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Sputtered copper oxide (CuO) thin films for gas sensor devices

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Abstract

Copper oxide (CuO) thin films were deposited using a reactive DC sputtering method for gas sensor applications. The structure of the films determined by means of an x-ray diffraction method indicates that the phase of copper oxide can be synthesized in the total pressure and temperature ranges of 6–8.5 mbar and 151–192 °C, respectively. The resistivity of the film synthesized at a substrate temperature of 192 °C increases from 0.104 to 0.51 Ω m after absorbing CO₂ gas at 135 °C. The gas sensitivity of the film synthesized at the substrate temperature of 192 °C increases up to 5.1 in the presence of CO₂ gas at 160 °C. The gas sensitivity in the presence of N₂ gas reaches only 1.43 even at 200 °C.

1. Introduction

Copper oxide finds some potential applications in solar energy devices, gas sensor applications, high- T_c superconductors, nanowires [1], nanoscale quantum dots [2] and some materials with giant magnetoresistance. Previously, the gas sensing properties of copper oxide based compounds have been studied by some other researchers [3, 7] although it is difficult to find any report related to the gas sensor applications of sputtered single phase copper oxide thin films. Thin films of copper oxide have been previously fabricated by the sol–gel synthesis method [4] and the molecular-beam epitaxy growth method [5]. Ultra-thin CuO islands on SnO₂ have been synthesized for gas sensing applications [6].

According to our early studies, most of the materials can be crystallized in thin film form above some minimum crystallization temperature [8–11]. Therefore all these films have been synthesized above a substrate temperature of 151 °C. The amount of residual air in the sputtering chamber was sufficient to crystallize the phase of CuO in this reactive sputtering method. Argon was used as the sputtering gas, and the total pressure in the chamber was varied from 6 to 9 mbar.

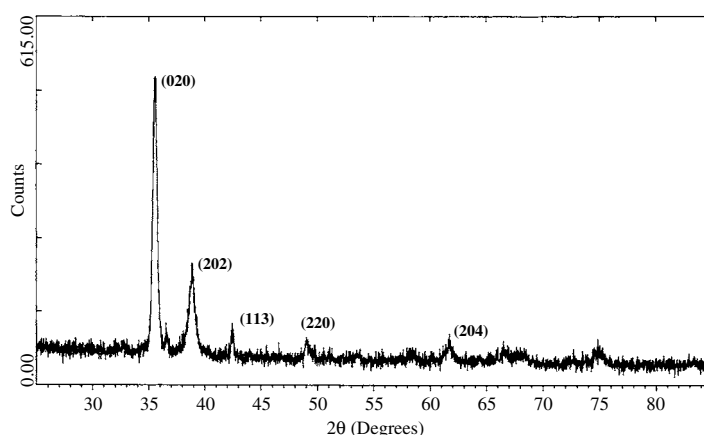


Figure 1. XRD pattern of the film deposited at substrate temperature 192 °C and 7.5 mbar total pressure.

2. Experimental details

All the films were synthesized on conductive glass substrates of area 2 cm × 2 cm using an Edwards S150B sputter coater with base pressure of 4.2 mbar for 6 h. A pure Cu plate of diameter 6 cm was used as the sputtering target and the separation between the target and the substrate was kept at 1.5 cm. The argon gas was introduced into the chamber through a flow controller with fine controlling in this dynamic process. The total pressure in the sputtering chamber was increased by raising the argon gas flow rate. Because the residual amount of air inside the sputtering chamber contributes to the 4.2 mbar base pressure inside the chamber, the difference between the total pressure and the base pressure gives the argon partial pressure inside the chamber. The composition of the atmosphere in the sputtering chamber at atmospheric pressure of 762.6 mm Hg, relative humidity of 60% and room temperature of 26 °C was found to be 78% of N₂, 21% of O₂ and 1% of other gases. The conductive glass substrate was heated using a heater coil coupled to a power supply, and the substrate temperature, in the range from 151 to 192 °C, was measured by means of a thermocouple attached to the substrate.

The structure of the deposited copper oxide films was determined by an x-ray diffraction (XRD) method. The resistivity of the CuO films was measured using a LEADER LCR745 LCR meter. The copper oxide film was placed inside a glass tube, and the film was heated using a heater coil attached to a power supply. The temperature of the film sample, in the range from 40 to 265 °C, was measured using a digital thermocouple attached to the substrate. A mixture of CaCO₃ and HCl acid was used to make dry CO₂ gas which flowed through the glass tube with the CuO film sample. At the beginning, the tube was flushed three times with CO₂ gas to remove the atmospheric gases in the tube. The resistivity of the CuO sample was also measured in pure N₂ gas. The thickness of all the films measured using the profilometer method is 12.7 μm; the thickness remained constant within this substrate temperature and sputtering pressure range.

