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Thickness effect on sensing properties of pure Cu$_2$O thin films under sub-ppm O$_3$ levels

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Abstract

The sub-ppm ozone (O$_3$) sensitivity of pure cuprous (Cu$_2$O) thin films based sensors have been investigated by utilizing conductivity measurements at different temperatures varies from 150 to 200 °C. The structural and morphological properties of Cu$_2$O sensitive layers have been investigated by the scanning electron microscope (SEM) and x-ray diffraction (XRD) respectively. The detection properties of Cu$_2$O layers have been strongly altered by the electrode geometries and sensitive layer thickness. The sensors’ responses and structural investigations revealed that the ozone sensitivity has improved with the increase in the degree of crystallinity along the preferential direction (1 1 1). Ab-initio calculation shows that O$_3$ adsorption mechanism could be semi-dissociative of O$_3$ molecule on the Cu$_2$O (1 1 1) surface, giving O$_2$ molecule remaining in interaction with the surface and an adsorbed oxygen O$_{ads}$.

1. Introduction

Precise detection of the ozone amount existing in the atmosphere is of great importance since this gas is a strong oxidizing agent, which has both positive or negative effects in medicine and various technological processes [1]. Various materials have been investigated for their potential application as based ozone gas sensors [2, 3]. For instance, n-type materials such as In$_2$O$_3$ [4] and WO$_3$ [5–8] thin films have received a great deal of attention during the last few years. In particular, In$_2$O$_3$ nano-crystalline films have been found to operate and detect ozone concentrations as low as few ppb at room temperature, this makes them as a good promising candidates for the conception of low energy consumption and low-cost devices [9, 10]. Other interesting materials have also revealed the suitability to be used as ozone sensors such as SnO$_2$ [11], SrTi$_{1-x}$Fe$_x$O$_3$ thin films [12], CuCrO$_2$ nanocrystals and microcrystals [13] and Cd$_{1-x}$Zn$_x$O [14].

It is well-known that most sensors were mainly based on n-type metal oxides. Although, the synthesis of semiconductor p-type metal oxide provides novel complementary sensing devices,

The Cu$_2$O cuprous oxide is a typical semiconductor p-type that utilized in different applications such as energy conversion [15], organic catalysis reactions [16], oxidation of copper [17], lithium batteries [18], and gas detection [19]. No enough attention has been paid to fabricate metal oxides p-type based sensors. In order to fulfilled this gap, the present work is devoted to manufactured and investigate Cu$_2$O based sensors as a semiconductors p-type oxides.

We believe that this work presents the first trial to test the sensitivity of sputtered pure p-type Cu$_2$O thin layers as ozone sensor. The present research has investigated the sensitivity of nano-structured Cu$_2$O thin layers that obtained by the annealing of metallic copper Cu thin films deposited by the reactive magnetron sputtering technique. The ozone sensing performance of Cu$_2$O films has been examined via evaluating the response magnitude as a function of operating temperature using electrical characterization methods. The different
sensors parameters such as layers and electrodes thicknesses, layers structure and morphologies and their effects on the sensors responses under ozone were explained. Ab-initio calculation was used in order to find the most probable ozone/Cu$_2$O sensing mechanism. Finally the sensing results were compared to literature for validation.

2. Experimental details

2.1. Sensing device preparation
Sensing devices were obtained by depositing Cu$_2$O layers onto SiO$_2$/Si substrates with interdigitated Pt electrodes grown on top (Figure 1). The electrodes with interdigitated shape, have been used to minimize the sensor resistance. This is due to the high resistivity of Cu$_2$O layers. Electrodes were obtained by photolithography with lift off processes. 50 $\mu$m was the distance between electrodes and their thickness was about 50 nm.

The Cu$_2$O layer was elaborated via thermal oxidation of Cu films deposited by magnetron sputtering. A 99.995% pure Cu target of 100 mm of diameter was used as the cathode of magnetron. The substrate was putted parallel to the surface with a substrate to surface distance of 100 mm. During sputtering, the substrate was kept at the ambient temperature and the flow rate of argon (Ar) was 20 cm$^3$ min$^{-1}$ controlled by mass flow controllers. The annealing of the obtained Cu films was performed under specific experimental conditions to synthesize pure Cu$_2$O sensitive layers as reported in our previous work [20].

In total, three Cu$_2$O based sensors were prepared, named: Film(30 s), Film(1 min) and Film(2 min), using three different sputtering durations of 30 s, 1 min and 2 min, respectively. The thicknesses of the Cu$_2$O sensitive layers (40 nm, 70 nm and 145 nm) have been estimated via ellipsometry measurements.

