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Enhanced ethanol vapour sensing performances of copper oxide nanocrystals with mixed phases

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ABSTRACT

Copper oxide nanostructures are fascinating nanomaterials due to their remarkable electrical, optical, thermal, and sensing properties given that their tunability and the stabilization of specific phases are uniquely possible at the nanoscale dimensions.

The present study reports on nano-crystalline copper oxide thin films via a simple synthesis from chemical solutions (SCS) followed by two types of thermal annealing, namely rapid thermal annealing (RTA) and conventional thermal annealing (TA). We report on the enhanced ethanol sensing performances of the device structures based on synthesized copper oxide nanocrystals with one and two distinctly different phases, namely Cu_2O, CuO, as well as mixed phases CuO/Cu_2O.

A gradient in phase change of nano-crystals was observed for annealed samples starting from CuO on the top to Cu_2O in their central region. RTA effects on the gas response of the Cu_xO_y nano-crystals have been identified as unprecedented selectivity and sensitivity to ethanol vapours at different temperatures. An increase in resistance value of about one order in magnitude was detected for samples treated by conventional-TA at 400 °C for 30 min at optimal operating temperature of 300 °C and RTA at 525 °C for 60 s at lower optimal operating temperature of 275 °C. It has been observed that the response and recovery times for pure copper oxide-based sensors can be significantly improved by Zn-doping, e.g. from ~4.1 s and ~10.5 s to about 3.3 s and 7.2 s, respectively.

The obtained results were discussed in details and it provide an exciting alternative for fast, sensitive, and selective detection of trace gases, which could be of several benefits in the technologies dealing with public securities and environmental monitoring applications.

1. Introduction

Nanoscale heterojunctions of semiconducting oxide nanocrystals have attracted a great attention due to their enhanced performances as gas sensors with a specific sensing mechanism. The properties of the nanoscale heterojunctions in nano-crystals can dominate the gas sensing behaviour of the entire device due to the surface and interface effects, which can lead to considerable enhancement of sensors sensitivity and selectivity [1]. The most reported heterojunction types are *p*–*n* and *n*–*n* configurations, demonstrating possibilities of gas response enhancement and of its integration in e-nose systems for a more reliable selective detection [2,3]. However, in such a case a new nanoscale *p*-type semiconductor oxide is required, which can be grown via versatile, cost-effective, and simple technologies. From the other side, the literature demonstrates that almost very less attention has been paid to *p*–*p* type nanoscale heterojunctions [3,4]. The most promising *p*-type materials for gas sensing applications are CuO, Cu_2O, NiO, Co_3O_4, and Cr_2O_3, which showed quite promising sensing properties for rapid and reliable detection of acetone C_3H_6O, C_2H_5OH, NH_3, H_2, CO, NO_2, and H_2S gases [5].

In this context, sensors based on copper oxide nano-crystals have attracted considerable attention due to simple synthesis methods, e.g., thermal oxidation of Cu foil in air, possibility for

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synthesis of various types of morphologies, such as mesoporous and nanostructured films [6–8], nanowires and nanorods [9,10], nanocubes [4], quasi-spherical and urchin-like micro-architectures [9], worm-like and fibre-like structures [9,11], and other nanostructures [12–14]. All of the reports have demonstrated quite promising potential of the CuO and Cu_2O for ethanol vapour and other volatile organic compounds (VOCs) sensing applications.

According to the literature review and as per demands from different gas sensing technologies, it appears a clear necessity for a reliable and efficient synthesis process which yields high quality CuO/Cu_2O nanoscale heterojunctions. In this context, nanotechnologies with rapid thermal annealing (RTA) can be an efficient approach to solve real problems for engineering. Few studies were reported on properties of RTA treated copper oxide nanostructures [15]. However, the control of the surface, interface, and gas sensing properties of the CuO/Cu_2O nanoscale heterojunctions obtained by a cost-effective RTA process in Cu_xO_y nano-crystals has so far not been reported in accordance with literature.

The control of crystallite size in copper oxide thin films within nano-scale dimensions is known to modify optical and electrical properties due to quantum confinement and enhanced surface effects [16]. However, there are only very few reports on copper oxide nanoparticulate or nanocrystalline thin films and their modified surface properties [16]. The existing recent studies are indicative of an increased interest in the synthesis and characterization of nanoparticles and nanocrystalline *p*-type Cu_2O thin films as an attractive semiconductor oxide material for the fabrication of sensors, low cost solar cells, and other opto-electronic devices [16]. Despite the above-mentioned relevant results, a detailed research work needs to be carried out to develop a nanotechnology for synthesis of high quality nanocrystalline copper oxide thin films with semiconductor properties. Along with this, it is important to understand the modified structural, electronic, and electrical properties due to the quantum confinement and surface effects of such oxide thin films.

