NOVEL TECHNIQUES FOR MEMS-BASED VOC SENSORS USING NANOSTRUCTURED METAL OXIDES

by

HARDIK JEETENDRA PANDYA

Instrument Design Development Centre

Submitted

in fulfillment of the requirements of the degree of

Doctor of Philosophy

to the

Indian Institute of Technology Delhi

MAY 2012

DEDICATED

TO

MY BROTHER

NISHANT

Certificate

This is to certify that the thesis entitled, **"Novel Techniques for MEMS-Based VOC Sensors Using Nanostructured Metal Oxides"**, being submitted by **Mr. Hardik Jeetendra Pandya** for the award of the degree of **Doctor of Philosophy (Ph.D.)** to the Indian Institute of Technology Delhi, New Delhi, is a record of bonafide research work carried out by him under our guidance and supervision.

In our opinion, the thesis has reached the standard of fulfilling the requirements of all the regulations related to the degree. The results contained in this thesis have not been submitted in part or full, to any other University or Institute for the award of any degree or diploma.

Prof. A.L. Vyas
Instrument Design Development Centre (IDDC)
Indian Institute of Technology Delhi
INDIA

Prof. Sudhir Chandra
Centre for Applied Research in Electronics (CARE)
Indian Institute of Technology Delhi
INDIA

ACKNOWLEDGEMENTS

I would like to take this opportunity to thank all those persons who have assisted in the production of this thesis, either in technical manner, or through philosophical guidance, moral support and camaraderie.

Firstly, I would like to express my deepest gratitude to my supervisors Prof. Sudhir Chandra and Prof. A.L. Vyas for their invaluable guidance, continuous interest, generous support and constant healthy encouragement throughout this research work. They have devoted lot of time for technical discussions, editing papers and finally in thesis writing. Their expertise and wide knowledge in Microelectronics, MEMS and Instrumentation helped me in better understanding of the subjects that played a very important role in the accomplishment of this work. They were always there whenever I needed help not only in academic matters but also at personal level. Indeed, my gratitude to them cannot be expressed in a few words and it is my honor to be their student.

I am extremely thankful to Prof. N.K. Jain and Prof. S. Tuli for helping me with administrative matters and many other personnel talks. I am also thankful to Prof. Chandrashekhar for encouraging me to do better research. Special acknowledgements to Prof. Sunil Bhand [BITS, Pilani-K. K. Birla Goa Campus] for his advice, motivation and support during my entire research work.

I extend my deepest gratitude to Dr. Chattar Singh for helping me in SEM characterizations of the samples.

I would like to thank all IDDC and CARE faculty and staff members who helped me directly or indirectly during my stay in IDDC and CARE for successful completion of my research work. I am highly thankful to Sr. Lab Technicians Mr. M.S. Channa and Mr. Govind Ram for providing me very valuable technical support for operating and maintaining the equipments used during the course of the work. Mr. Govind Prasad (Lab. Attendant) has given highly appreciable support in the labs during my research work.

I especially appreciate the company of fellow researchers at CARE and IDDC: Atul Vir Singh, Bhaskar Thakkar, Ruchi Tiwari and Bhagaban Behera who have made useful contributions to this work by way of discussions and suggestions from time to time.

I would also like to acknowledge the financial support that I have received from Indian Council of Agricultural Research (ICAR), through the sponsored project during my research work.

I would like to express my gratitude to the Government of India and The Indian Institute of Technology Delhi for giving me the opportunity to undertake a PhD program in India.

Finally, I would like to thank my younger brother Nishant for his love, financial and personal support throughout my research work. I would like to express my deepest feelings and gratitude to all family members, especially my mom for their constant encouragement and unconditional love. I would like to thank to the most beautiful person in my life Ameeta for always motivating me during hard times and supporting me selflessly.

Finally, I want to thank God for giving me life, salvation, vital human relationships, and the opportunity, strength, and perseverance to successfully complete this research work.