2.2. Sensitive layers characterization
The characterization of Cu$_2$O structural obtained layers was carried out using an x-ray diffractometer (Philips X’Pert PRO), in the Bragg-Brentano configuration. The $2\theta$ values were varied from 30 $^\circ$ to 80 $^\circ$ with a scan-rate of 0.02 $^\circ$s$^{-1}$ using Cu-K$_\alpha$ radiation ($\lambda = 1.54178$ Å$^-$).

Layers morphology has been investigated using a Philips XL scanning electron microscope (SEM) operating with accelerated voltage of 25 kV.

2.3. Sensor measurements
The gas sensing properties of the different active materials produced were tested under ozone (O$_3$) gas environment. To conduct gas tests, ozone was generated using a commercial device (Model 306 Ozone Calibration Source). This ozone generator allows the delivery of very precise and constant amounts of O$_3$.

Sensor responses, namely electrical resistance versus time, were measured under O$_3$ concentrations varying from 100 ppb to 1000 ppb the electrical resistance being monitored by a Source/Pico-ammeter (HP4140B). The applied DC voltage was 0.1 V. During each measurement cycle, the exposure time to the ozone gas was about 1 min.

Figure 1. Schematic top view of SiO$_2$/Si substrate equipped with platinum interdigitated electrodes.
In order to avoid the humidity influence, all experiments were studied using dry air as the carrier gas and the total flow rate was about 1 L.min\(^{-1}\).

Before the O\(_3\) detection experiment, the sensor resistance was measured under a dry air flow until a stable level was obtained; this level was set as the reference resistance.

The sensor responses were recorded at different working temperatures, varying from 150 °C to 200 °C. To assess the reproducibility of the results, each measurement was repeated several times. The sensor response \( S \) was determined by calculating the following ratio

\[
S = \frac{R_{\text{gas}}}{R_{\text{air}}}
\]

where \( R_{\text{gas}} \) is the resistance of the sensor under a given O\(_3\) concentration and \( R_{\text{air}} \) is the baseline resistance of the sensor in dry air.

The response time, \( \tau_{\text{res}} \), of sensor can be defined as the time the sensor takes to reach 90% of its maximum resistance value after O\(_3\) stream flow. Conversely, the recovery time, \( \tau_{\text{rec}} \), is the sensor time takes to be within 10% of the resistance value it had under dry air before exposure to O\(_3\) stream.

3. Results and discussion

3.1. XRD characterization of Cu\(_2\)O thin films

X-ray diffraction patterns of the Cu\(_2\)O films are shown in figure 2. The patterns revealed the polycrystalline nature which composes of the cubic Cu\(_2\)O phase. A comparison with expected relative intensities shows that the preferential orientation is (111).

According to Scherrer’s equation [21], the crystallite size can be calculated using the full width at half maximum (FWHM) values. It was found that the average crystallite size for the Cu\(_2\)O films was around 10 nm (figure 3 and table 1).

3.2. SEM characterization of Cu\(_2\)O thin films

SEM images of the Cu\(_2\)O sensitive layers are presented in figure 4. It can be noticed that films deposited over 30 s (figure 4(a)) have a compact and smooth surface composed of regular Cu\(_2\)O nano-crystallites. With increasing sputtering duration, which was proportional to the layer thickness, the crystallites agglomerate to form dense and rough granular surfaces with clear grain boundaries as seen in figures 4(b) and (c), for deposition times of 1 min and 2 min, respectively.

Previous studies have reported that the size of the grains, the size of crystallized domains, and the relative thicknesses of layers and electrodes are important parameters for determining the response of gas sensors [7]. Consequently, their effects on the response of Cu\(_2\)O based sensors under ozone will be discussed in the following section.
3.3. Gas sensing characterization of Cu$_2$O thin films

3.3.1. Cu$_2$O resistance variation under O$_3$

To study the effect of ozone concentration on the behavior of the films’ resistivities, further measurements were performed at different concentrations in the range of 100 to 1000 ppb at different working temperatures varying from 150 °C to 200 °C. The optimum temperature was found to be 175 °C (figure 5).

As shown in figure 5, when ozone was injected into the test chamber, a decrease of resistance was observed. While an increase of resistance was noticed back to its initial value after removing the ozone. Similar behavior has been recorded in case of all of ozone concentrations. Previous observed behavior shows the p-type semiconductor character, of our Cu$_2$O layers. In order to deduce the mechanism of O$_3$–Cu$_2$O interaction, a stability investigation was performed.

