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Copper oxide nanowires prepared by thermal oxidation for chemical sensing

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Abstract

Copper oxide nanowires (NWs) were prepared grown by thermal oxidation of metallic Cu thin layer deposited by RF sputtering on various substrates. A strong relation between oxidation parameters and morphology has been detected, and thus optimal growth parameters were found. The preliminary response of this alternative p-type 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.

Copper oxide; Chemical sensors

1. Introduction

An intensive scientific research is being performed on nanostructored material, mainly because of their interesting properties and their potential technological applications, due to the efficient transport of electrons and excitons within the smallest dimension. Metal oxide nanowires (NWs), nanobelts and nanorods deserve a special mention among the most promising nanostructures. So far the research focused on the investigation of n-type metal oxide semiconductors materials, such as ZnO [1], SnO_2 [2], TiO_2 [3], and so on. Few studies have been reported on the use of p-type material NWs as chemical sensors, like for example Copper Oxide [4, 5].

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Two different structures could be formed by the interaction of oxygen with copper: CuO and Cu_2O. Copper (II) oxide, or cupric oxide (CuO), is a black-coloured p-type semiconductor with a narrow bandgap of 1.2eV and has monoclinic crystal structure. It's currently employed in field emission sources [6] [7], magnetic storage media [8], high-T superconductors [9], solar cells [10] [11] and heterogeneous catalysts [12]. In literature several different ways were presented to prepare CuO NWs. Among these methods, thermally-oxidized CuO NWs seem more crystalline and with higher aspect ratios compared to those prepared via other methods. In this work CuO NWs were grown using this method on different substrates and the conductometric performances of a mat-based device towards various target gases has been evaluated.

2. Experimental

2.1. Nanowire preparation

The thermal oxidation has various advantages over other techniques: it works in atmospheric pressure; it's scalable and it has a high yield, in a view of large-scale production; it's possible to control the growth pattern, via, for example, shadow masking. Silicon substrates were used for structural investigations, while alumina substrates were used for conductometric chemical response measurements.

Growth process consisted into four main steps: 1) substrates cleaning, in acetone using ultrasonic cleaner for 10 minutes, to remove dust and organic compounds; 2) metallic copper layer deposition, by RF magnetron sputtering ($5.3x10^{-3}$ mbar, 50W RF argon plasma at room temperature, thickness of Cu layer 2µm); 3) metal layer etching, to remove oxide spontaneously produced by the interaction of copper and oxygen in air, via plasma etching with argon plasma at 15W for 5 minutes; 4) thermal oxidation in a tubular furnace, with a fixed 300sccm flow of a mixture of argon and oxygen, in different ratios (from 100% O_2 to 10% O_2 – 90% Ar). Furnace temperature was varied from 200°C to 600°C. Oxidizing time was held constant at 15 hours.

In the oxidation process the metallic Cu firstly oxidize to Cu_2O ($Cu + O_2 \rightarrow Cu_2O$) and then the Cu_2O film further oxidize to CuO ($Cu_2O + O_2 \rightarrow CuO$), producing CuO NWs and leading to a complete oxidation [13].

2.2. Morphological and structural characterization

A field emission scanning electron microscope SEM LEO 1525 was used, operating in 3-5 kV acceleration voltage range, for the observation of the morphology of nanowires over the insulating substrates.

The morphology and crystallographic structure of the nanowires were further characterized with atomic resolution investigation performed in Barcelona with a TEM Jeol 2010F field emission gun microscope with a 0.19 nm point to point resolution.

2.3. Functional characterization

Alumina substrates were used to prepare the final mat-based sensing device to measure the conductometric response towards target gases. Because metal oxide interaction with the surrounding gases is thermal activated, a platinum heater was deposited by DC sputtering on the backside of the substrate. On the front side interdigitated platinum contacts were deposited with the same technique. The substrates were then soldered on a TO5 package with gold wires.

Electrical characterization was carried out by volt-amperometric technique in a climatic chamber, kept at 20°C. The applied voltage ranged from 0.1-1V and film conductance was measured by a Keithley 486 picoammetter. Relative humidity was controlled and fixed at 50%. A constant flow of synthetic air of 0.3 l/min was used as carrier gas, into which the desired concentration of test gases was mixed. Samples were held at the desired temperature for 8 hours for stabilization. After the 30 minutes exposure to a fixed concentration of target gas, the flow of synthetic air is restored for 90 minutes for the recovery.

3. Results

The oxidizing temperature in the furnace is the parameter that has the strongest influence on the growth of nanowires, and it allows to easily controlling their morphology, in both density and diameter. Figure 1 report samples oxidized at different temperature in the furnace, keeping the other conditions constant. At 400°C NWs seem almost vertical aligned and with an average diameters of 170 nm, while at 300°C and 250°C they are thinner (50-80 nm) and randomly arranged. The best temperature in terms of density is 300°C.

