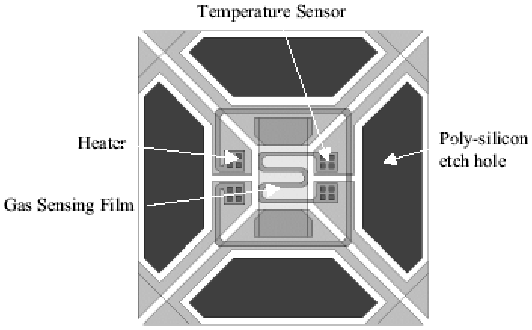

Fig. 2. Layout of the integrated gas sensor.

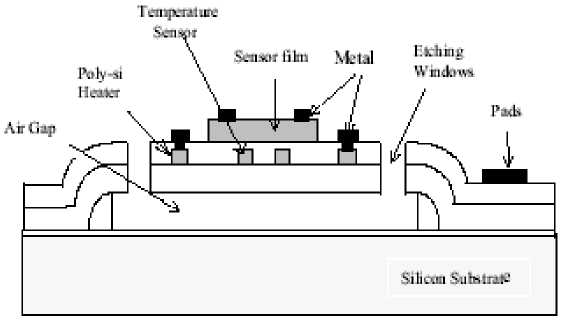

Fig. 3. Final gas sensor cross-section.

The micro-hotplate with dimensions 128 µm by 128 µm is suspended by the four microbridges at the four corners. The bridges are 34 µm wide and 52 µm long. The low stress silicon nitride is used as the base of bridges due to its stiffness and low residual stress. This step is followed by deposition of low temperature oxide (LTO). These composite layers provide adequate mechanical support and good thermal insulation to MHP. The area outside the MHP remains at the silicon substrate temperature. On our design, polysilicon heater ring is placed at the outer perimeter of the MHP. This improves the temperature uniformity on the MHP. The polysilicon resistor, at the center, monitors the temperature of MHP. The insulating air-gap is formed by etching away polysilicon sacrificial layer. One of the major problems with surface micro-machined structure is the large step encounter by crossing metal interconnections resulted from the thick sacrificial polysilicon layer (Fig. 5a).

The device is fabricated by using a seven mask process. The fabrication sequences are summarized in Figure 5. Initially, 200nm thick thermal silicon oxide (SiO_2) is grown on n-type, [100] oriented silicon wafer. The 2 µm thick LPCVD polysilicon is deposited on the SiO_2 as the sacrificial layer. The first mask defines the micro-hotplate area. After etching the polysilicon, the side-wall spacer is formed for better step coverage (Fig. 5b). The micro-hotplate membrane base is deposited using 400nm thick densified LPCVD silicon oxide, 800nm low stress LPCVD Si_3N_4 and 400nm LPCVD densified silicon oxide. The temperature sensor and heater elements are formed using 350nm LPCVD polysilicon deposition. The phosphorus diffusion is carried out at 950^0C for 20 minutes to obtain polysilicon sheet resistance 20-25 ohm/square. A 400nm densified LPCVD oxide is deposited on these polysilicon heater and temperature sensor elements. It is used as an insulating layer, which provides isolation to polysilicon heater and temperature sensor with other layers. The etching windows are opened and micro-hotplate structure is defined by etching the LPCVD oxide and LPCVD low stress Si_3N_4. The windows are used for polysilicon sacrificial layer etching for the air gap formation. The MHP is released by etching polysilicon sacrificial layer (Fig. 5c). Next, the tin oxide gas sensitive thin-film is sputtered and patterned using lift-off photolithography technique (Fig. 5d). The sensor thin-film is sintered at temperatures from 400 to 700°C, to stabilize the film.