This work reports on new approaches developed to improve performances of CuO/Cu_2O nanoscale heterojunctions-based sensorial structures. The effects of conventional thermal annealing in furnace – TA and of rapid one – RTA on the copper oxide nanocrystals characteristics and gas responses have been investigated in detail. The size-dependent structural, electronic, vibrational, and sensor characteristics of these Cu_xO_y nano-crystals are discussed in detail. Faster response and recovery times for ethanol vapour have been found for developed sensors based on CuO/Cu_2O nanoscale heterojunctions. Next, by Zn-doping in Cu_xO_y samples based sensors it was possible to further considerable reduce the response and recovery times. The mechanism of ethanol sensing based on interaction with ionosorbed oxygen species and based on decomposition and/or oxidation reaction of ethanol molecules has been tentatively proposed to explain the obtained results for both pure and Zn-doped copper oxide samples.

2. Experimental details

2.1. Chemical deposition of Cu_2O nanostructured films on glass substrate

The synthesis from chemical solution (SCS) was performed for growing cuprous oxide (Cu_2O) nanostructured films on the commercial microscope glass slides (76 mm × 25 mm × 1 mm). Substrates have been carefully cleaned before processing in many subsequent steps to remove all contaminations from the glass surface as described in the previous works [17,18] and then sensitized in $SnCl_2{\cdot}2H_2O/HCl$ solution [19]. Starting materials for copper thiosulfate complex solution, used as the cation precursor, were 1 M of copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) and 1 M of sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$). All chemicals were analytical grade without further purification. The $Na_2S_2O_3{\cdot}5H_2O$ was gradually added to $CuSO_4{\cdot}5H_2O$ under stirring until mixed solution becomes transparent. The involved synthesis reaction can be expressed in terms of chemical complexation equilibria [20]:

$$2Cu^{2+} + 4S_2O_3^{-} \Leftrightarrow 2[Cu(S_2O_3)]^{-} + [S_4O_6]^{2-} \quad (1)$$

Further, by adding respective quantities of deionised water (DI), the solution was diluted to obtain 0.1 M of copper ion concentration. The anionic complex solution represents 2 M of NaOH in DI water. During the Cu_2O nanostructured film deposition the beaker containing copper sulphate solution was maintained at room temperature, while the beaker with anionic complex solution was maintained at 80 °C. The glass substrate was immersed vertically in the solutions by using a home made microprocessor based deposition system developed especially for the chemical deposition SCS techniques, and represents an articulated robot. Advantage of such deposition system is a precise control of the substrate dipping time and number of performed SCS cycles, which exclude errors due to human factor. The pre-cleaned glass substrate was attached to a Teflon holder mounted on the mini-robot arm. Due to repetitive and precise movements of the robot arm, the nanostructured films have been deposited more uniformly in comparison with manual deposition process. All of these factors allow us to synthesize more reproducible samples and in larger quantities, which can be easily up-scaled for industrial production. One SCS deposition cycle of Cu_2O nanostructured film can be generalized by the following steps: (1) immersion of the pre-cleaned glass substrate in the hot (at 80 °C) anion solution for adsorption of hydroxide anions (OH^-); (2) immersion of the glass substrate in the copper complex solution for reaction of Cu^+ cations with adsorbed OH^- anions. The resulting reaction can be expressed by [20,21]:

$$2Cu^{+} + 2OH^{-} \rightarrow 2CuOH \rightarrow Cu_2O + H_2O \quad (2)$$

The Cu^+ cations are formed by complex dissociation equilibrium [20]:

$$[Cu(S_2O_3)] \Leftrightarrow Cu^{+} + S_2O_3^{2-} \quad (3)$$

To precisely control the thickness of the nanostructured films, a certain number of SCS cycles has been performed, according to a preliminary measured graph. After chemical deposition the as-grown nanostructured films were rinsed thoroughly with DI water and dried in a hot air flux (∼150 °C) for 1 min. The post-growth thermal annealing was performed by rapid thermal annealing RTA for 60 s and thermal annealing TA in electrical furnace for 30 min at different temperatures in air. The experimental data are shown below in dependence of annealing temperature and operating temperature of the sensors.

2.2. Morphological, structural, vibrational, and chemical studies of the grown samples

The morphologies of the synthesized pure and Zn-doped copper oxide nanostructured films were examined by a scanning electron microscope (SEM, Zeiss, 7 kV, 10 μA). X-ray powder diffraction (XRD) was performed after the sample preparation to confirm that the SCS depositions are initially cuprous oxide nanocrystals. For XRD studies a 3000 TT Seifert X-ray diffractometer unit (with 40 kV and 40 mA, CuKα1 radiation with λ = 0.1540598 nm) was used and the average crystal lattice parameters have been determined by the Scherrer method from the diffraction peaks. The micro-Raman spectrometer of WITec system was used in this study. A 532 nm line from Nd-YAG laser at an output power of 8 mW was used as the excitation source.