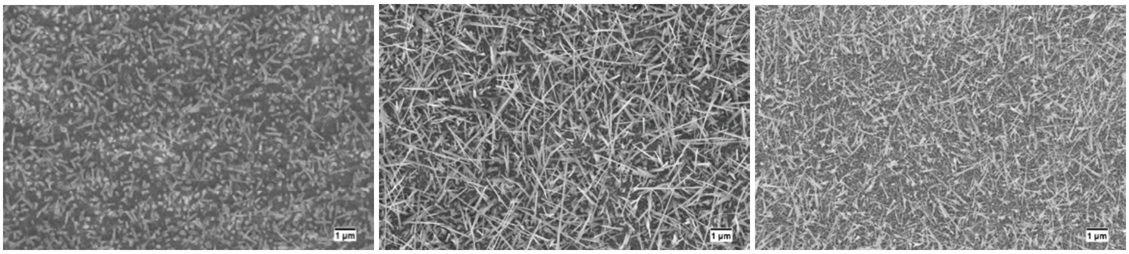

Figure 1: Influence of oxidation temperature: 400°C (left), 300°C (middle) and 250°C (right). The atmosphere composition is 80% O_2 and 20% Ar, while Cu film sputtered is 2µm at RT.

The ratio of oxygen and argon in the atmosphere does not affect much the density of NWs in case of favorable oxidation temperature (250°C-.400°C), but has an effect on their dimensions. To a decrease of the oxygen rate correspond an increase of the diameters of the nanowires.

Figure below (Figure 2) shows a HRTEM image of one of these nanowires. The crystalline structure observed in the nanowire perfectly match with the Tenorite CuO crystal. The NWs grow along the (011) planes.

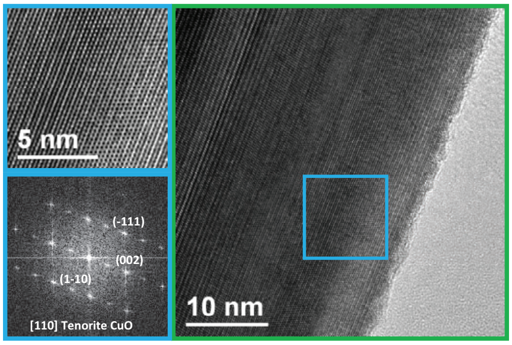

Figure 2: HRTEM picture of a single CuO NW grown on a 2µm Cu film sputtered at RT on silicon substrate. The atmosphere composition was 80% O_2 and 20% Ar and the oxidation temperature was 300°C.

Different target gases were used to measure the performances of a CuO NWs mat-based device. The measured current decreased in presence of reducing gases (Figure 3), a typical behaviour observed for *p*-type oxide semiconductors [4]. This observation is in line with the results of compositional and structural analyses, indicating the presence of *p*-type CuO as the main phase in the analyzed samples. Figure 3 reports the response of copper oxide nanowires to selected concentration of two different gases tested (ozone and ethanol) for a working temperature of 400°C (ethanol) and 300°C (ozone) with 50%RH@20°C.

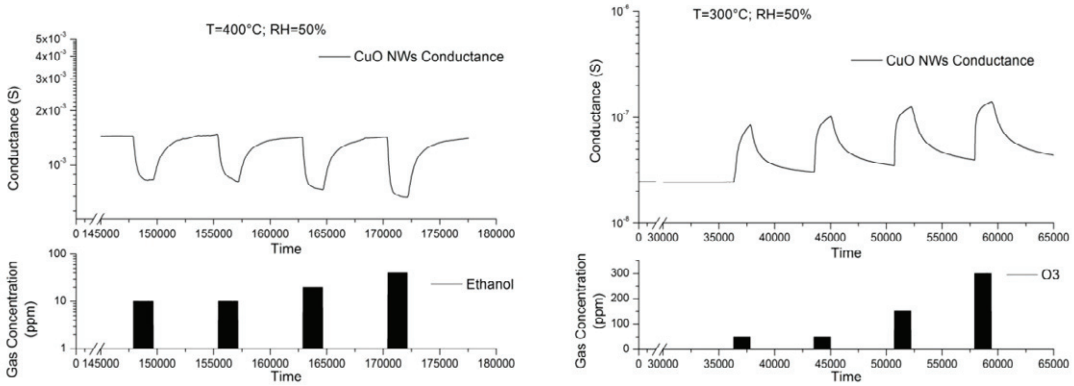

Figure 3: Dynamic response of CuO NWs mat-based sensor toward two different target gases. As expected, the conductance decrease with the injection of ethanol, as normal for a p-type semiconductor, and almost completely recover in air.

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