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Fabrication of MEMS composite-polymer gas sensor arrays for electronic nose

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Sensor arrays capable of sensing different gases combined with a sampling system and a means of pattern classification and recognition comprise a basic system for an 'Electronic Nose' In the present work, a complete process for the fabrication of micro-cavities with sensing electrodes and volumes ranging from 2.5 to 12 nano-liters for the development of polymer gas sensors has been reported. An array of eight sensing cells in four sizes have been fabricated using SU-8 negative tone resist through UV-LIGA process developed at CEERI, Pilani. The length and width of the SU-8 cavities are: 250 × 250, 300 × 300, 500 × 500 and 500 × 600 micron and the depth of each of them was optimized to be 40 micron. These cavities filled with different polymer composites comprise the basic sensing cells for a variety of gases. The current paper presents the salient features of the fabrication process in detail and the results obtained in ethanol and methanol ambient using a polymer composite developed through dissolution of styrene and polyaniline in PMMA. A number of other composites such as Pc-Ppy, Pr-Ppy, Fc^{+}-PPy have also been synthesized and tested for a high sensitivity in carbon monoxide.

Keywords: Polymer gas sensor, Composite polymer, Conducting polymer, Electronic nose, Sensor array, Sensitivity, Selectivity

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1 Introduction

Chemical gas sensors have been widely used in environmental monitoring and control, industrial processing, olfactory systems, in hazardous, toxic and inflammable environments for human safety[1]. Some of these applications require a quick determination and recognition of a group of volatile compounds or gases. It is accomplished with the help of an array of sensors[2] comprising 'electronic nose'. With the evolution of MEMS technology, it is now possible to fabricate an array of sensors which could be easily scaled down and integrated with an on-chip or off-chip conditioning circuitry. This technology has provided a number of platforms[3] to use wide variety of materials for the sensing of several kind of gases. These platforms include micro-hot plate[4], cantilevers and micro-cavity based sensors. The materials used are metal oxides, solid electrolytes and polymers. The first two kind of materials generally require heating to constant temperatures and hence lead to higher device power consumptions. Moreover, the fabrication process becomes complicated. The third kind of materials, i.e. polymers have paved their way for this application after a great deal of research. Electrically conducting[2,5,6] organic polymers have been used significantly mainly because of three distinct advantages: a wide range of available polymers which could be blended in a variety of combinations to be sensitive to a broad range of gases and vapours, ease of deposition and the ability to operate at room temperatures leading to low device power consumption[5].

2 Composite-Polymer based MEMS Gas Sensors

Electrically conducting[1,3,5,7] organic polymers comprise an extremely important class of materials for various kind of applications in semiconductor and sensing devices. These polymers have evolved as materials of great research interest for nearly one decade. Among these polymers, polyacetylene, polypyrrole[8], polythiophene and polyaniline[9] have been identfied as having a number of interesting features that make them potentially important materials for various type of sensors such as chemical sensors, gas sensors, piezo sensors, thermal switches, opto-electronic sensors, bio-sensors etc. Other orga-

nic polymers e.g. phthalocyanin, porphyrin and ferrocenium, blended in different compositions have shown marvellous gas sensing capabilities. Consequently, they are poised to play a significant role in several kind of MEMS sensors.

3 Fabrication Process

Fabrication of the device was carried out on 100 mm diameter silicon substrates. Fig. 1 shows a complete fabrication flow chart. A dry thermal oxide of thickness 200 nm was grown as a basic isolating