Hardik Jeetendra Pandya

ABSTRACT

In the present dissertation, an attempt has been made to develop a few novel techniques for fabricating low-cost sensors for detecting vapours of volatile organic compound (VOC) using Micro-Electro-Mechanical-Systems (MEMS) technologies. For this purpose, different metal oxides have been investigated as sensing material. One of the objectives of the present work is to develop sensors, which are capable of detecting VOCs at nearby room temperatures (30°C - 100°C). This has been accomplished by using nanostructured metal oxides rather than the thin films of these materials.

The metal oxides used in present study are: indium tin oxide (ITO), zinc oxide (ZnO) and copper oxide (CuO). The ITO films are prepared by RF magnetron sputtering using a 3-inch diameter ITO target in argon atmosphere in the pressure range 5-20 mTorr at RF power of 100-300 W. The target-to-substrate spacing is fixed at 50 mm. Films having thickness in range of 0.1-0.3 μm are investigated. The effect of deposition parameters (RF power and sputtering pressure) on various properties such as deposition rate, crystallinity and surface morphology are investigated. As these films are to be used for sensing purpose, the crystallinity is an important issue as improved crystallinity of the films enhances the sensitivity of detection. The ITO film prepared at 200W RF power and 10 mTorr sputtering pressure and annealed at 450 °C for 1 h show a nano-crystalline phase having fairly uniform grain size. Accordingly, we have used these parameters for preparing nano-crystalline ITO film. The ITO film is deposited and patterned using lift-off technique on the MEMS platform having an integrated heater. A low cost material (Ni) is used for microheater fabrication while aluminum is used for inter digital electrode (IDE) to measure the resistance of the

sensing layer. The lift-off technique is used for patterning the ITO as its etchant affects the Al IDE (and vice-a-versa). The complete process of fabricating MEMS based sensor having integrated microheater and using ITO as sensing film is presented. A set up was especially established to test the sensors for different concentrations of VOCs. The sensors are tested for different VOCs (methanol, acetone, ethanol and IPA).

The nanostructured ZnO was prepared in a novel manner. Zn film is deposited on oxidized silicon substrate using thermal evaporation technique. The Zn films are annealed at different temperatures in air for different durations. It is demonstrated that Zn film is converted into nanostructured ZnO on annealing in air. It has been further demonstrated that the use of nanostructured ZnO results in considerable reduction in the operating temperature of the sensor. The power consumption to achieve the desired operating temperature is also significantly reduced by making the sensor on a thin diaphragm obtained by MEMS technologies. The nanostructured ZnO films are integrated with the MEMS processing steps to form a complete sensor. The sensors are tested for different VOCs. It is observed that the sensors fabricated using nanostructured ZnO are capable of detecting VOCs at operating temperatures as low as 100 °C.

An innovative technique for fabricating sensors on planar thermally isolated MEMS platform is presented. The sensors fabricated using this technique have high mechanical strength and also consume low power.

Copper oxide is the third (and last) material investigated as sensing layer in the present work. A new and simple technique for preparing long and uniformly aligned copper oxide (CuO) nanowires, by annealing the copper (Cu) film deposited on oxidized silicon, is presented. The Cu films are deposited using RF magnetron sputtering technique. The annealing time and temperature are optimized. The sensor is fabricated using CuO nanowires using a simple 2-mask process. The Cr–Au film is used as inter digital electrode in this case. The copper film of about 3 µm thickness is prepared by RF sputtering process. Thereafter, the wafer is subjected to annealing process at 700 °C in air for 6 h, which converted the Cu film into CuO nanowires. The sensors are tested for different VOCs. It is observed that the sensor is capable of detecting VOC even below 50 °C operating temperature. These sensors have higher sensitivity and faster response time compared to sensors fabricated using other metal oxide materials (ITO and ZnO).

An electronic module for displaying concentration of VOCs is designed and developed. The module is equipped with signal conditioning unit, microcontroller and liquid crystal display device. Thus, a completed sensor system with electronics is designed and developed in the present work.

The thesis concludes by suggesting the scope of further research in this area.

TABLE OF CONTENTS