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MO_x/CNTs hetero-structures for gas sensing applications: role of CNTs defects

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Abstract

The preparation, characterization and sensing properties of CNT composites with a thin metal oxide (MO_x) surface layer is presented. Atomic layer deposition (ALD) was applied for the coating of the inner and outer CNTs walls with thin films of ZnO and SnO_2 of precisely controlled thicknesses. Differently treated CNTs with different degree of surface functionalization were used as support for the oxide films. The sensing properties of the obtained composite materials towards NO_2 were investigated and related to the morphological and microstructural characteristics of both the coating and support. SnO_2-based composites on CNTs treated at 700 °C show enhanced performance as sensors, making them suitable for practical applications.

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Keywords: Carbon nanotubes; MOx coating; MOx/CNTs heterostuctures; NO_2 sensors.

1. Introduction

High surface area composite hetero-structures based on metal oxides (MO_x) and carbon nanotubes (CNTs) exhibit unique electrical properties that are related to the presence of a p-n hetero-junction. Their electric conductivity can be influenced by the surrounding atmosphere. Therefore, these structures present a substantial potential as new gas sensing materials [1]. Despite their growing impact in the field, an incomplete understanding of the sensing behavior still remains. In order to study these hetero-systems, thin films of ZnO and SnO_2 have been deposited by atomic layer deposition (ALD), a surface-gas phase

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process based on sequential, self-limiting surface reactions. A fine control of the morphology and thickness of the deposited films can be achieved by this technique [2].

In view of gas sensors applications, great interest is devoted on semiconductor MO_x layers with a thickness in the order of the Debye length [3]. Previously it was shown that the tailoring of the type and degree of functionalization of the CNTs surface allows to tune the MO_x coating from selectively decorated up to fully coated CNTs [4]. Tessonnier et al. demonstrated that the carbon nanotubes surface graphitic character influences the type and density of surface groups created during functionalization by nitric acid treatment [5]. Commercial CNTs with different degree of graphitization, prepared by different thermal treatments prior to a standard acid treatment, were here used as carbon support [2]. The gas sensing properties of the obtained hetero-structures towards NO_2 were investigated. Based on these results, the mechanism accountable for the observed gas sensing properties will be discussed.

2. Experiment

Carbon nanotubes (Pyrograf Products, USA) were heat treated in inert atmosphere at either 700, 1500 or 3000 °C in order to graphitize the layer of pyrolytic carbon, hence decreasing the density of structural defects in a controlled manner. The CNTs exhibit average outer and inner diameters of 85 and 40 nm, respectively, independently of the applied annealing temperature. The three CNTs samples were subsequently functionalized with concentrated nitric acid (70%) at 100 °C for 10 h.

The SnO_2- and ZnO-CNTs composites were prepared as follows. Each metal oxide was deposited simultaneously on the functionalized CNTs previously deposited on a silicon wafer from dispersions in ethanol. The three types of carbon material were inserted and coated at the same time, in the same chamber, in order to have exactly the same deposition conditions. Acetic acid (Aldrich) was used as oxygen source, whereas Tin ter-butoxide (STREM) and Diethyl zinc (Aldrich) were used as tin and zinc precursors, respectively. Metal precursors and acetic acid were introduced subsequently by pneumatic ALD valves from their reservoirs. Pure nitrogen was used as a carrier gas. The number cycles varied from 50 to 1000. More detailed information about the preparation of the samples can be found elsewhere [3]. The microstructure and morphology of the CNTs and MO_x/CNTs hetero-structures were investigated by SEM, TEM, EDX, XRD, TGA-DSC, FT-IR and Raman spectroscopy.

The sensing device consists of an alumina substrate with Pt interdigitated electrodes on one, and a Pt heater on the other side. The active sensing layer was deposited by screen printing. Gas sensing tests were carried out inside a chamber under controlled atmosphere. Mass flow controllers were used to adjust desired concentrations of target gas in dry air. The electrical resistivity measurements and the sensors responses were recorded using the four point probe method, by means of an Agilent 34970A multimeter.

3. Results

A detailed morphological and structural characterization of the differently heat treated carbon nanotubes used as support has been reported elsewhere [4]. Briefly, an increase of the surface graphitization has been observed with the increase of the annealing temperature. In particular, the CNT700 is characterized by a structural disorder of the outer and inner surface layer of the tubes. The annealing at 1500 °C leads to the appearance of some connections between the inner rims of subsequently stacked cups and only a thin layer of structurally ill carbon is present. Annealing at 3000 °C results in a straightening of the graphitic sheets and highly graphitized walls which show connections between stacked cones, forming steps on the inner and outer surface.

