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RESEARCH ARTICLE

CO-Sensing Properties of Cu_xO-Based Nanostructured Thin Films Grown by Reactive Pulsed Laser Deposition

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Undoped copper oxides (Cu_2O and CuO) thin films were grown by reactive pulsed laser deposition on SiO_2 substrates at 20 and 40 Pa oxygen pressures and deposition temperature of 120 °C. The surface morphological and structural properties of the obtained thin films were investigated by Atomic Force Microscopy (AFM) and by Scanning Electron Microscopy (SEM), respectively. Furthermore the Cu_xO nanostructured thin films were tested as potential carbon monoxide (CO) sensing layers towards two concentrations, 3000 and 5000 ppm CO in air flow, at selected operating temperatures between 150–200 °C. The influence of the oxygen partial pressure on the structural, electrical and gas sensing properties of the films was examined.

Keywords: Copper Oxide, CO Sensing, Operating Temperature, PLD, AFM, Nanostructured Thin Films.

1. INTRODUCTION

In the last years, in order to develop efficient CO gas sensors, many semiconducting metal oxides, like SnO_2,[1–3] ZnO,[4] TiO_2 [5] etc. were investigated as potential sensing elements but their operating temperature was quite high (350–450 °C). Copper oxides thin films (Cu_2O and CuO) are *p*-type semiconductors that have attracted much interest due to their potential applications for photovoltaic cells and gas sensors.[6,7] In particular, compound oxides consisting of copper oxide and *n*-type metal oxides such as ZnO/CuO, SnO_2/CuO and CuO/$Cu_xFe_{3-x}O_4$ have been studied as gas sensors.[8–10] The use of single-crystalline CuO nanowires as sensing elements was also investigated to improve the sensor performance.[11] However, the research on copper oxide alone as gas sensor is far from being satisfactory and issues such as the high operating temperature and stability of gas sensors remain unsolved.

In the present paper the PLD Cu_xO nanostructured thin films on SiO_2 substrates are characterized and the optimized sensing properties towards CO gas are investigated.

2. EXPERIMENTAL DETAILS

Undoped *p*-type Cu_xO thin films have been grown on SiO_2 substrates by pulsed laser deposition technique (PLD). An Nd:YAG laser beam ($\lambda = 355$ nm (THG), $\tau_{FWHM} \sim 10$ ns) at 10 Hz repetition rate was focused on a metallic Cu target. The laser fluence incident on the target surface was set at ~2 J/cm^2. The Cu_xO films were grown under a dynamic oxygen pressure of 40 and 20 Pa for 90 min deposition time at substrate temperature of 120 °C.

The surface morphology of the deposited thin films was investigated by atomic force microscopy (AFM) in contact mode with a Veeco CP-II instrument. The structural properties of the Cu_xO thin films were investigated by Scanning Electron Microscopy (SEM). Resistivity and Hall coefficient measurements, in a 0.63 T magnetic field, were performed using the four-point van der Pauw configuration in order to obtain the conductivity type, the carrier concentration p_H and the mobility μ_H of Cu_xO films. Relative sensor response measurements were performed towards 3000 and 5000 ppm CO concentrations in air flow ambience at operating temperatures between 120 and 200 °C in a stainless-steel tube.

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3. RESULTS AND DISCUSSION

3.1. Morphological and Surface Characterization

The root-mean square (rms) average surface roughness of Cu_xO thin films deposited on SiO_2 substrate, as determined from the AFM measurements, are shown in typical 3D-AFM images below (Fig. 1). It is shown that the roughness depends on the pressure of the oxygen ambient during the deposition.

The Cu_xO films grown under 20 Pa showed a smoother surface with area rms roughness of 5.60 nm. On the contrary, the film surface of the Cu_xO film deposited under 40 Pa showed that the roughness value increased to 11.34 nm (Table I).

Table II shows that the density of grains on the surface, is larger for the film grown under lower oxygen partial pressure. Moreover the average size of the grains, determined from linear analysis of the AFM data is 51 and 47 nm for the films grown at 20 and 40 Pa, respectively. The SEM micrographs confirmed that the films grown under oxygen pressure of 20 Pa exhibited higher grain density than the films grown under 40 Pa.

3.2. Electrical Properties and Gas Sensing Response

Hall-effect measurements were carried out at room temperature in a magnetic field of 0.63 T. Table III shows the results obtained by using the four-probe van der Pauw method with Ag as Ohmic contacts. The Ohmic contact of the Cu_xO/Ag interface was confirmed by the linear dependence of I–V characteristics. The carrier concentration (p_H) and the Hall mobility (μ_H) were obtained from the combined Hall coefficient and electrical resistivity (ρ) measurements.

As shown in Table III the films were found to exhibit p-type conductivity, due to copper vacancies and oxygen interstitials.[12] The films grown under 40 Pa oxygen partial pressure exhibited lower carrier mobility and higher carrier concentration than the films grown under 20 Pa oxygen pressure. This mobility reduction could be attributed to the increase of the ionized acceptor states implying in smaller mobility values in the film grown under 40 Pa.

