Novel Cu$_2$O gas sensor prepared by potentiostatic electrodeposition on IDE electrodes

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Abstract. This paper introduces a new approach for preparation a gas sensor based on the potentiostatic electrodeposition of Cu$_2$O on interdigitated electrodes. Four Cu$_2$O gas sensors with different deposition charges were prepared from lactate-stabilized copper sulphate on Au IDE electrodes. Prepared sensors were characterised by scanning electron microscopy and electrical measurements in the air and H$_2$ ambient. It was found that the key aspect for high gas sensitivity is to achieve an appropriate rate of crystal interconnection between IDE electrodes. Low deposition charge results in an air gap between IDE electrodes, while high deposition charge causes strong, bulk-like interconnection of Cu$_2$O crystals. The low rate of Cu$_2$O interconnection formed by connection of individual crystals, where the conductance is affected by the surface area of the crystals, is shown as a most appropriate sensor. The sensitivity of 3.75 to 1000 ppm H$_2$ concentration and 200 $^\circ$C operation temperature is achieved for the optimised Cu$_2$O based IDE sensor.

1. Introduction

Development of a gas sensor with the ability to attain high sensitivity and low fabrication cost is a key issue for industrial applications. Intensive research is focused mainly on metal oxides that provide high sensitivity and can be fabricated by sputtering [1], spray pyrolysis [2], sol-gel [3], or hydrothermal method [4]. Among the metal oxides, cuprous oxide (Cu$_2$O) attracts strong attention due to the possibility to tune the conduction type and crystallographic structure by altering the deposition conditions [5]. All such aspects make Cu$_2$O a very interesting material with high expectations for gas sensing applications.

In this paper, a new approach for Cu$_2$O gas sensor fabrication based on potentiostatic electrodeposition on interdigitated electrodes (IDE) is introduced. Electrodeposition is a simple, low cost technique for preparation of metal oxides. Altering the deposition bath, deposition voltage or deposition time can be used to tune the crystallographic and electrical properties of Cu$_2$O layers [6] and thus the sensitivity to the gas. Electrodeposition has already been used for fabrication of Cu$_2$O gas sensor on porous pSi substrate with achieved sensitivity of 4.5 to 1 ppm NO$_2$ [7]. Our approach is based on potentiostatic electrodeposition of Cu$_2$O on Au IDE electrodes, where the electrodeposited Cu$_2$O crystal causes interconnection and thus electrical contact between IDE electrodes. Potentiostatic electrodeposition provides better control over the nucleation and grown of the initial Cu$_2$O layers. The influence of the deposition charge on the interconnection between IDE electrodes and their impact to the gas sensing properties is analysed and discussed.
2. Experimental setup
Electrodeposition was carried out in a three-electrode configuration with a Pt electrode as a counter electrode, saturated Ag/AgCl reference electrode and an interdigitated electrode (IDE) as a working electrode. A thin-film interdigitated electrode with 180 pairs of gold 5 µm wide electrodes and with 5 µm gap between the electrodes from MicruX was used as a IDE electrode. Copper (II) sulfate (CuSO\(_4\), 0.4 mol/L) with L-lactic acid (3 mol/L) adjusted by LiOH to pH 12.5 was used as a deposition electrolyte. All depositions were carried out at deposition voltage –450 mV vs. Ag/AgCl and deposition temperature 45 ºC controlled by a water bath. The amount of deposited material was controlled by the monitoring of deposition charge transported between Pt and IDE working electrodes. IDE electrodes prepared by deposition charge of 50, 100, 120 and 170 mC marked as IDE50, IDE100, IDE120 and IDE170 are described in the following study. The gas responses were investigated in the temperature range of 25 – 250 °C. The electrical response of the Cu\(_2\)O films was measured under laboratory conditions for hydrogen. The gas measurements of Cu\(_2\)O layers were provided in gas chamber CascadeMicrotech PLV50 using 4 probes with gold tips. Sensing the electrical response of the gas sensor to test gas was performed by measuring the electrical resistance of the gas sensitive layer between IDE electrodes using SourceMeter Agilent B2902B.

3. Results and discussion
The critical aspect for the preparation of Cu\(_2\)O based gas sensor on IDE electrodes is the rate of crystal interconnection between IDE electrodes. While the Cu\(_2\)O grows in all directions, the thickness of the Cu\(_2\)O layer and hence the air gap between IDE fingers decreases with the deposition time. Figures 1a-c show three possible situations, which can arise during the electrodeposition of Cu\(_2\)O on IDE. Figure 1a) shows a low amount of deposited Cu\(_2\)O and hence a gap between the IDE fingers. With increasing deposition time, the thickness of the deposited layer increases in all directions and the fingers are interconnected by Cu\(_2\)O crystals (figure 2b). This case is characterized by a large surface area of interconnected crystals. With a further increase of the deposition time, the size of the crystals increases and causes stronger interconnection between IDE electrodes (figure 3c). In this case, the electrical conductance between IDE is determined by bulk Cu\(_2\)O crystals which have a weak connection with the ambient gas. Since the gas sensing mechanism is caused mainly by the interaction of the Cu\(_2\)O surface with the target gas, the case b) has the best condition to achieve high sensitivity.