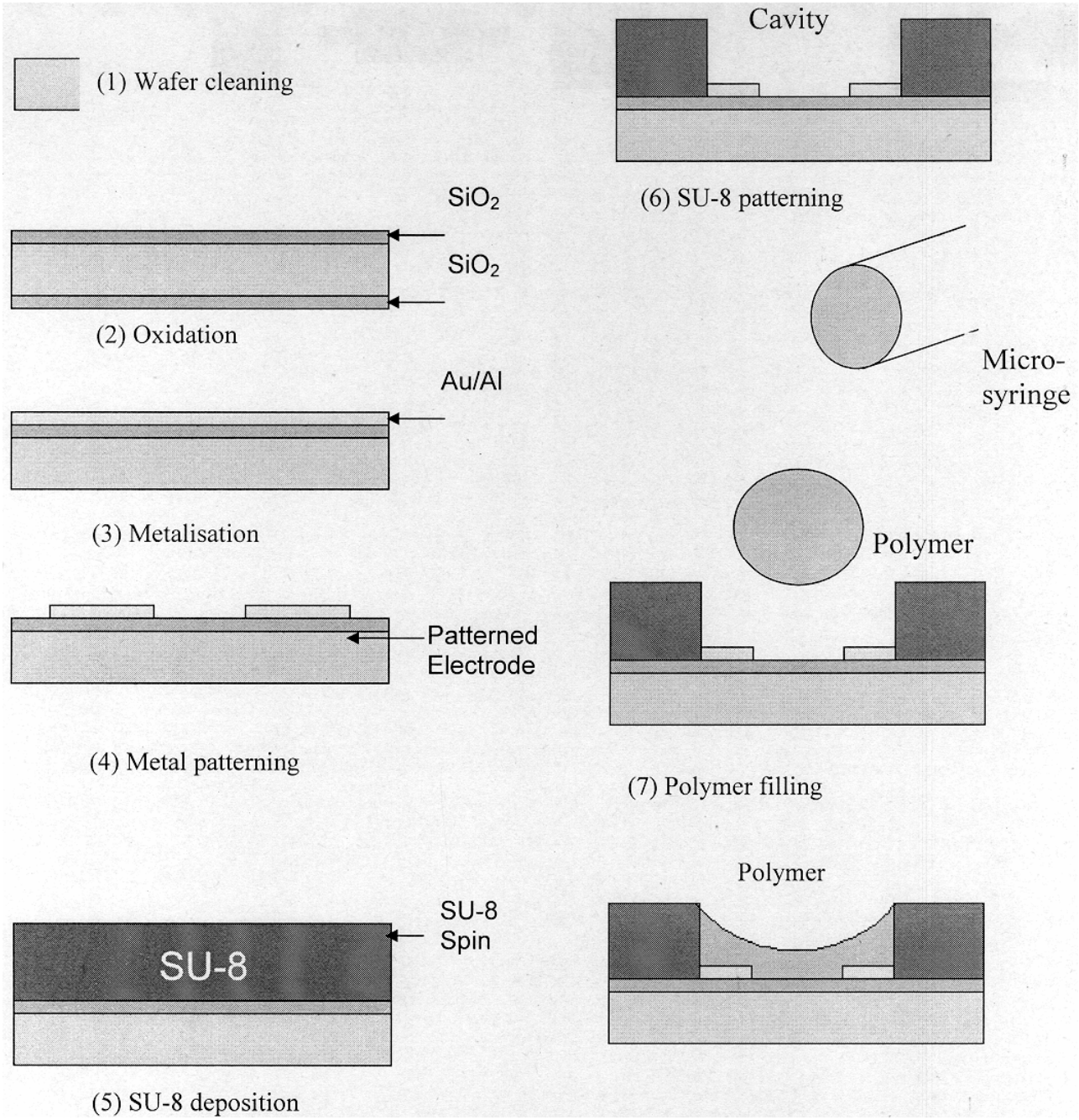

Fig. 1—Fabrication flow chart of the polymer gas sensor

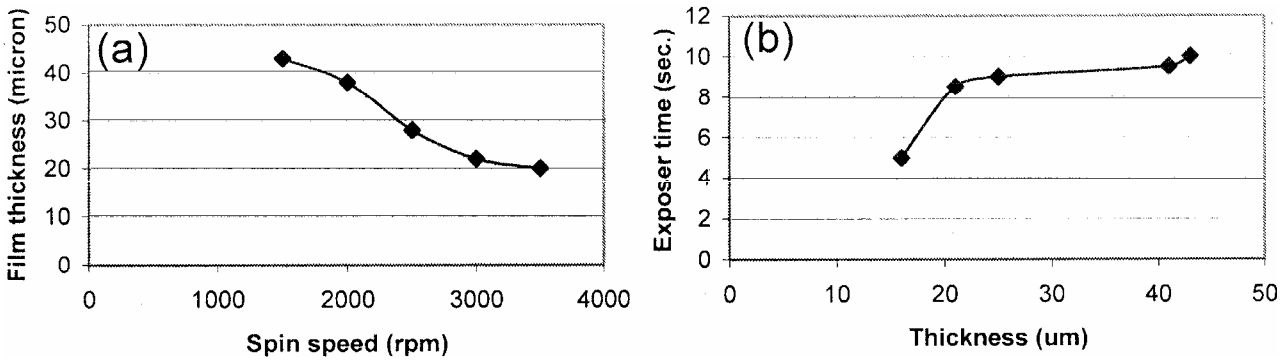

Fig. 2—(a) Spin speed versus thickness and (b) thickness versus exposure time for SU-8 2025 resist