With increasing heat treatment temperature, a progressive decrease in the electrical resistance of the CNTs was registered (Fig. 1). This is due to the reduction of the amount of amorphous carbon and related defects within the structure of CNT700 which are responsible for a reduced carrier density. The enhanced electrical conductance of annealed CNTs is therefore attributed to the increased graphitization of carbon nanostructure.

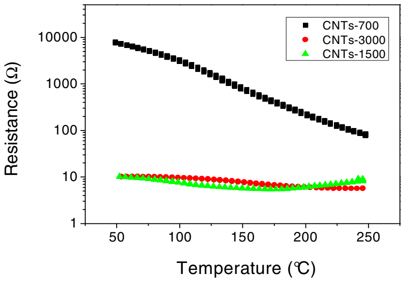

Fig. 1. Electrical resistivity of the as received CNTs heat treated at various temperatures.

Previous sensing tests on SnO_2/CNTs have demonstrated that the metal oxide layer thickness is a factor influencing the sensor response [3]. In order to compare different metal oxide films as sensing layer, a constant thickness has been chosen in the ALD process for ZnO and SnO_2. However, depending on the CNTs type and MO_x nature, different metal oxide morphologies were observed (Fig. 2).

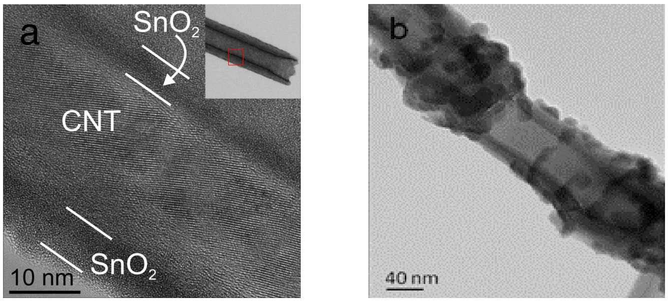

Fig. 2. TEM images showing the difference in SnO_2 morphology obtained by ALD on CNT700 (a) and CNT3000 (b).

Sensing tests, carried out with NO_2 as target gas, have shown strong differences in the behavior of the various composites tested (Fig. 3). The SnO_2/CNT700 sensor responded to nitrogen dioxide with very high sensitivity. In contrary, the response registered for the SnO_2/CNT3000 sensor was very poor. A negligible sensitivity was also observed for the ZnO/CNTs-based sensors, independent of the CNT type.

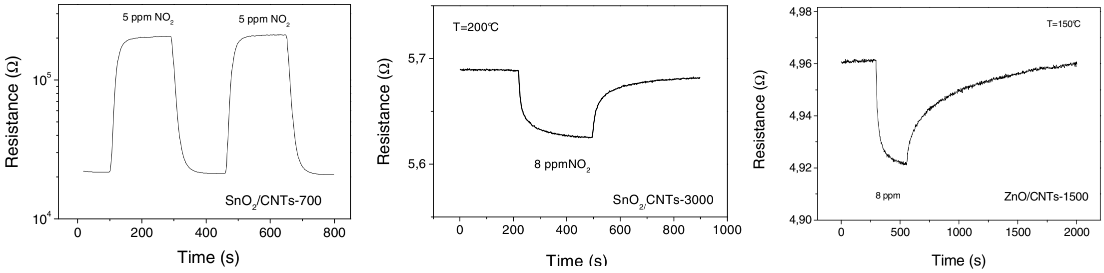

Fig. 3. Dynamic response of SnO_2- and ZnO-based composites to NO_2 gas.

From previous investigations, it was ascertained that MO_x coating appears to be involved in the receptor function, while the CNTs provide mainly the electronic conduction path (transducer function) [1, 3]. The nature and morphological/microstructural characteristics of both coating and support also play a prominent role in addressing the sensor response. These characteristics determine the electrical transport properties of the sensing layer, and in turns, affects the sensing ones. SnO_2 and ZnO are generally considered n-type semiconductors, while CNTs demonstrates a p-type behavior. In the case of SnO_2/CNT700, the SnO_2 coating is continuous and electrical conduction is expected to occur through the CNT-MOx interface. This creates a p-n hetero-junction which barrier height is modulated by NO_2 interaction with the n-type SnO_2 layer. On the opposite other hand, on the sample SnO_2/CNT3000 sample, due to the discontinuous partial coverage of the nanotubes by SnO_2, the electrical conduction flow mainly through the CNT-CNT contacts, leading to originating the p-type response of the device. These observations are also well in good agreement with the different electrical characteristics and resistance variations observed between in these two samples (see Fig. 3) i.e. the resistance is high and increases during NO_2 exposure for the SnO_2/CNT700 whereas it is low and decreases in the case of the SnO_2/CNT3000.

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