3. Results and discussion

The XRD pattern of the film deposited at substrate temperature 192 °C and 7.5 mbar total pressure is given in figure 1. All the peaks in the XRD pattern belong to the crystal structure

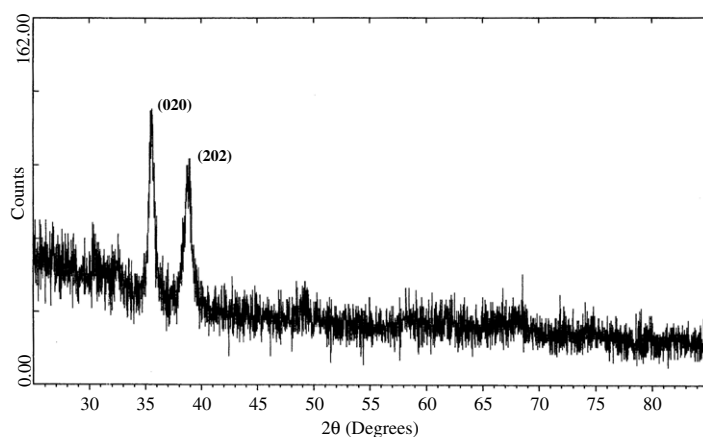


Figure 2. XRD pattern of the film deposited at substrate temperature 192 °C and 9 mbar total pressure.

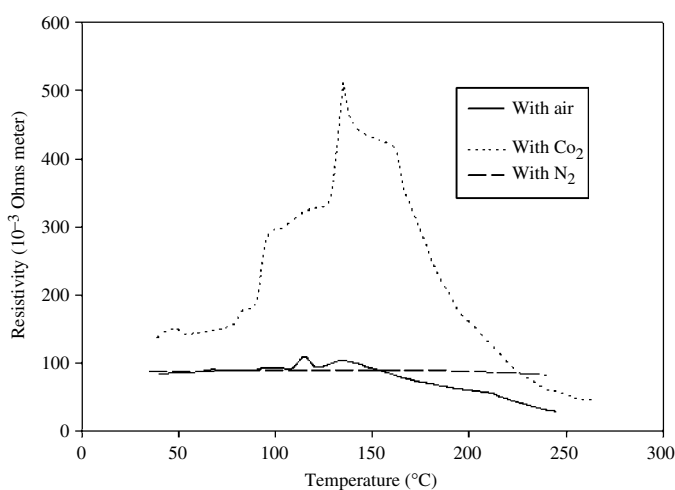


Figure 3. Plots of the resistivity of the film sputtered at 7.5 mbar and 192 °C versus the measuring temperature in the presence of CO₂ (dotted line), air (solid line), and N₂ (dashed line).

of copper oxide, indicating that the film contains the phase of copper oxide. The XRD pattern of the film deposited at 192 °C and 9 mbar is given in figure 2. These XRD patterns imply that the crystallization can be improved at lower total pressures. At the lower total pressure the oxygen partial pressure is higher, and providing enough oxygen may possibly improve the crystallization [12]. The ratio of the intensities of the first and second XRD peaks in these XRD patterns indicates that the orientation of the film changes slightly in this total pressure range. At the lower total pressure, the XRD pattern indicates a strong (020) orientation.

The electrical conductivity of the sample can be given as the reciprocal of the measured resistivity of the copper oxide sample. The sensitivity of the sensor is the ratio of the resistivity of the copper oxide film sample in the presence of CO₂ gas (E_1) to the resistivity of that sample in the air (E_2). Because the CO₂ percentage in atmospheric air is 0.04% in our laboratory, the effect on resistivity due to CO₂ gas in the atmospheric air can be neglected. Plots of the

resistivity of the sample and the measuring temperature in CO₂ gas (dotted line) and air (solid line) are shown in figure 3. The surface adsorption alters the underlying charge carriers in the CuO film or the electrical conduction between individual crystal grains in the film.

The resistivity of the sample measured in N₂ gas (dashed line) is also plotted in figure 3. The ratio of the resistivity in the presence of N₂ to that in air (or the gas sensitivity in N₂) slightly varies with temperature. This sensitivity reaches the highest value at 200 °C and it is about one quarter of the highest sensitivity measured in CO₂. This implies that CuO is highly sensitive to CO₂ compared with N₂.

4. Conclusion

Copper oxide is a prime candidate in the application of CO₂ gas sensors. The copper oxide phase remains unchanged in the total pressure and temperature ranges of 6–8.5 mbar and 151–192 °C, respectively. But the sputtered copper oxide films indicate a strong (020) orientation at lower total pressures, and hence at higher oxygen partial pressures. The sample deposited at 192 °C and 7.5 mbar provides the highest sensitivity at measuring temperature 160 °C. The sensor response time and recovery time are 3 s and 25 min, respectively, indicating that this sensor quickly responds to CO₂ gas. The thickness of the film (12.7 μm) does not vary in this sputtering temperature and pressure range. The sensitivity measured in N₂ gas with respect to air is very low compared with that in CO₂ gas.

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