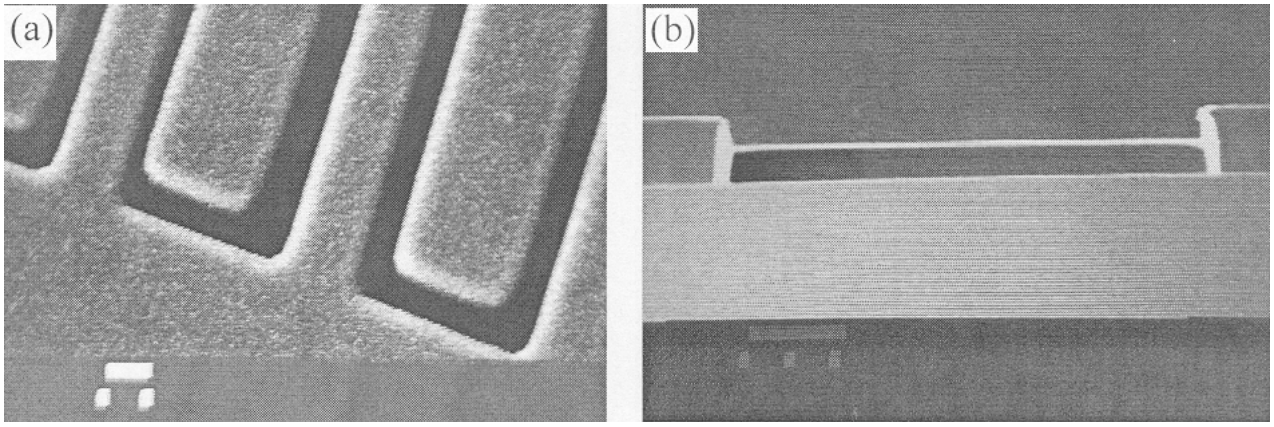

Fig. 3—(a) 40 micron thick comb drive structures in SU-8-2025, (b) Cross-section of 40 micron deep SU-8 cavity

layer between the device and the substrate. Initially, aluminium with a thickness of one micron was sputter deposited and patterned for the sensing electrodes, but for subsequent runs a 200 nm gold was finalized to be the electrode material. After patterning of electrodes, formation of the micro-cavities was carried out using a negative tone resist SU-8 2025. Experiments related to the characterization of this resist were first carried out separately. Fig. 2(a) shows the spin speed versus thickness graph and Fig. 2(b) shows the exposure time for optimum development of SU-8 2025. Soft baking times were 15 minutes at 65°C and 95°C in a convection oven. It was then implemented on the planar wafer. Micro-cavities with the depth of 40 micron were patterned over the bottom electrodes. These cavities were hard baked at 140°C for half an hour in a convection oven. It makes them chemically immune and stable. Fig. 3(a) is a SEM micrograph of interdigited patterns in SU-8 with a depth of 40 micron, Fig. 3(b) is a cross-section of the cavity. Fig. 4 is a SEM micrograph of the fabricated polymer composite gas sensor chip in a size 3.5 mm × 4.5 mm with eight number of arrays before filling the polymers. Fig. 5 is a single cell with SU-8 cavity. Composite polymers were developed separately at NCL, Pune. These composite polymers were then filled into the cavities with the help of a micro-syringe. Die bonding was carried out on a circular metallic header. After wire bonding of the die pads with header connecting pads, a perforated cap was used to cover the header to facilitate the exposure of the device with the ambient gas.

4 Results and Discussion

Initially two composites (i) styrene in PMMA and (ii) PMMA blended polyaniline conducting polymers were tested for change in their conductivity in methanol and ethanol ambient. These composites show a relatively poor response time. Polyanilin composite was also tested for CO sensing. It has shown sensitivity to ethanol and methanol vapours with somewhat a slow response. Fig. 6 is a res-

