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Effect of Chlorine Doping on Gas Sensing Properties of Electrodeposited n-type Cuprous Oxide Thin Films

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ABSTRACT

Effect of chlorine doping on gas sensing properties of electrodeposited n-type cuprous oxide thin films were investigated using liquefied petroleum (LP) gas as the test gas. Doping was achieved by adding a 0.02 M cuprous chloride ($CuCl_2$) into the electrolyte solution during deposition of Cu_2O thin films. The conductivity type of the deposited films was determined using spectral response measurements. The gas response of the chlorine doped n-type Cu_2O thin films to the LP gas was monitored by measuring the electrical resistance (R), using the contact probe method, enclosing the film inside a gas sensing chamber. Effect of temperature on the gas response was investigated by maintaining a constant gas flow rate of 0.005 ml/s. In contrast to the undoped n-type Cu_2O thin films that showed a negative response ($\Delta R < 0$) at all temperatures, chlorine doped n-type Cu_2O thin films initially showed a positve response ($\Delta R > 0$) to the LP gas which then reversed its sign to give a negative response. Increasing temperature caused the positive response to decrease and vanish at 42 ºC yielding only a negative response similar to the undoped n-type Cu_2O thin films. The chlorine doped Cu_2O thin films showed a maximum negative response at 52 ºC. The gas response variations shown by the chlorine doped n-type Cu_2O thin films at lower temperatures would make them practically suitable materials for gas sensing applications.

1.0 INTRODUCTION

Environmentally hazardous gases are being released continuously to the atmosphere due to natural processes and human activities. Therefore, monitoring of environment has been of extreme importance for the safety and well being of human and animal life and the nature in general. As a result, gas sensing has become an important area of research and the development of devices that enables the monitoring of various types of gases is of outmost importance. Sri Lanka, a country which is rapidly developing as an industrial nation, is no exception with regard to the monitoring of environment and taking measures important for its safety. For example, in Sri Lanka, highly inflammable Liquefied Petroleum (LP) gas is one of the most widely used fuels domestically. At most times leakage of LP gas from production plants or from cylinders occur during their storage, transport and usage. These leakages at most times can be found from the odor of gas, however, by then a significant amount of gases may have leaked out to the surroundings. Gas sensor devices enable the early detection of such leakages thus

preventing accidents and wastage while helping maintain a safer and cleaner environment.

With the pioneering work reported in 1962 by *Seiyema et. al.*[1], much technological effort has been made in the field of gas sensing aiming towards improvement of the gas response, selectivity, stability and feasibility for practical use. A principal mechanism employed in gas sensing is the monitoring of the electrical resistance of the sensor material upon its exposure to a particular gas of low concentration. Among the many sensor materials available, use of polycrystalline oxide semiconductors as the sensing material is rapidly expanding. Extensive studies have been made on oxide semiconductors such as SnO_2 and ZnO_2 for their gas sensing applications for various types of gases[2,3]. Recently, there have been a few studies on the use of p- type Cu_2O as a potential gas sensing material. *Alahapitiya et. al.*[4] has used thermally oxidized p-type Cu_2O for methane sensing. *Shishyano et. al.*, has used electrodeposited p-type Cu_2O for NO_2 gas sensing[5]. For LP gas sensing, *Dhawale et. al.*, have explored the possibility of using Electron Beam Irradiated chemically deposited TiO_2 thin films[6].

It has been demonstrated that the electrodepostion can be used to control the conductivity of Cu_2O thin films while changing the surface morphology of the resulting films. Ability to control the conductivity, the surface morphology etc. coupled with the ease and associated low cost of fabrication make electrodeposted Cu_2O thin films a suitable candidate for gas sensing applications. However, the high resistance of the electrodeposited Cu_2O thin films is considered a drawback associated with this deposition technique and thus the resulting device. Recently, it has been demonstrated that the resistivity of these films can be lowered by using suitable doping methods. For example, chlorine doping during the electrodeposition has lowered the resistivity of Cu_2O thin films significantly[7]. We have previously reported the use of electrodeposited n-type Cu_2O films for LP gas sensing[8]. This paper reports the use of electrodeposited chlorine doped n-type Cu_2O thin films for monitoring of LP gas. The variation of the gas sensing sensitivity with the temperature is discussed. Further studies are required to understand the reaction mechanisms that cause the results reported in this work.