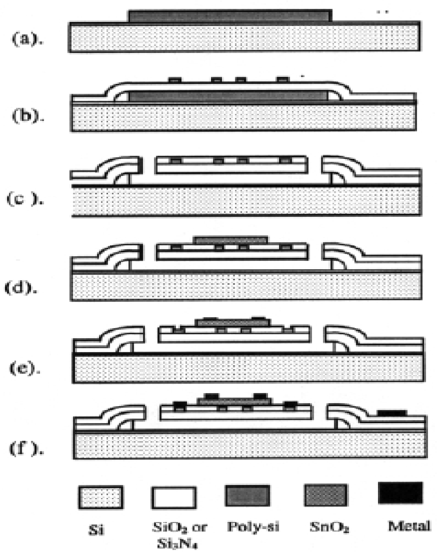

Fig.5. Device fabrication process flow.

Table 1

Sensitivity	Concentration of CO	R_{SnO2}(air)	R_{SnO2}(fromCO)
15	60 ppm	645 Ω	43 Ω
14	50 ppm	645 Ω	46 Ω
13	40 ppm	645 Ω	49 Ω
12	30 ppm	645 Ω	54 Ω
11	20 ppm	645 Ω	58 Ω

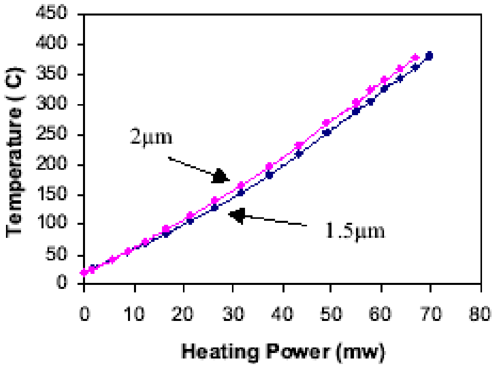

Fig.6. Sensor temperature as a function of heating power with 1.5µm and 2 µm air gap thermal insulation.

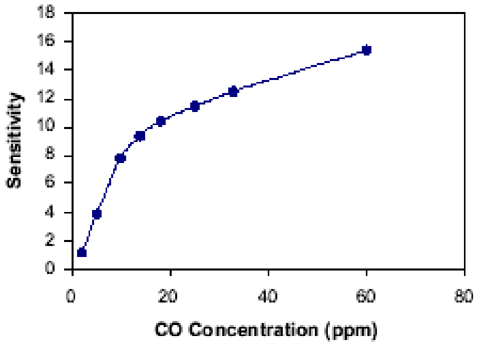

Fig.7. The sensitivity as a function of CO concentration at 290ºC.

The process is designed in such a way, that the high temperature sintering can be carried out before the deposition of interconnection metallization which cannot withstand the high sintering temperature. The sensor metal electrodes Au (or Pt) are sputtered and patterned. The contact holes to the temperature sensor and heater are opened (Fig. 5e). The metal interconnection Al/Ti-W (or Pt/Ti) for the heater, temperature sensor and gas sensor are deposited and patterned (Fig. 5f).

CALCULATION THE CHEMICAL SENSOR ELEMENTS.

Resistance of the polysilicon heater, sensing film of the SnO_2 and temperature sensor could be found by:

$$R = \rho \frac{l}{S}\ , \Omega$$

where: S = w.d; w – width of resistive path; d – length of resistive path; ρ - specific resistance of the material; l - the length of the fabricated resistor; S – resistor's cross section;

The sensitivity of the chemical sensor could be defined as:

$$S = \frac{R_{air}}{R_{CO}},$$

where: R_{air} resistance of the sensing layer in air; R_{CO} resistance of the sensing layer in CO.

Table 1 shows the change of sensing layer resistance end from concentration of CO. Increasing the concentration of CO, the resistance of the sensing layer decrease.

The quantity of heat of the heater is:

$$Q = A = I^2 Rt = \frac{U^2}{R} t = UIt = Pt \text{, J}$$

where: I – current across polysilicon heater; R – resistance of heater; t – time;

When we measured resistance of temperature sensor we don't forget that resistance is variable at different temperatures:

$$R = R_o(1 + \alpha t)\text{, }\Omega$$

where: R_0 - resistance at 0 °C; t - temperature; α – temperature coefficient of the resistance.

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