Sensors and Actuators B 141 (2009) 270–275

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Chemical vapor deposition of copper oxide films and entangled quasi-1D nanoarchitectures as innovative gas sensors

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ARTICLE INFO

Article history:
Received 8 April 2009
Received in revised form 22 May 2009
Accepted 27 May 2009
Available online 12 June 2009

Keywords:
Copper oxides
Films
Nanoarchitectures
Chemical vapor deposition
Gas sensors

ABSTRACT

Supported copper oxide nanosystems were synthesized by chemical vapor deposition (CVD) on Al_2O_3 substrates and characterized by means of glancing incidence X-ray diffraction (GIXRD), secondary ion mass spectrometry (SIMS) and field emission scanning electron microscopy (FESEM). The analyses showed an evolution from polycrystalline Cu_2O nanodeposits to CuO samples with an entangled quasi-1D morphology upon increasing the growth temperature from 350 to 550 °C. For the first time, the sensing properties of CVD copper oxide nanosystems were probed in the detection of volatile organic compounds (VOCs; *e.g.* CH_3COCH_3, CH_3CH_2OH). The obtained results revealed good responses even at moderate operating temperatures, with characteristics directly dependent on the system composition and nano-organization.

1. Introduction

Copper oxides (Cu_2O and CuO) are important *p*-type multifunctional semiconductors that have been extensively investigated for various technological applications, such as field emission devices, batteries, solar energy conversion, photovoltaic materials, heterogeneous catalysts, gas sensors [1–13]. In view of such utilizations, intense efforts have been devoted to the development of many kinds of morphologies, such as wires, cubes, spheres, cages, whiskers and so forth [8,10]. In fact, organized nanostructured materials feature unique properties and attractive performances thanks to their large surface-to-volume ratio, the presence of size effects and of various defects, often resulting in an unexpected reactivity [9–11]. In the field of gas sensing, the combined influence of the above phenomena is significantly advantageous in order to achieve a high gas sensitivity and a rapid response [14].

In this context, Cu_xO ($x = 1,2$) nanosystems have received an increasing attention for various applications, from enzymatic glucose biosensors [15] to solid state gas sensors. In particular, several research activities have been aimed at CO detection, not only by means of pure copper oxides [7,11,14,16], but also by ZnO–CuO composite systems [8,17–19]. Other reports have been focused on the sensing properties of Cu_xO systems towards carbon dioxide [20], NO_x [12,14,16,21,22], ethanol [10,11,13], as well as alcohols, gasoline and H_2S [8,22]. Despite these works, the research on nano-organized Cu_xO ($x = 1,2$) as gas sensors is still far from being satisfied [11,16]. In fact, the majority of reports on oxide-based gas sensing devices has been devoted to the use of *n*-type semiconductors [9,11], whereas the performances of *p*-type Cu_xO, especially in the form of supported quasi-1D nanomaterials, have been scarcely investigated [12,14] and undoubtedly deserve further studies [9].

Up to date, most of functional 1D, 2D and 3D Cu_2O and CuO nanoarchitectures have been mainly prepared in the form of powders, *e.g.* by thermal oxidation [1,14,16], solution routes [3,8,11,13,20], hydrothermal [7,9,10,15], solvothermal and electrochemical methods [4,5,7]. Indeed, advances in the tailored preparation of the above systems still represent a challenging issue and is therefore a strategic subject of ongoing investigations.

As a part of a comprehensive research project on multifunctional copper oxide nanosystems for applications in innovative Li-ion batteries and photocatalytic water splitting for H_2 production [6], we have recently developed a novel chemical vapor deposition (CVD) route to Cu_xO nanosystems on Si(1 0 0) substrates starting from a copper(II) hexafluoroacetylacetonate (1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, hfa) adduct with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) [$Cu(hfa)_2$·TMEDA], endowed with favorable properties in terms of volatility, stability and mass transport [23]. In particular, we have

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doi:10.1016/j.snb.2009.05.038

shown the possibility to tailor the phase composition from Cu_2O to CuO, as well as the system nano-organization, by controlled variations of the growth temperature. The present paper is devoted to a further insight into the system properties, with particular attention to the analysis of functional performances in solid state gas sensors. To this regard, depositions were performed on polycrystalline Al_2O_3 substrates and the systems were subjected to preliminary structural, compositional and morphological investigations. Subsequently, the sensing properties were tested in the detection of selected reducing gases, in particular CH_3COCH_3 and CH_3CH_2OH, of interest for applications in food quality monitoring and breath analyzers [24,25]. It is worth highlighting that, whereas previous works have reported on the gas sensing performances of Cu_xO (x = 1,2) nanosystems in CH_3CH_2OH detection, to the best of our knowledge their response towards acetone has never been investigated up to date.

2. Experimental

Copper oxide nanodeposits were synthesized by means of a custom-built cold-wall CVD reactor [26,27] under electronic grade O_2-based reaction atmospheres, using $Cu(hfa)_2$·TMEDA as precursor. Based on previous results [23], the growth temperatures were fixed at 350 and 550 °C, in order to obtain Cu_2O and CuO nanodeposits, respectively.

