Preparation of copper oxide nanowire-based conductometric chemical sensors

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ABSTRACT

CuO nanowires (NWs) were grown by thermal oxidation of metallic Cu thin layer deposited by sputtering on different substrates. Optimal growth parameters were found, studying the influence of the oxidizing temperature and the atmosphere during the oxidation process. A strong relation between oxidation parameters and morphology has been detected. The preliminary response of this sensing material, using nanowire's mat-based device, to various oxidizing and reducing target gases has been evaluated, in order to corroborate the functional properties of the CuO NWs as potential sensing material under certain conditions and to confirm the p-type conductometric response of the material.

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1. Introduction

Nanostructured materials are subject of an intensive scientific research because of their interesting properties and potential technological applications, compared to their bulk or micro-sized counterparts, due to the efficient transport of carriers and excitons within the smallest dimension. Among the most promising nanostructures, metal oxide nanowires (NWs), nanobelts and nanorods deserve a special mention. Due to the high surface area/volume ratio and high crystallinity [1], nanostructured materials, in particular metal oxide NWs, are promising in the field of gas sensing [2–5], for third generation solar cells [6,7] and as field emitters sources [8,9].

So far the research in this field focused on the investigation of n-type semiconductors materials, such as ZnO [6,10], SnO_2 [11–13], TiO_2 [14,15], and so on. Few studies have been reported on the use of p-type material NWs as chemical sensors, like for example copper oxide [16,17].

Oxygen can interact with copper forming two different structures: CuO and Cu_2O. Copper (II) oxide, or cupric oxide (CuO), is an intrinsically p-type semiconductor mainly due to Cu vacancies [18] with a narrow bandgap of 1.2 eV, has monoclinic crystal structure and black color. It can be found in nature as tenorite rocks. It's currently used in field emission sources [19,20], magnetic storage media [21], high-T superconductors [22], solar cells [23,24] and heterogeneous catalysts [25].

Copper (I) oxide, or cuprous oxide (Cu_2O), a p-type semiconductor as well, has an energy gap of 2.1 eV and a cubic crystal structure. It's mainly used for water photodecomposition [26], photodegradation of organic pollutants and as electrode in lithium ion batteries [27,28]. It's found as red mineral called cuprite. It's less stable than CuO, and usually degrades to that form in moist air. Both oxides have been poorly studied for gas sensing applications [29,30] in spite of the potential interest that p-type sensing materials have owing to the transduction mechanisms changes originated by the carrier availability and surface band bending potential values.

In literature several different techniques were presented to prepare CuO NWs including wet chemical methods [31,32], templating method [33], thermal decomposition [34], anodization [35], thermal oxidation [36–38] and electrospinning [39]. Among these methods, CuO NWs prepared via thermal oxidation seem more crystalline and with higher aspect ratios compared to those prepared via other methods. In this study, CuO NWs were prepared grown by thermal oxidation of metallic Cu thin layer deposited by sputtering on various substrates. Then, the preliminary response of this sensing material, using nanowire's mat-based device, to various oxidizing and reducing target gases has been evaluated, in order to corroborate the functional properties of the CuO NWs as potential sensing material under certain conditions.

2. Experimental

The proposed fabrication approach has many advantage compared to others reported in literature. It mainly consists in a tubular furnace working in atmospheric pressure, without the need of vacuum equipment. It has a high yield with no risk of cross contamination due to the low temperature processing (from 300 °C to 400 °C). It's possible to selectively pattern the nanowire area on the device substrate, which is not easy using for example solution-based transfer methods reported in literature [29]. Moreover, the reproducibility of the devices is increased, because all the deposition steps could be done automatically without the operator contribution, and all these steps can be easily scaled up and integrated in a large-scale production. In this work the sputtering technique was used to deposit a metallic film on substrates, however it's possible to use other techniques also, such for example thermal evaporation, to further decrease the costs of the whole fabrication process. The overall advantages of the proposed synthesis technique could be summarized in: (1) synthesis of the nanostructures directly on the functional substrate, (2) high yield and increased reproducibility, and (3) compatible with mass-production. The only disadvantage is the time required for the synthesis of the nanostructures (several hours to form micron-long nanowires).

In this work different substrates were used, according to the target application: silicon, for structural investigations like HRTEM and EDX; alumina, for investigations on the functional properties of CuO nanostructures; glass substrates and kapton substrates, as a proof-of-concept for their possible integration in different or flexible devices. Growth process consisted into four main steps: (1) substrates cleaning, (2) metallic layer deposition, (3) metal layer etching and (4) thermal oxidation.

Cleaning is necessary in order to remove dust and most organic compounds from the substrate. Samples were cleaned in acetone using ultrasounds for 10 min and afterwards dried with a synthetic air flow.