Table 1. Crystallite size and degree of crystallinity following the preferred direction for Cu$_2$O layers deposited on a SiO$_2$/Si substrate.

| Sensor name   | Crystallinity rate of (111) | Crystallite size (nm) | (111) | (200) | (220) | (311) |
|---------------|-----------------------------|-----------------------|-------|-------|-------|-------|
| Film (30 s)   | 89.94%                      | 9.80                  | 6.61  | 7.43  | —     |
| Film (1 min)  | 85.08%                      | 10.50                 | 8.61  | 6.39  | 7.34  |
| Film (2 min)  | 85.29%                      | 11.42                 | 8.25  | 7.26  | —     |

Figure 4. SEM images of Cu$_2$O sensitive layers obtained from annealing of thin Cu layers prepared with different sputtering times: (a) 30 s, (b) 1 min and (c) 2 min.
3.3.2. Stability and detection mechanism investigations under O₃

The stability investigations of the three Cu₂O layers against pulses of 1000 ppb of O₃ at optimum working temperature are reported in figure 6. The exposure time was kept constant at 1 min for each test. The last investigation exhibits total reversibility, and good stability of the baseline for Film (30 s) and Film (1 min).

However, the thicker layer response was characterized by weak amplitude and a constant drift of the baseline.

The adsorption ozone mechanisms by Cu₂O could be described as follows:

For the thinnest Cu₂O layers the O₃ adsorption is mainly localized on layers’ surface according to the following irreversible (or weakly reversible) chemical reactions [22]:

\[
A + O₃ \rightarrow (A - O) + O₂(g)
\]
Table 2. Cu$_2$O sensors response and recovery times versus working temperature for 100 ppb of O$_3$.

| Working temperature °C | Response time, $\tau_{\text{res}}$/s | Recovery time, $\tau_{\text{rec}}$/s |
|-------------------------|---------------------------------------|--------------------------------------|
| 150                     | 47                                    | 8/10                                 |
| 175                     | 44                                    | 2/5                                  |
| 200                     | 46                                    | 80                                   |
| 200                     | 135                                   | 92                                   |
| 200                     | 123                                   | 98                                   |

Table 3. Comparison of the sensing characteristics of some materials based ozone sensors with the present work.

| Sensor material | Fabrication approach | Sensing Temp.(°C) | Response $S = R_g/R_{air}$ | $\tau_{\text{res}}/\tau_{\text{rec}}$ (sec) | O$_3$ Conc. (ppb) | References |
|-----------------|----------------------|-------------------|-----------------------------|---------------------------------------------|-------------------|------------|
| nCo$_2$O$_4$    | Co-precipitation     | 200               | 0.23                        | 8/10                                        | 80                | [24]       |
| SrTi$_{0.85}$Fe$_{0.15}$O$_3$ | Electron beam deposition | 260               | 0.33                        | 26/72                                       | 100               | [25]       |
| Zn$_{0.95}$Co$_{0.05}$O | Spray pyrolysis      | 250               | 0.40                        | 46/62                                       | 20                | [26]       |
| NiAl            | Hydrothermal         | 175               | 2.2                         | 4/5                                         | 15                | [27]       |
| CuO             | RF sputtering        | 150               | 1.8                         | 200/500                                     | 300               | [28]       |
| SnO$_2$ (triton) | Spin coating         | 175               | 3                           | 15/720                                      | 500               | [29]       |
| ZnO             | Hydrothermal         | 150               | 3                           | 9/300                                       | 60                | [30]       |
| Zn$_{0.95}$Co$_{0.05}$O | Polymeric precursors | 200               | 3                           | 46/360                                      | 42                | [31]       |
| In$_2$O$_3$     | MOCVD                | 175               | 4                           | n/a                                         | 10                | [32]       |
| In$_2$O$_3$     | Sol-gel              | 175               | 20                          | n/a                                         | 200               | [33]       |
| Cu$_2$O         | RF sputtering        | 175               | 26.31                       | 44/92                                       | 100               | Present work |

$\text{(A} - \text{O}) + e^- \rightarrow \text{(A} - \text{O})^-$ \hspace{1cm} (3)

where ‘A’ is one free adsorption site.

The electron trapped by the oxygen at the Cu$_2$O surface (equation (3)) decreases the layer resistance by increasing the major charge carrier (hole) concentration [23]. When the test chamber is purged, ozone is replaced by dry air. Then the adsorbed oxygen resulting from O$_3$ decomposition is removed from the surface of Cu$_2$O, according to the following reaction:

$O_{(\text{ads})} \leftrightarrow \frac{1}{2} O_{2(g)} + e^- + A$ \hspace{1cm} (4)

The electron produced by this oxidizing process is injected into the Cu$_2$O layer, which induces an increase in the layer resistance and the baseline is well restored.