2. METHODOLOGY

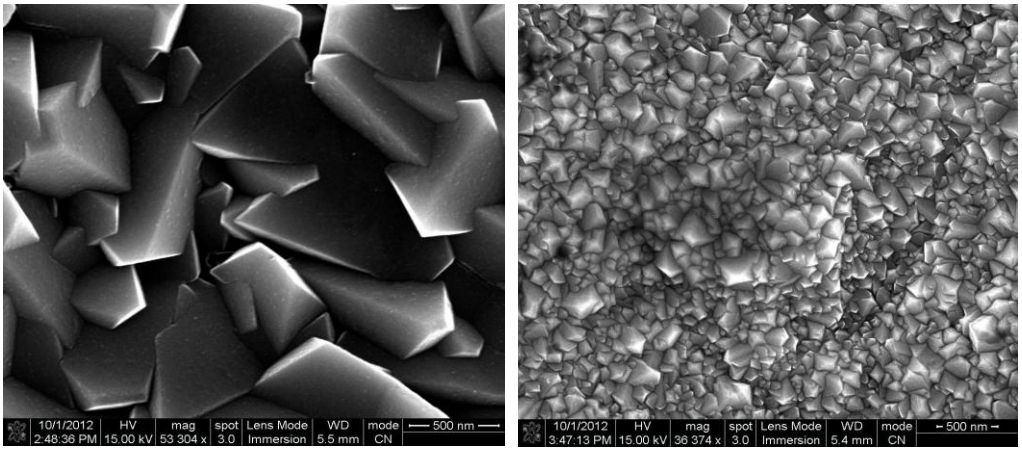
Chlorine doped Cu_2O thin films were deposited on Ti substrates. Prior to the deposition, the substrates were cleaned thoroughly with detergent, dilute nitric acid, in an acetone bath, and lastly with distilled water. For deposition, a three electrode electrochemical cell was employed[7]. This cell contained aqueous solutions of 3 M lactic acid, 0.45 M cupric sulfate, 4 M sodium hydroxide, and cuprous chloride. Sodium hydroxide was used to adjust the pH of the electrolyte. 0.02 M Cuprous chloride was used as the chlorine precursor. The deposition was carried out for a period of 45 minutes, at a constant temperature of 60 ºC, under potentiostatic conditions. The conductivity type of the deposited films was determined using the spectral response measurements[7]. The surface morphology of the films was determined using Scanning Electron Microscopy (SEM).

A film was then enclosed in a gas sensing chamber made of stainless steel. Chamber contained two compartments; the top through which the gas was flown and the bottom where the heating element was housed. In order to measure the electrical resistance, contact probes were fixed on to the surface of the film which was placed on an asbestos heating platform. Externally, the probes were connected to a multimeter, which in turn was connected to a computer data logger.

All the measurements were made at atmospheric pressure by using a flow through technique. The exposure time of the LP gas on the thin film was 30 s. A gas flow rate of 0.005 ml/s was maintained and the temperature was varied between 30 ºC and 100 ºC while monitoring the temperature with a thermocouple (type K) which was in contact with surface of bare substrate (area of the substrate which was not covered by the Cu_2O film). The temperature was controlled using a thermostat with a temperature controller. The electrical resistivity measurements were made using a Keithley 2100 $6\frac{1}{2}$ digital multimeter, that was connected to a computer. The measurements were taken over a period of approximately 120 s upon the gas was sent in to the chamber. This procedure was repeated at different temperatures in order to determine the temperature that corresponds to the maximum gas sensitivity.

3.0 RESULTS AND DISCUSSION

Fig.: 1(a) and Fig. 1 (b) show the SEM pictures of electrodeposited undoped and chlorine doped Cu_2O samples indicating that both films have a uniform coverage with polycrystalline grains. While the undoped films have grain sizes in the micron scale SEM picture of the chlorine doped film shows smaller polycrystalline grains of both nano and micro scale indicating that the doped films have a larger effective surface area which is an additional advantage to interact with the test gas.



1(a) 1(b)

Fig. 1: (a) SEM pictures of undoped Cu_2O sample 1(b) SEM pictures of chlorine doped Cu_2O sample

Conventionally, the variation of the resistance can be represented in terms of the sensitivity, which can be defined for the case of LP gas as

$$Sensitivity \quad , S = \left| \frac{R_{LPG} - R_{air}}{R_{air}} \right| \qquad (1)$$

Where, R_{LPG} is the resistance of the film upon exposure to LP gas and R_{air} is the resistance of the film when it is under normal atmospheric conditions. Previously, it was found that when the undoped Cu_2O films were exposed to the LP gas, film showed a negative response, i.e. the resistance of the film decreased with the exposure time and when the gas flow was stopped, the resistance gradually recovered to its value under the normal atmospheric conditions[8]. In a magnitude of sensitivity vs. time graph, this behavior is depicted by a single response peak. In contrast, upon exposure to LP gas, the resistance of the chlorine doped Cu_2O films increased ($R_{LPG} > R_{air}$) initially showing a positive response and then showed a negative response ($R_{LPG} < R_{air}$) as in the case of undoped Cu_2O films yielding two peaks in the magnitude of sensitivity vs. time graph.