Polycrystalline alumina slides (3 mm × 3 mm; thickness = 254 μm) were used as substrates and suitably cleaned before each deposition, in order to minimize the presence of surface contaminants. Depositions were performed at a total pressure of 10.0 mbar and a precursor heating temperature of 70 °C, with a total O_2 flow rate of 200 sccm (total duration = 2 h). The gas lines between the precursor vaporizer and the reaction chamber were maintained at 120 °C throughout each deposition in order to prevent undesired precursor condensation phenomena. At the end of each experiment, samples were cooled down to room temperature under flowing O_2.

GIXRD measurements were performed at a constant incidence angle of 0.5° by means of a Bruker D8 Advance diffractometer, equipped with a Göbel mirror and a Cu Kα source powered at 40 kV, 40 mA. The angular accuracy was 0.001° and the angular resolution was better than 0.01°. The Scherrer equation was used to estimate the mean crystallite dimensions.

SIMS depth profiles were recorded by means of an IMS 4f mass spectrometer using a Cs^+ primary beam (14.5 keV, 10 nA) and by negative secondary ion detection. Beam blanking mode was used to improve the depth resolution, interrupting the sputtering process during magnet stabilization periods. In order to take into account the influence of matrix composition, the erosion speed was evaluated at various depths through measurements of the corresponding crater heights by a Tencor Alpha Step profiler. For a reliable evaluation of sample thickness, the effects of both the instrumental response function, as well as of the substrate and the deposit roughness, must be properly considered, since they result in an apparent broadening of the deposit–substrate interface width. Whereas the former two were determined by means of standard approaches [28], the effect of the deposit roughness was modelled by considering a Gaussian distribution. In this case, the deposit is described as a step (with thickness equal to the mean value) modulated by a sequence of peaks and valleys whose amplitude is estimated in terms of standard deviation from the average. On this basis, in the present work the nanodeposit thickness values were obtained by the Cu signal, after correcting the measured profile by the instrumental function and the substrate roughness contributions.

FESEM analyses were performed by means of a Zeiss SUPRA 40VP instrument, at a fixed accelerating voltage of 5.0 kV. The mean nanoaggregate sizes were evaluated through the SmartSEM™ software, by averaging over 20 independent measurements.

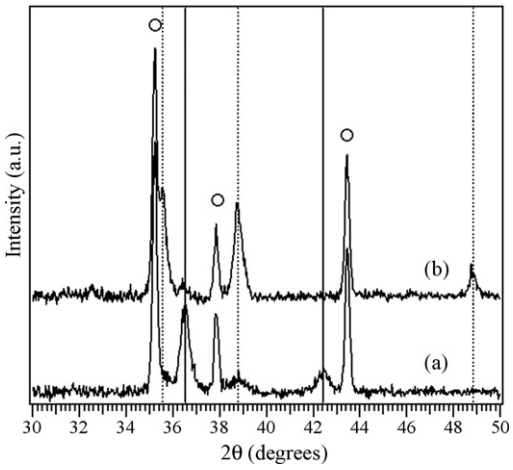

Fig. 1. GIXRD patterns for copper oxide specimens deposited at: (a) 350 °C; (b) 550 °C. The reflections reported for bulk Cu_2O [29] and CuO [30] are evidenced by continuous and dashed lines, respectively. The Al_2O_3 substrate diffraction peaks [24] are marked by circles.

For the fabrication of sensors, a platinum interdigitated electrode structure [24] and a Pt heater were deposited by sputtering over copper oxide nanosystems and on the substrate backside, respectively. The sensor operating temperature was achieved by applying a constant voltage to the heater, using the same Pt resistance also as a thermometer. In order to calibrate the actual temperature of the sensing layer, combined measurements of the power dissipated by the heater and thermal measurements with an infrared camera were performed. These tests indicated a negligible gap between the temperature of the sensing material and that measured on the back of the device, as expected by considering the very low substrate thickness.

Gas sensing properties were tested by means of the flow-through technique [24] at atmospheric pressure, using a constant synthetic air flow (0.3 l/min) as carrier gas for the analyte dispersion. Measurements were performed in the 100–400 °C range under a constant humidity level of 40%, in a sealed chamber maintained at a fixed temperature of 20 °C throughout each experiment. The sensor resistance was monitored by means of the volt-amperometric technique at constant bias voltage. Herein, the sensor response S is defined as the relative resistance variation upon the target gas exposure [12] (estimated uncertainty = ±5%). The response and recovery times were calculated as previously described [11,25]. Before measurements, all samples were pre-stabilized at the working temperature for 8 h. Under these operating conditions, the assembled sensors presented a stable response and did not show significant activity losses upon repeated utilization, the maximum deviations not exceeding 10%.

3. Results and discussion

The obtained copper oxide nanodeposits were homogeneous and well adherent to the alumina substrates. On increasing the deposition temperature from 350 to 550 °C, a color evolution from yellowish to dark brown could be observed.

The system structural properties were investigated by GIXRD (Fig. 1). For T = 350 °C, the pattern was dominated by two diffraction peaks located at 2θ = 36.5° and 2θ = 42.4°, attributed to the (1 1 1) and (2 0 0) crystallographic planes of cubic Cu_2O [29]. Conversely, an increase of the growth temperature resulted in the appearance of signals at 2θ = 38.8° and 48.8°, corresponding to the (1 1 1) and