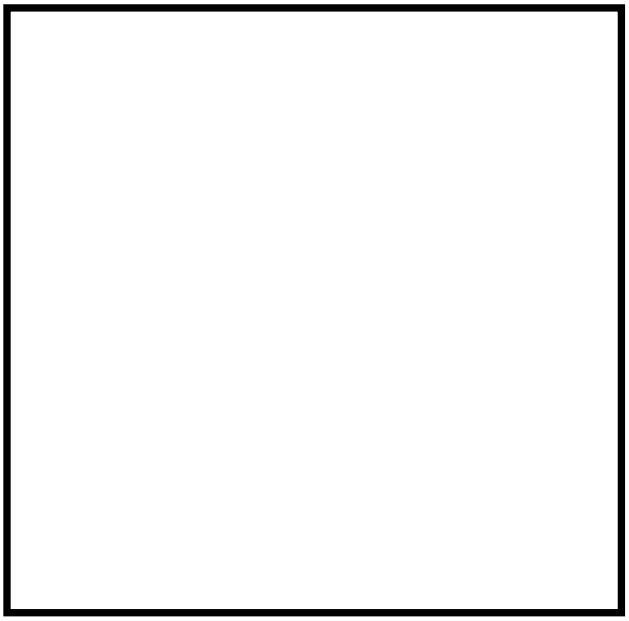

Fig. 4—Polymer composite Gas Sensor Chip before filling of polymer composite

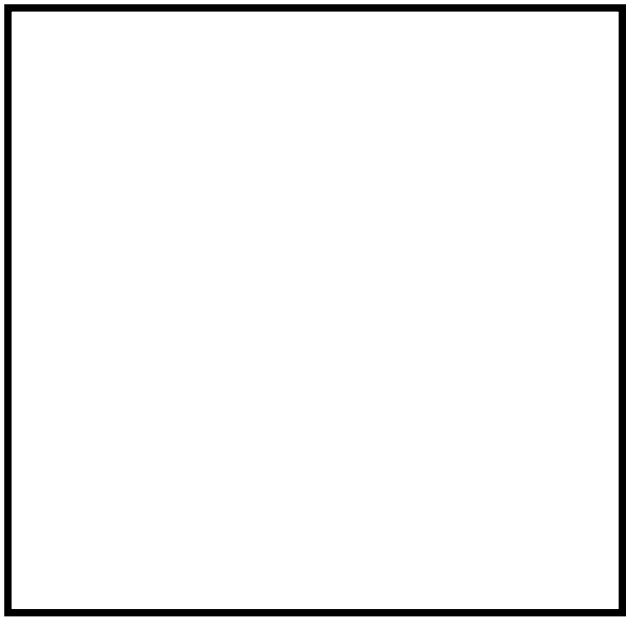

Fig. 5—A single cell

Fig. 6—Response curve for polyaniline composite sensors in CO ambient with different concentrations

ponse curve in CO + N_2 mixture with different concentrations of CO for polyaniline composite. Several kind of other compositions based on Pc-Ppy, Pr-Ppy, Fc^+-PPy Pc-Ppy, Pr-Ppy, Fc^+-PPy were synthesized for high sensitivity to CO, NO and NO_2. Sensitivity tests were carried out. These conducting polymers were further modified to convert them solution based compositions in order to make them compatible with device processing.

Conducting polymers modified with ferro-complexes were characterized for higher CO sensing. Fig. 7 shows the sensitivity curve for ferrocene

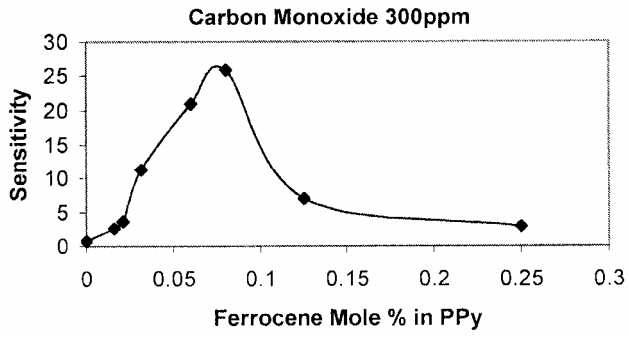

Fig. 7—Sensitivity curve for ferrocene modified ICP sensors

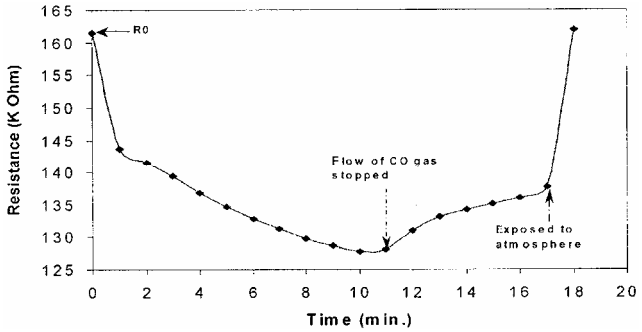

Fig. 8—Response curve for 5% Pc-Ppy (phthalocynaninin polypyrrole) in 100 ppm carbon monooxide

modified ICP sensor for CO sensing. Fig. 8 shows the response of a single cell filled with 5% Pc-Ppy (phthalocynaninin polypyrrole) in 100 ppm carbon monoxide environment.

5 Conclusion

A complete process for the fabrication of composite polymer gas sensor has been developed. It is a low-cost process based on UV-LIGA with a potential of further reduction in cost by using a glass or ceramic substrate. Sensitivity and selectivity to wide variety of gases can be obtained through new formulations of polymer composites.

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