Table I. AFM area analysis measurements of Cu_xO thin films deposited on SiO_2 substrates.

Oxygen pressure [Pa]	Area R_a [nm]	Area RMS [nm]	Avg. height [nm]	Max. range [nm]
20	2.15	5.6	1.85	87.36
40	4.02	11.34	4.10	188

Table II. AFM grain analysis measurements of Cu_xO thin films deposited on SiO_2 substrates.

Oxygen pressure [Pa]	Grains/μm^2	Avg. grain volume [μm^3]	Mean grain size [nm]
20	4	0.0019	51
40	3	0.0048	47

Table III. Electrical properties of Cu_xO thin films.

Oxygen pressure [Pa]	ρ [$\Omega \cdot$cm]	μ_H [cm^2/V$\cdot$sec]	p_H [cm^{-3}]	Dominant carrier type
20	33	70	$2.6E+15$	p
40	32	20	$9.8E+15$	p

3.3. CO Sensing Tests

The relative response (sensitivity) of the sensors was calculated by the following formula:

$$S = \frac{R_g - R_0}{R_0} \tag{1}$$

where R_0 and R_g are the film resistance in air and target gas, respectively.

Under the flow of CO gas the resistance of Cu_xO films was increased. This behavior was expected as the concentration of holes in the p-type semiconductor decreased due to the charge transfer between CO molecules and Cu_xO surface in oxygen environment.

In Figures 2(a) and (b) are shown typical relative response curves of two Cu_xO samples towards 3000 and 5000 ppm CO gas concentration and at operating temperatures between 150 and 200 °C. It is shown that increasing the operating temperature, the response of the film grown

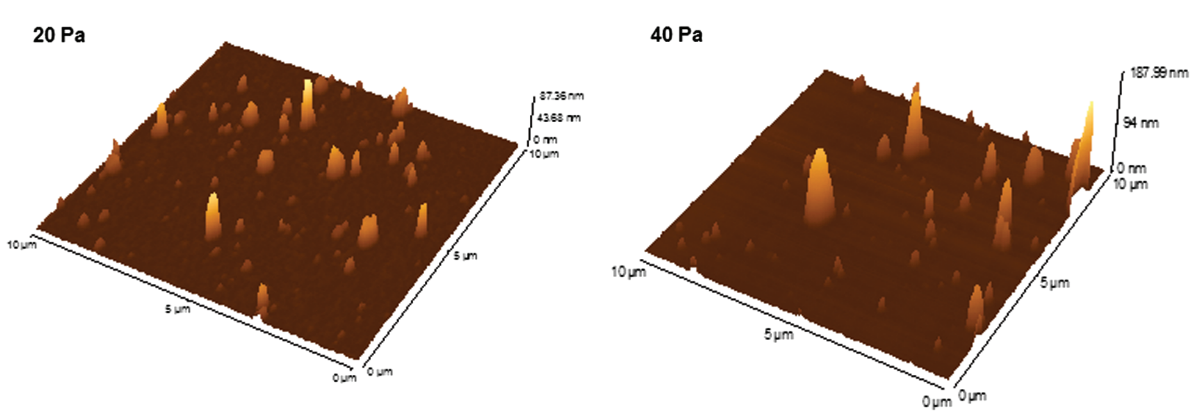

Fig. 1. 3D-AFM images of Cu_xO nanostructured thin films.