![Figure 1](image_url)

**Figure 1.** a) IDE electrodes with a low amount of deposited Cu\(_2\)O and with an air gap between electrode fingers, b) IDE electrodes with interconnection between individual Cu\(_2\)O crystals, c) IDE electrodes with a high degree of Cu\(_2\)O interconnection, d) prepared MicruX IDE electrode with deposited Cu\(_2\)O layer.

3.1. Sample fabrication
Potentiostatic electrodeposition is characterized by a decreasing deposition current and thus deposition speed with time. Because of this, the amount of the deposited material can be more precisely controlled by monitoring the deposition charge. This charge is equal to the deposited Cu\(_2\)O. Figure 2
Figure 2. a) Current as a function of time during electrodeposition. b) Deposition charge as a function of time measured during electrodeposition.

3.2. SEM characterisation

Figure 3 shows SEM images of studied samples. All Cu$_2$O samples exhibit crystals with an octahedral shape. Such crystals are defined by (111) facets [8]. It was shown that crystals with (111) facets exhibit a higher sensitivity to H$_2$ and CO compared to crystals with (100) facets presented in cubic or truncated octahedral Cu$_2$O crystals [8]. The size of crystals increases with the increased deposition time and deposition charge. Sample IDE50 exhibits crystals with a low size and air gaps between IDE fingers. The low deposition charge was not sufficient to attain conductive interconnection between IDE fingers. The sample IDE100 exhibits interconnection between IDE fingers formed by the connection of individual crystals. With a further increase of the deposition time and charge the size of Cu$_2$O crystals increases causing a higher coverage of Au IDE electrodes and a higher degree of conductive interconnection between IDE electrodes. Sample IDE170 is characterized by strong interconnection between Cu$_2$O crystals forming a bulk-like nature of the connections between IDE electrodes.

3.3. Electrical characterisation

The resistance between IDE fingers of the prepared sensors was used to gain a deeper insight in the electrical interconnection between measured Cu$_2$O crystals. In addition, the temperature dependent resistance was measured to provide an insight in the carrier transport in the structure. Figure 4 shows Arrhenius curves of the resistance for samples IDE100, IDE120 and IDE170. Sample IDE50 exhibited...
Figure 3. SEM pictures of IDE100, IDE120 and IDE170. Inset shows the detail of interconnection between Cu$_2$O crystals.

an infinitely large resistance confirming an air gap between IDE fingers. The resistance of sample IDE100 is significantly higher compared to samples IDE120 and IDE170. Decreased resistance with increased deposition charge confirms the higher degree of Cu$_2$O interconnection between the fingers of the IDE electrode. IDE100 exhibits a linear behavior of the Arrhenius curve with a slope of 0.27 eV. This slope represents the activation energy of the thermal process responsible for the current transport. Energy levels between 0.12 and 0.45 eV were observed for p-type Cu$_2$O material [9, 10] and were associated with the native acceptor in Cu$_2$O formed by negatively charged copper vacancies [11]. The activation energy of 0.27 eV is within this range and thus in our case can be associated with copper vacancies. Such copper vacancies are the source of intrinsic p-type doping of the Cu$_2$O and are located near the valence band level of Cu$_2$O. Due to the low interconnection between IDE fingers of IDE100, the carrier transport is limited by a few individual Cu$_2$O crystals which are in contact with each other. Such crystals are in the air ambient and thus contain a hole accumulated layer at the surface formed by the interaction of Cu$_2$O with oxygen form the air. Modulation of this accumulated layer upon the interaction with target gas is the source of the sensor response to the gas. Samples IDE120 and IDE170 exhibit a significantly lower resistance with nonlinear behavior in the Arrhenius representation of the resistance (figure 4). The nonlinear behavior of the resistance was previously observed on bulk metal oxides and was associated with scattering mechanisms at the grain boundaries [11]. For such structures, the current transport is facilitated by a higher amount of interconnected crystals which are not in the contact with the ambient atmosphere.

3.4. Gas sensing properties
The gas sensing properties were investigated by monitoring the sensor response to H$_2$. The response of the structure to the gas was calculated as a ratio between resistances measured in H$_2$.
Figure 4. Temperature dependence of the resistance for studied IDE electrodes.

Figure 5. a) Sensitivity of Cu$_2$O electrodes IDE170, IDE120 and IDE100 to H$_2$ at 200 °C and 250 ppm. b) Sensitivity of IDE100 to H$_2$ at 150 °C and 200 °C temperatures and 250, 1000 ppm H$_2$ concentration.
4. Conclusion
A new approach for fabrication of Cu$_2$O gas sensors by potentiostatic electrodeposition on Au IDE electrodes was introduced in this paper. It was shown that the key factor for achieving a high gas response is the appropriate interconnection between Cu$_2$O crystals deposited on Au IDE electrodes. This interconnection can be controlled by monitoring the deposition charge. The best H$_2$ sensitivity was achieved with IDE sensor prepared at a deposition charge of 100 mC and interconnection between individual crystals. Such crystals are in connection with the ambient and the current transport between crystals is determined by interaction of the Cu$_2$O surface with the gas. Sensitivity of 3.75 was achieved with the optimized IDE electrode at 200 °C and 1000 ppm H$_2$ concentration. A more precise control of the crystal size grown is required for further improvement of the proposed Cu$_2$O based IDE sensor.

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