A thin layer of metallic copper was deposited on target substrates by RF magnetron sputtering, using an argon plasma. The gas flow was kept constant (7 SCCM) for all depositions, resulting in a pressure inside the chamber of 5.3×10^{-3} mbar. A power of 50 W was set on the RF power supply. Others parameters were varied (deposition time and temperature) in order to determine the best conditions to promote the synthesis of the nanowires. Different metal layers were deposited at room temperature (RT), 200 °C, 300 °C and 400 °C, while layer thickness ranged from 300 nm (30 min deposition) to about 3 μm (5 h deposition).

Copper is very reactive in environmental atmosphere, and the interaction with oxygen (always presents in air) spontaneously produces a thin layer of copper oxide. This thin layer of native oxide is detrimental for NWs growth, so it has to be removed before the thermal oxidation. In this work two different methods were used to remove this layer: wet chemical etching and plasma etching. Wet chemical etching was performed using HCl. Samples were washed in ethanol for 5 min and then rinsed in deionized water. Afterwards samples were kept in 1.5 M HCl for 10 min, rinsed in deionized water and then dried with synthetic air [40]. Despite of the fact that it gave acceptable results on rough substrates like alumina, it sometime led to a complete layer detachment on flat substrates, like glass or silicon. An alternative method to remove the native copper oxide layer is plasma etching. An application of a 15 W Argon plasma for 5 min was enough to clean the samples. This method was less aggressive than HCl cleaning, thus avoiding the detachment of the metallic films from the substrates. This cleaning process greatly reduces the native oxide on the surface of the metallic layer, promoting the growth of NWs.

After the copper oxide layer removal, samples were undergone to a forced oxidation in a Carbolite tubular furnace. Samples were placed in a quartz holder inside the alumina tube at chosen temperature, gas flow, atmosphere composition and duration. Gas flow was set at 300 SCCM and oxidation time was fixed at 15 h, in order to reduce the number of parameters to investigate. In particular, the duration of the oxidation process mainly influences the length of NWs. The selected duration (15 h) was enough to synthetize nanowires long several micrometres. The atmosphere inside the furnace consisted in a mixture of argon and oxygen, in different ratios (from 100% O_2 to 10% O_2–90% Ar). For alumina, silicon and glass substrates oxidation temperature was varied from 200 °C to 600 °C, while for kapton HT the highest oxidation temperature was 400 °C, the maximum operating temperature for commercial kapton HT according to the datasheet. During the warm-up of the furnace the heating rate was fixed at 2 °C/min for all substrates and all oxidation temperatures.

The oxidation process consists firstly in the oxidation metallic Cu in a Cu_2O film ($Cu + O_2 \rightarrow Cu_2O$), as reported in literature [41]. Afterwards, the Cu_2O film further oxidize into CuO ($Cu_2O + O_2 \rightarrow CuO$), producing CuO NWs and leading to a complete oxidation.

To investigate the morphology of prepared samples, a field emission scanning electron microscope (FE-SEM) LEO 1525 was used. Samples were attached with carbon glue to metallic stubs, to reduce charging effects due to the electron beam. The morphology and crystallographic structure of the nanowires were further characterized with atomic resolution by means of high resolution transmission electron microscopy (HRTEM) in a Jeol 2010F field emission gun microscope with a 0.19 nm point to point resolution. For TEM and HRTEM characterization, NWs were mechanically removed from their substrates and deposited over carbon-coated copper grids [42].

Alumina (99.9% purity, 2×2 mm) substrates were used to prepare sensing devices. CuO NWs were synthetized at 300 °C, starting from a 1.8 μm copper layer (3 h deposition, at room temperature), directly on alumina substrates. Gas flow was set at 80% oxygen–20% argon ratio.

Metal oxide interaction with the surrounding atmosphere is thermally activated, thus, to reach the desired operation temperature, a platinum heater was deposited on the backside of the substrate by DC magnetron sputtering (70 W argon plasma, 300 °C, pressure 5.3×10^{-3} mbar, thickness 900 nm), whereas on the front side interdigitated platinum contacts were deposited. The substrate was finally mounted in a TO4 package by electro-soldering using 50 μm gold wires.

To investigate the conductometric response of the sensors a homemade test chamber was used, able to measure up to ten sensors simultaneously [43]. The test equipment consists in a stainless steel chamber (1 L volume) placed inside a thermostatic chamber (Angelantoni, Italy, model MTC 120) set at 20 °C, to avoid the influence of the external temperature. Humidified air was produced by flowing the dry air through a Drechsel bottle, held in a thermostatic bath at 25 °C, and then in a condensation vessel in order to favour the condensation of saturated vapour. The humidified air was mixed with dry air in order to obtain the desired relative humidity (RH) content, in these measurements fixed at 50% @ 20 °C (chamber temperature). A humidity sensor (Vaisala, Finland, model HMI 36) was used to monitor the atmosphere of the test chamber and to adjust the flows of dry and humid air. Test gases with a certified composition, supplied by SIAD SpA, (Italy) were mixed in a carrier of dry synthetic air by MKS Instrument mass flow controllers. The total flow inside the chamber was set at 500 SCCM.

Sensor temperatures were controlled by modulating the electric power applied to heaters by Thurlbly-Thandar PL330DP power