In the case of thicker Cu$_2$O layer (Film(2 min)), two adsorption processes could take place during ozone decomposition according to the reaction (equation (2)). The first process is the surface O$_3$ adsorption like in the case of thinnest Cu$_2$O layers. In this case a part of surfacic adsorbed oxygen could diffuse in the bulk. When the test chamber is purged, only surfacic adsorbed oxygen is easily removed while the diffused one could react irreversibly with oxygen vacancies in the bulk and become hardly desorbed. As a consequence, after each ozone cycle exposure, the baseline doesn’t reach its initial previous resistance level, which explains the permanent decreases of the baseline resistance. It can be concluded that only surfacic adsorbed oxygen contributes to the Cu$_2$O layers responses. Diffused oxygen affects only the overall baseline resistance level.

3.3.3. Morphological and structural effects on the Cu$_2$O responses

At the optimum working temperature for 100 ppb of O$_3$, the layers Film(30 s) and Film(1 min) exhibit the smallest response and recovery times as reported in Table 2.

Also, the sensitivity was found to be around 26.31 (figures 5(a)) and 18.87 (figure 5(b)) respectively, as compared to the very low sensitivity of Film(2 min) (figure 5(c)).

This result was compared to some recent materials based sensors as tabulated in Table 3 [24–33].

According to W. Gopel [34], the flat-band conditions are fulfilled to a good approximation when $L_{Q} > \sqrt{2}$; where $l$ is the measured grain diameter and $L_Q$ is the space charge region width. This means that the conductivity is mainly influenced by surface effects. This phenomenon will be more pronounced for the thinnest Cu$_2$O sensitive layers, which is in good agreement with our experimental observations where the best responses are obtained for layers of 40 nm and 70 nm for sensors fabricated from Film(30 s) and Film(1 min), respectively (see figure 5(a) and b). Increasing the thickness of the sensitive layer degrades the sensors sensitivity (figure 5(c)).

However, the lower thickness limit of the thinnest Cu$_2$O sensitive layers must be of the same order of magnitude.
as the electrode thickness, which corresponds to a sputtering time of around 40 s, when considering a linear behavior of the thickness versus deposition time. This condition is important to avoid the degradation of sensor’s sensitivity.

Finally, in case of sensor with layer of 70 nm (Film(1 min)), saturation has been achieved when the amount of ozone became higher than 600 ppb. However, a state of non-saturation has been noticed in the case of the thinnest layer (Film(30 s)).

In general, the response of oxide materials is related to the number of available adsorption sites \( \theta \) which depends on the working temperature and ozone concentration \([28]\). The number of available adsorption sites can be correlated to the degree of crystallinity along the preferential direction (111). We have noticed that the sensor (Film(30 s)) with a 40 nm sensitive layer thickness, may have the highest \( \theta \) because it reveals non-saturation state. In addition, this sensor presents the highest degree of crystallinity in the (111) direction as shown in table 1. Also, it has been found that the crystallinity decreases with the increase in sensor thickness which makes the saturation of the response is more pronounced. In the literature it was found that the Cu2O (111) surface is the most favorable adsorption surface for NO, CO, H2O, H2 and O2 \([35–39]\). In line with this, we suggest that Cu2O (111) surface could also be the most favorable adsorption surface for O3 molecules. So a theoretical calculations was performed for this surface and presented in following section.

3.3.4. Mechanism of O3 adsorption on Cu2O (111) surface.

In order to investigate the effect of Cu2O (111) surface on the O3 adsorption and deduced the probably adsorption mechanism on this surface. For that purpose an Ab-initio calculations were carried out for the Cu2O (111) surface presented in figure 7, where Cu1 was a copper atom in the center between two oxygen atoms and Cu2 the copper atom attached to a single oxygen atom. In addition, the copper atoms were organized in parallel rows of Cu2 alternating with rows formed by an alternation between Cu1 and Cu2 atoms. All calculations were performed with a O3 molecule initially close to sites with a positive charge using the siesta code \([40, 41]\).

After the system relaxation, we found two equilibrium situations, in the first situation O3 molecule was adsorbed without dissociation when each extreme oxygen atoms of O3 were on one copper atom (figure 8(A)). The second situation O3 molecule was adsorbed with dissociation on the surface (111) when one of its oxygen extremities is on Cu1 copper atom (figure 8(B)).

