A material for room temperature FET sensor to detect ammonia and hydrocarbon gases

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Cobalt oxide has been reported as a new material for room temperature FET gas sensor. Thin films of cobalt oxide have been prepared by DC magnetron sputtering on oxidized silicon substrates and used as gas sensitive layers in a capacitively controlled field effect transistor (CCFET) structures. CCFET is a MOSFET with an extended gate electrode. Gas sensing behaviour of these films has been investigated at room temperature for different gases of varying concentrations, ranging from 10 ppm to 10,000 ppm. Gases such as CH₄, C₂H₆, NH₃, CO, NO and H₂ have been used to study the sensor performance. Since the measured sensor signal is not amplified, it is a direct measure of sensitivity of the film to a gas to which it is exposed. The CCFET structure, preparation of sensitive films and measurements are described in this paper. The results indicate that cobalt oxide is selectively sensitive to ammonia and hydrocarbon gases only with a little or negligible response to other gases. Signals of 5 mV and 30 mV for 10 ppm of the hydrocarbons and ammonia respectively have been observed.

Field effect transistors (FET) based on silicon were introduced as a hydrogen gas sensor about 25 years ago by Lundstrom et al using Pd as its gate material. Since then, the research efforts concentrated on development of FET-sensors for other gases. FET sensors are preferred because of small size and low power consumption. Since silicon based devices operate below 200°C, so low temperature sensing materials are needed to develop FET sensors. A number of catalytic metals, metal oxides and mixed oxides are known to be sensitive to different gases. Though metal oxides such as SnO₂, MoO₃, Nb₂O₅ and NiO-Al₂O₃ are excellent materials for conductivity type sensors but these are not acceptable to FET sensors because of high operating temperature above 300°C. In view of this, efforts are concentrated to identify a low temperature material for realization of silicon FET-sensors. Although, some metals show acceptable sensitivity at low temperatures but their cross sensitivity to other gases is a major drawback. For example Pd-FET of Lundstrom is sensitive to hydrogen as well as all other hydrogen containing gases. Recently, high Tc cuprates have been demonstrated to detect ammonia and nitrogen oxide gases at room temperature. Operating the device at room temperature has an additional advantage as signal processing and conditioning circuits can be incorporated along with FET sensor to realize an integrated sensing system.

In this paper, we report cobalt oxide as a new material for FET-gas sensors. We have observed that films of cobalt oxide are selectively sensitive to ammonia and hydrocarbon gases at room temperature. These films are used as a sensitive layer in capacitively controlled field effect transistor (CCFET) structures. Film preparation and experimental results on gas sensing properties of cobalt oxide are presented here.

Experimental Procedure

Thin film of cobalt was deposited on oxidized silicon substrates, using dc magnetron sputtering technique. The film was annealed in oxygen ambient at 600°C for 3h to convert it in to cobalt oxide. The film showed a sheet resistance of 0.5 Ω/Square after annealing. Using Telestep measurement, it was found that the thickness of the film was approximately 3500 Å. Samples of 5 x 8 mm² were prepared for this study.

These films were used as sensitive layers to construct discrete structures of CCFET sensors. The device consists of an air gap capacitor coupled with silicon FET. A gas sensitive film and a gold layer form two plates of the capacitor. One of the plates is connected to gate electrode of the FET. Details of the CCFET structure and its operation are reported elsewhere.

For characterization of sensors, a laboratory fabricated test system, as shown in Fig. 1, was used. It
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Fig. 1 — Schematic diagram of the test system used for characterization of gas sensors

consists of four mass flow controllers (MFCs) and an optimally designed circular sensor chamber. Test gas cylinders containing a certified concentration were used for the measurements. By using dry synthetic air, further dilution of the test gases was carried out. Temperature of the sensor chamber was measured with the aid of a thermocouple mounted in the chamber near the device. An appropriate standard electronic circuit was used to measure the sensor signal voltage. No signal amplification was done and it was recorded directly through an emitter follower circuit. The details are reported elsewhere9,10.

A simplified schematic diagram of CCFET structure is shown in Fig. 2. For a clear presentation, the chip containing FETs is omitted in the figure and only sensor FET is shown outside the housing. As depicted in the figure, a gas-sensitive film and a gold layer constitute two plates of the capacitor. A gap of 50-μm provides space to a test gas for interaction with the sensitive surface layer. Gold has been used as a reference electrode as it is non-sensitive to most of the testing gases. Either one of the plates has a floating potential and is connected to the gate electrode of the sensor FET. The other plate has a definite potential and is connected to the source electrode of the transistor. To minimize the leakage current, a guard ring surrounds the floating electrode. The ring is held at the same potential as the CCFET gate.

Fig. 3 represents the measurement circuit used for testing the gas-sensing properties of the sensitive film such as cobalt oxide. The floating gate electrode potential, needed for the guard function, is delivered by the CCFET. This is connected as a source follower in the circuit. The reference transistor T2 and the operational amplifier OP1 compensate the CCFET threshold voltage. The operational amplifier OP2, the transistor T3 and the band gap voltage reference V1 hold the sensor transistor T1 and T2 at a constant operating point, so that the parasitic gate, source-to-gate and drain-to-gate capacitors need not be recharged. This circuit provides the floating electrode potential with a low output resistance.

Results and Discussion

Gas sensing properties of the cobalt oxide films were studied using NH3, CH4, C3H8, CO, NO and H2 gases at different concentration levels. Test gas dilutions from 10 ppm to 10,000 ppm were done with the synthetic air and the signal voltage was recorded using an electronic x-t recorder. Before starting the experiments, the sensor chamber was purged with
The sensor response for the propane gas is similar
to methane as shown in Fig. 6. However, in this case the rise and fall time are long. Further, like in case of ammonia for higher concentrations the signal is not reaching a saturation value.

Sensor response at a temperature of 21°C to carbon monoxide is shown if Fig. 7. It is obvious that the polarity of the sensor signal for carbon monoxide is opposite to that for ammonia and hydrocarbon gases. Also, as observed in case of ammonia and propane in Fig. 4 and Fig. 6 respectively, the response times are large in this case too.

The sensors response to H$_2$ and NO is depicted in Fig. 8. It is clear that from these results that cobalt oxide is not sensitive to these gases even for 10,000 ppm of concentration of these gases. Commonly, the materials which are sensitive to ammonia, are also sensitive to H$_2$ and hydrocarbons. But, in the present case the cobalt oxide based FET is sensitive to ammonia and hydrocarbons but shows almost no sensitivity to hydrogen. Thus, this material is selectively sensitive to ammonia, CH$_4$ and C$_3$H$_6$ gases.

Conclusions

In this study, the gas sensing properties of the cobalt oxide films for various gases have been examined. The films were used in CCFET structures for this purpose. The films are sensitive to NH$_3$, CH$_4$ and C$_3$H$_6$. Its cross sensitivity to H$_2$ and NO gases was also tested and observed that it is not sensitive to these gases. This concludes that thin films of cobalt oxide are highly sensitive to ammonia and hydrocarbon gases, at room temperature, with little or negligible response to other gases. This material, therefore, can easily be used in the silicon based CCFET-sensors for detecting ammonia and hydrocarbons at room temperature.

References