CuO-ZnO SEMICONDUCTOR GAS SENSOR FOR AMMONIA AT ROOM TEMPERATURE

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ABSTRACT
Pure nanostructure thick films, prepared by screen printing technique, were almost insensitive to NH₃ at room temperature. Pure nanostructure thick films were surface activated with CuO by dipping them into an aqueous solution (0.01M) of CuCl₂ for different intervals of time and fired at 500°C for 12h. CuCl₂ is known to be unstable above 200°C and transforms into CuO upon firing above 200°C. The grains of CuO would disperse around the grain of ZnO base materials. The CuO activated ZnO films dipped for 5 min were observed to be sensitive and highly selective to 100ppm of NH₃ sensor in the presence of NH₃ and other gases were studied and discussed. The better performance could be attributed to an optimum number of surface misfits in terms of CuO on the ZnO films.

I. INTRODUCTION
Ammonia is produced and utilized extensively in many chemical industries, fertilizer factories, refrigeration systems, food processing, medical diagnosis, fire power plants, etc. A leak in the system can result in health hazards. Ammonia is harmful and toxic [1, 2] in nature. The exposure of ammonia causes chronic lung disease, irritating and even burning the respiratory track, etc. Environmental pollution [3, 4] is a burning global issue. Therefore, all industries working on and for ammonia should have an alarm system detecting and warning for dangerous ammonia concentration levels. Detection of low concentration of ammonia is not only important for the points discussed above, but also it is very important for the view of chemical pollution in the production of silicon devices in clean rooms. It is therefore necessary to monitor ammonia gas and to develop the ammonia gas sensors which should detect ammonia at room temperature.

Among various materials ZnO [5, 6, 7] is the most promising semiconductor to detect toxic and hazardous gases. The utilization of metal oxides for gas detection in the atmosphere has been recently discussed [8]. Applications for NH₃ gas sensing have been published concerning ZnO [8, 9] or have also introduced [10] doped metal oxides. Hence the sensors operable at room temperature with low cost metal additives must be developed for large applicability. In the present work, the efforts are made to develop a room temperature sensor with a low cost additive (CuO) using dipping technique, a simplest method of modification.
II. EXPERIMENTAL WORK

AR grade Zinc oxide powder calcined at 600°C for 1h in air. The tixotropic paste was formulated by mixing the resulting ZnO fine powder with a solution of ethyl cellulose as a binder in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and trupineol. The ratio of inorganic to organic par was kept as 39:61 in formulating the paste. The paste was then used to prepare thick films. The thixotropic paste was screen printed on a glass substrate in desired patterns. The films prepared were fired at 500°C for 24 h. These films were surface activated by dipping them into a 0.01M aqueous solution of CuCl₂ for different intervals of time and were dried at 80°C, followed by firing at 300°C for 1 h in ambient air. The particles of CuCl₂ dispersed on the films would be transformed to CuO during firing process, and sensor elements with different mass% of CuO were obtained. CuCl₂ is not thermally stable above 200°C. These surface-activated films are termed as CuO-activated films. Silver contacts were made by Silver Paint.

III. MATERIAL CHARACTERIZATION

III.1 Thickness Measurement
The thicknesses of the films were observed to be in the range from 25µm to 35µm. The reproducibility of the film thickness was achieved by maintaining the proper rheology and thixotropy of the paste.

III.2 Thermoelectric power (TEP) Measurement
The p-type semiconductivity of thick films of CuO and n type semiconductivity of thick films of ZnO were confirmed by measuring thermo electromotive force of the thick film samples.

IV. ELECTRICAL MEASUREMENT OF THICK FILMS

IV.1 Current-Voltage Characteristics
Figure 1 depicts the I–V characteristics of the pure and CuO-activated ZnO films. It is clear from the symmetrical I–V Characteristics at the silver contacts on the films were ohmic in nature.
IV.2 Electrical Conductivity

Figure 2 shows the variation of log (conductivity) with temperature. The conductivity values of all samples increase with operating temperature. They are nearly linear to $1/T$ in the range from 100°C to 250°C. The increase in conductivity with increasing temperature could be attributed to the negative temperature coefficient of resistance and semiconducting nature of the CuO-activated ZnO films. The conductivity increases exponentially during 250°C to 350°C and suddenly increases beyond 350°C. It is observed from Fig. 2 that the electrical conductivity of the pure ZnO film was larger than activated ZnO films in ambient air. It may be due to the intergranular potential barrier. Pure ZnO has only one kind of grains arranged uniformly, where in the case of activated films the grains are of different natures such as CuO and ZnO. The modification causes the formation of heterogeneous intergrain boundaries of CuO-ZnO. Thus increased barrier heights of the intergranular regions of activated ZnO may be responsible to decrease the conductivity.
V. SENSING PERFORMANCE OF THICK FILMS

Fig. 3: Variation of NH₃ gas response at different temperatures

The relative response to a target gas was defined as the ratio of the change in conductance of a sample upon exposure to the gas to the original conductance in air. Figure 3 depicts the variation of response to NH₃ gas (100 ppm) with operating temperature of CuO-activated ZnO thick films. The largest response of CuO-activated ZnO was observed to be 13.7 (Sensitivity) at room temperature. The ammonia response at room temperature is expected to be monitored by adsorption of moisture on the activated ZnO film. The cumulative effect would decrease the film resistance, giving a response to ammonia gas at room temperature. At room temperature, there would be no oxygen adsorption. Therefore, the oxygen adsorption–desorption mechanism is not employed to sense the NH₃ gas. When raising temperature above room temperature, the moisture from the film surface evaporates and hence the response would decrease further. The sample with a dipping time of 5 min of CuO was observed to be the most sensitive at room temperature.

VI. CONCLUSION

From the results obtained, the following statements can be made for the sensing performance of CuO-activated ZnO sensors. Pure ZnO thick films were observed to be insensitive to NH₃ gas at lower temperature. Surface properties of the films were conveniently customized (without affecting bulk properties) by modifying the CuO-ZnO film surface using dipping technique. CuO activated ZnO sensors have shown crucial response to NH₃ gas at room temperature.

References