For the first situation the, adsorption energy, \( E_{\text{ad}} \), is determined by the following equation:

\[
E_{\text{ad}} = E(\text{Cu}_{2n}O_n + O_3) - E(\text{O}_3) - E(\text{Cu}_{2n}O_n)
\]  

(5)

where \( E(\text{Cu}_{2n}O_n + O_3) \) is the Cu2nO_n surface energy with adsorbed ozone, \( E(\text{Cu}_{2n}O_n) \) is the energy of the clean Cu2O surface and \( E(\text{O}_3) \) is the ozone molecule energy.

We found an \( E_{\text{ad}} = -2.89 \text{ eV} \), meaning that the reaction is thermodynamically favorable.

For the second situation, the molecule is dissociated according to the following reaction:

\[
\text{Cu}_{2n}O_n + O_3 \rightarrow \text{Cu}_{2n}O_{n+1} + O_2,
\]  

(6)
given one oxygen atom adsorbed on Cu1 atom and O2 dioxygen molecule. The reaction enthalpy was given by:

\[
\Delta H = E(\text{Cu}_{2n}O_{n+1}) + E(O_2) - E(\text{Cu}_{2n}O_n) - E(O_3)
\]  

(7)

where \( E(\text{Cu}_{2n}O_{n+1}) \) was the \( \text{Cu}_{2n}O_n \) energy on the surface with an adsorbed oxygen \( O_{\text{ad}} \), \( E(\text{Cu}_{2n}O_n) \) is the surfacic \( \text{Cu}_{2n}O_n \) energy for a surface with \( n = 24 \) atoms, \( E(O_2) \) was the energy of the triplet state (\( S = 1 \)) of O2 and \( E(O_3) \) is the free O3 energy. Then the calculated enthalpy was \(-2.64 \text{ eV} \), less than the dissociated adsorption energy \(-2.89 \text{ eV} \).

According to previous results the adsorption mechanism taking into account the O3 molecule dissociation, was energetically more favorable.

In this case O3 molecule was adsorbed with \( E_{\text{ad}} = -2.89 \text{ eV} \). After dissociation, a dioxygen molecule O2 could remain in interaction at the surface. This third situation of O3 semi-dissociation; which derived from the dissociative adsorption; was shown in figure 8(C), and given by the following the reaction:
With

\[ E_{\text{ad}} = E(Cu_{2n}O_{n+1} + O_2) - E(Cu_{2n}O_n) - E(O_2) \]

where \( E(Cu_{2n}O_{n+1} + O_2) \) was the surface with an adsorbed oxygen \( O_{\text{ad}} \) and dioxygen \( O_2 \) in interaction, \( E(Cu_{2n}O_n) \) was the energy of the \( Cu_{2n}O_n(111) \) surface and \( E(O_3) \) was the \( O_3 \) energy.

Then, taken into account the basis set superposition error (BSE) calculated as following:

\[ E_{\text{BSE}} = (E(O_3)_{O_3}^{(O_3 + Cu_{2n}O_n)}) - E(O_3)_{O_3}^{(O_3 + Cu_{2n}O_n)} - E(Cu_{2n}O_{n(111)})_{O_3}^{(O_3 + Cu_{2n}O_n)} \]

We obtain an adsorption energy \( E_{\text{ad}} = -2.49 \text{ eV} \). This adsorbed energy value signs an energetically more favorable situation compared to the \( O_3 \) adsorption without dissociation (\( -2.89 \text{ eV} \)) or with a complete dissociation of \( O_3 \) molecule (\( -2.64 \text{ eV} \)).

4. Conclusion

In conclusion, we demonstrated ozone detection using \( Cu_2O \) thin layers that deposited upon interdigitated platinum electrodes. \( Cu_2O \) layers were sensitive to ozone down to 1 ppm. The sensors exhibited a good response to ozone, which is strongly influenced by the thickness of the sensitive layer and structural properties. The sensitive layer should have a thickness comparable to that of the electrodes. Also, the \( (111) \) plane is the preferential orientation for ozone adsorption. By utilizing the advance detection mechanism, we have deduced that only surfacic adsorbed oxygen contribute to the \( Cu_2O \) layers responses. Whereas, the diffused oxygen affects only the overall baseline resistance level in the case of increasing the layer thickness.

Ab-initio calculation shows that \( O_3 \) adsorption could be semi-dissociative, giving \( O_2 \) molecule remaining in interaction with surface and an adsorbed oxygen \( O_{\text{ad}} \) on \( Cu_1 \) (\( E_{\text{ad}} = -2.49 \text{ eV} \)).

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