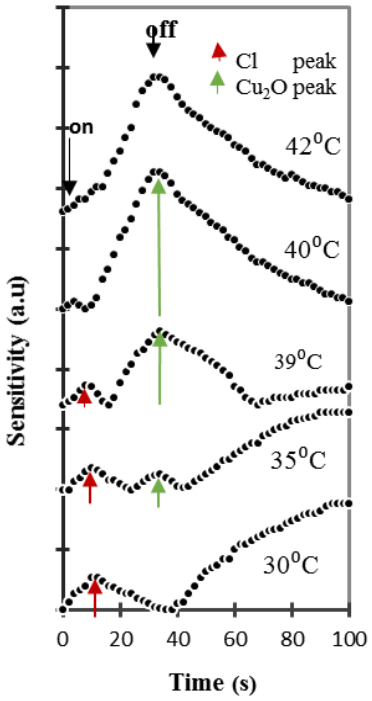


Figure: 2(a)

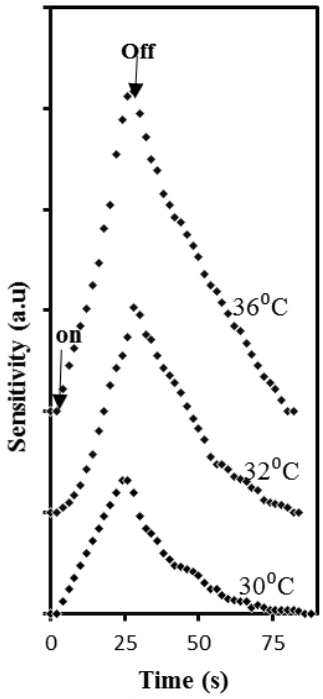


Figure: 2(b)

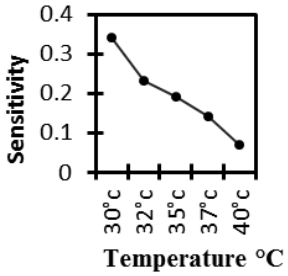


Figure: 2(c)

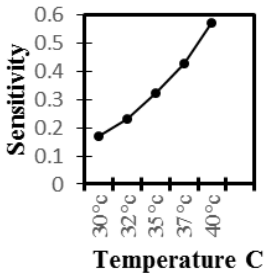


Figure: 2(d)

Fig. 2: (a) Sensitivity variation of 0.02M Cl doped Cu_2O thin film 2(b) Sensitivity variation of undoped Cu_2O thin film 2(c) Variation of maximum sensitivity in the chlorine peak of chlorine doped Cu_2O thin film sample with temperature and, 2(d) Variation of maximum sensitivity in the Cu_2O peak of the chlorine doped Cu_2O thin film sample with temperature

Fig. 2(a) shows the sensitivity variations at temperatures of 30 ºC, 35 ºC, 39 ºC, 40 ºC and 42 ºC obtained for chlorine doped Cu_2O thin films upon exposure to the LP gas. It can be seen that at temperatures of 30 ºC, 35 ºC and 39 ºC there are two responses, with the first peak appearing around 10 s whereas the second peak appearing around 30 s, before the gas is made to stop flowing. This is in contrast to the response given by undoped Cu_2O samples in which the variation of resistance gives rise to only a single peak as shown in Fig. 2(b). The second peak in the sensitivity vs. time graph in the fig. 2(a) is comparable to the peaks seen when undoped Cu_2O was used as shown in fig. 2 (b). Therefore, the first peak appears to have arisen due to the presence of chloride ions in the doped Cu_2O films. Thus for the sake of clarity, the first peak is termed as the chlorine peak whereas the second peak is termed as the Cu_2O peak. Furthermore, it can be seen that the chlorine peak reduces its intensity with increasing temperature disappearing completely at 42 ºC whereas the intensity of the Cu_2O peak continues to increase.