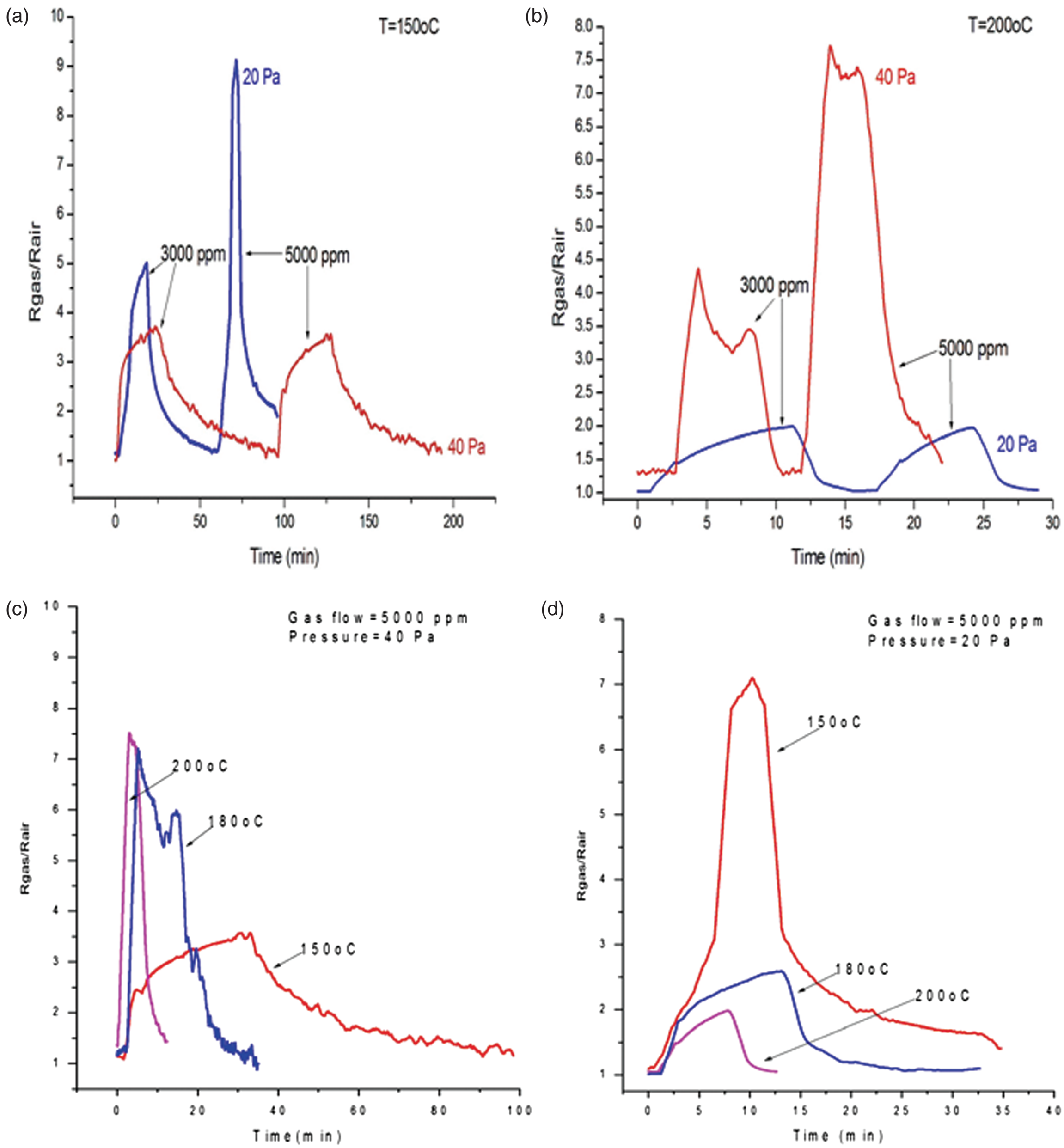

Fig. 2. (a) Relative gas sensing response of the film grown under 20 Pa oxygen pressure at optimum operating temperature of 150 °C, towards 3000 and 5000 ppm CO flow in air gas mixture. (b) Relative gas sensing response of the film grown under 40 Pa oxygen pressure at optimum operating temperature of 200 °C, towards 3000 and 5000 ppm CO flow in air gas mixture. (c) Relative gas sensing response of the film grown under 40 Pa oxygen pressure at 150, 180 and 200 °C operating temperatures. (d) Relative gas sensing response of the film grown under 40 Pa oxygen pressure at 150, 180 and 200 °C operating temperatures.

under 40 Pa oxygen pressure, increases reaching its optimum value at 200 °C (Fig. 2(c)) while the film grown under 20 Pa exhibited an optimum operating temperature at 150 °C (Fig. 2(d)) and then decreases as the temperature is increasing. This behavior is probably related to the different dominant sensing mechanisms between the two films having different surface roughness and mean grain densities as it is mentioned above. It is well known[13] that there are two gas sensing mechanisms: the physisorption which is the first reaction of the gas species with the surface of the films and the chemisorption process which involves the reaction of the CO gas molecules with the adsorbed O^- in the film surface, resulting in charge (electrons) transfer between the gas and the Cu_xO films. This process lead to a decrease of the hole density in the surface charge layer and thus an increase of the Cu_xO resistance.[14] The physisorption is dominant at low temperatures because it is an exothermic process while the chemisorption as an endothermic mechanism is dominant at higher temperatures. Moreover the recovery and response time were increasing as the temperature decrease. This effect could be attributed to the fact that adsorption rate increases at higher temperatures.

4. SUMMARY

Undoped copper oxide Cu_xO thin films were grown under two different oxygen pressures of 20 Pa and 40 Pa. The influence of oxygen pressure on the films morphological, structural, electrical and CO sensing properties has been investigated. Analysis of the results lead to the conclusion that the film grown under oxygen pressure of 20 Pa was smoother than the one grown under 40 Pa, while the density of grains on the surface, is larger for the film grown under lower oxygen pressure.

The response of the film grown under 20 Pa reduces when temperature increases, instead the response of the film grown under 40 Pa increases when temperature decreases. Both samples showed an increase at the response and recovery time with the temperature decrease.

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