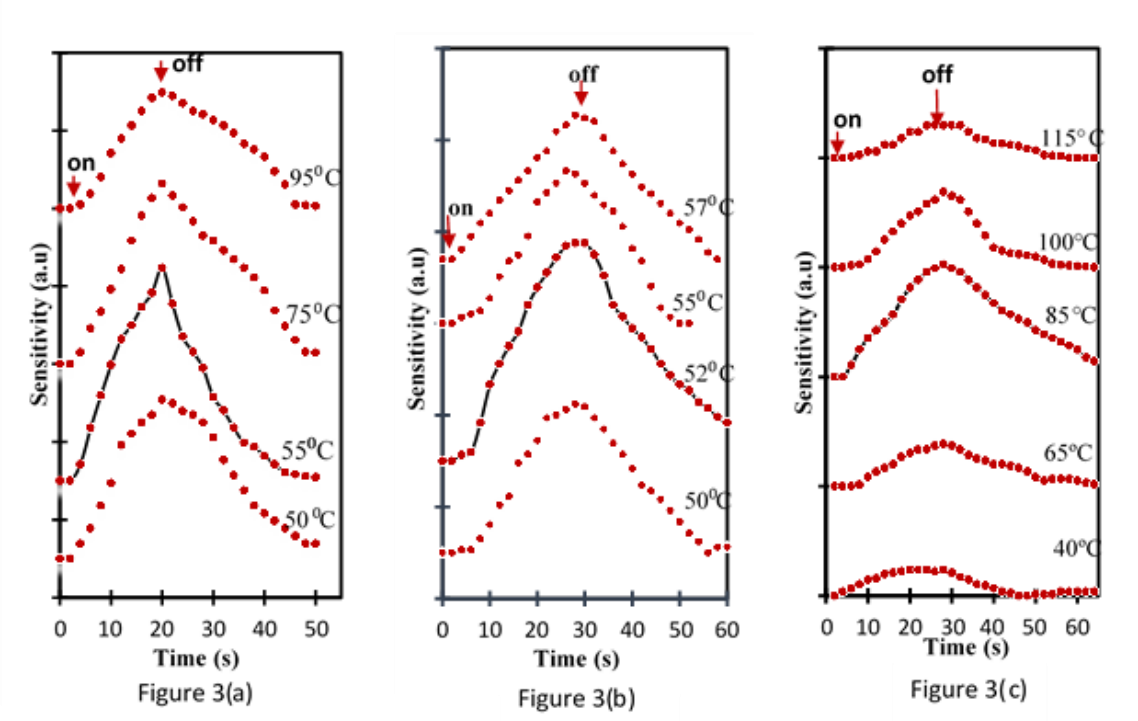


Fig. 3 (a) Sensitivity variation of chlorine doped Cu_2O thin films with time at the high temperatures Fig. 3(b) Senitivity variation of chlorine doped Cu_2O thin films with time at the high temperatures and Fig. 3(c) Senitivity variation of undoped Cu_2O thin films

Fig. 3 (a) and (b) show the sensitivity measurements of the chlorine doped samples when they were exposed to LP gas at higher temperatures. Measurements show that the intensity of the Cu_2O sensitivity peak of the chlorine doped sample increased further yielding a maximum sensitivity at 52 ºC and then decreasing with further increase in temperature. In contrast, the undoped Cu_2O films showed the maximum sensitivity around 85 ºC as shown by the Fig. 3(c).

Thus it can be clearly seen that the chlorine doping has altered the gas sensing behavior of Cu_2O thin films significantly. While chlorine doping causes the resistance of Cu_2O films to go down drastically, the presence of chloride ions in the film has resulted in an additional sensitivity peak that exists closer to the room temperature. It can be interpreted that the doping has caused LP gas molecules to interact initially with more active chloride ions providing a positive response, i.e. $\Delta R\ (= R_{LPG} - R_{air}) > 0$ and then with the other constituents of the Cu_2O film providing a negative response, i.e. $\Delta R < 0$ as in the case of undoped Cu_2O films. It can also be seen that the maximum sensitivity occurs at a lower temperature compared to the undoped Cu_2O films. Currently, studies are being conducted in order to investigate the mechanism/s through which the LP gas molecules interact with the chlorine doped Cu_2O films.

4.0 CONCLUSIONS

Compared to undoped n-type Cu_2O thin films that showed a negative response at all temperatures, chlorine doped n-type Cu_2O thin films initially showed a positive response to the LP gas which then reversed its sign to give a negative response. Increasing temperature caused the positive response to decrease and vanish at 42 ºC yielding only a negative response similar to the undoped n-type Cu_2O thin films. The chlorine doped Cu_2O thin films showed a maximum negative response at 52 ºC which is lower than the temperature at which the undoped n-type Cu_2O thin films show the maximum response.

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