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Study of the surface-ruthenated SnO_2/MWCNTs nanocomposite thick-film gas sensors

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were successfully coated with tin-dioxide (SnO_2) nanoparticles using both hydrothermal process and sol–gel technique under different solvent conditions. The obtained MWCNTs/SnO_2 nanocomposites had the weight ratio of the components 1:4, 1:8 and 1:50, respectively. The as-prepared nanocomposites were characterized in detail using scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). Gas-sensor structures are developed on the base of these materials. High response to methanol and ethanol vapour as well as i-butane gas at 200 °C operating temperature has been revealed for the functionalized with Ru nanocomposite thick-film sensor structures having the ratio of the components 1:8 and 1:50. The structures having 1:4 ratio of components exhibit the best selectivity toward methanol and ethanol vapors.

1. Introduction

The hybrid materials made of semiconductor metal oxides mainly SnO_2 as the most prospective and widely used gas-sensitive material and carbon nanotubes (CNTs) have been given much attention in recent years for their various applications. The special geometries and properties of such materials facilitate their great potential applications as high-performance gas sensors [1–4]. Previous research works have demonstrated that the hybrid materials gas sensors, for example SnO_2/CNTs have a better performance in comparison with the sensors based on separated same materials. One of reasons responsible for the enhancement of the sensing performance of the sensors based on CNTs/SnO_2 nanocomposite is attributed with their very large specific surface area and the advent of additional nanochannel in the form of hollow CNTs for gas diffusion [1,3,5]. On the other hand, it is known that the n–p heterojunction is formed at the interface between tin oxide and carbon nanotubes since SnO_2 is n-type semiconductor whereas carbon nanotubes form p-type semiconductor [3,4,6]. The adsorption of gas molecules changes both the depletion layers at the surface of SnO_2 nanoparticles and at the p-MWCNTs/n-SnO_2 heterojunctions. These two effects may be the other reason for improvement in sensitivity of tin oxide based nanocomposite gas sensors [7].

Surface modification of the CNTs/metal-oxide hybrid gas sensors and sensors based on the nanocomposites components with noble metals (Pt, Pd, Au, Ru, Rh) promotes increasing in sensitivity and improvement of the gas sensors selectivity [8–11] because of these metals or their oxides are the catalysts for chemical reactions taking place on the surface. So, high sensitivity, good selectivity and lower operating temperatures achieve for Ru incorporated SnO_2 hydrocarbon gas sensors [12].

In hybrid material metal oxides and CNTs can be connected with each other by different ways, namely: CNTs filled or coated by metal oxide as well as metal oxide doped with CNTs [2,13–15]. As shown in previous works, in all these cases we can expect an increase in sensitivity to certain gases as well as lowering the operating temperature. Particularly, MWCNTs and PtO_2-doped SnO_2 sensors had good performance in detecting of ethanol gas and LPG [16].

One of the aims of this work is finding simple methods to obtain SnO_2/CNTs composite materials having proper morphology

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intended for using as base material for gas sensors manufacturing. The choice of tin oxide as a component of SnO_2/MWCNTs nanocomposite structure is conditioned by the fact that SnO_2 is well known and studied basic material for metal-oxide gas sensors (see, for example, review papers [17,18]). Thus, high performance of SnO_2 gas sensors had been achieved in general by development of special sol–gel route which provides thermally stable metal-oxide nanoparticles with size lower than 10 nm [18–22]. We expect that coating of functionalized MWCNTs with SnO_2 nanoparticles with such sizes should provide further improvement of the gas sensor performance and lowering of its operating temperature.

In this work we prepared and studied thick-film gas-sensor structures using various precursors for wet chemical processes. The choice of corresponding treating conditions and regimes for CNTs functionalization were focused on obtaining sensitivity to such target gases as hydrogen, ethanol, methanol and i-butane. We would like to note that there are few published works on coating of CNTs with thick layers of different materials. We obtained and studied hybrid MWCNTs/SnO_2 surface-modified with Ru thick films. The results of these investigations are presented here.

2. Experimental

2.1. Samples

MWCNT and SnO_2 mixed nanopowders samples in this work were studied both with and without Ru catalyst.

The choice of the ruthenium as a catalyst was defined by its following properties:

a) Resulting from the sol–gel process ruthenium dioxide has a rutile structure likewise tin oxide. Moreover, the atomic radius of tin is very similar to that of ruthenium. Both these facts allow the formation of a solid solution [23].
b) It is well known that such catalysts as Pt, Pd are very effective catalysts first of all for hydrogen sensing. But, the goal of this work was to develop sensors to other gases with low cross-sensitivity to hydrogen. It is known that ruthenium in tin oxide matrix acts as an oxidative catalyst for hydrocarbons to achieve a considerable degree of sensitivity and selectivity [24].
c) Ruthenium dioxide (RuO_2) is a material having some advantages such as high conductivity, electrochemical reversibility, good compound adhesion and high stability in acidic solvents.

For ruthenium plating in our research works we used ruthenium (IV) chloride hydroxide ($RuOHCl_3$) as precursor material. The preference was given to the surface modification technology and not, for example, to Ru or RuO_2 doping processes since, according to [12], the high sensitivity to hydrocarbon gases, particularly to butane, should be expected namely with use of ruthenium as a surfactant.

2.2. Materials and sample preparation

MWCNTs/SnO_2 nanopowders for thick film preparation were made by the following two ways: using sol–gel preparation technique (obtaining samples with MWCNTs/SnO_2 ratio 1:50, further marked as ECS7) as well as hydrothermal synthesis (samples with MWCNTs/SnO_2 ratio 1:4 and 1:8, further marked as KCS1 and KCS2, respectively).

To prepare the samples according to the first way MWCNTs membranes made in EPFL (Lausanne, Switzerland) were used for preparation of nanocrystalline MWCNTs/SnO_2 powder by wet chemical method. Millimeter long MWCNT grown by CVD were used to prepare membranes by vacuum filtration form a suspension in isopropanol [25–28]. To make a functionalization of nanotube walls with oxygen-containing hydroxyl (OH), carbonyl (C=O), and carboxylic (COOH) functional groups, MWCNTs from the membranes were transferred to slurry in HNO_3/H_2SO_4 acids mixture during 1 h. Such a functionalization of outermost walls of the CNTs is very important and necessary for the following synthesis of SnO_2 nanoparticles on the MWCNTs surface since, as is well known, these oxygen-containing groups act as sites for nucleation of nanoparticles. After rinsing by distilled water and drying at 80 °C MWCNTs were poured in 5 ml of deionized water and treated in ultrasonic bath for 5 min.

Later, tin chloride pentahydrate ($SnCl_4{\cdot}5H_2O$) was added to obtained suspension in the ratio of 1:7 with thorough mixing for 5 h at 140 °C. After that, precipitate was collected for the following synthesis of hybrid material. 346 ml 0.5 M $SnCl_4$ was added to 77 mg all of precipitate. Obtained mixture was exposed to ultrasonic treatment for 5 min. Ammonium was used for keeping pH of solution at the level of 8.3. The mixed suspension was left overnight at 80 °C, whereupon MWCNTs/SnO_2 composite powder with 0.1% addition of the MWCNTs was rinsed, dried, grinded and annealed in air at 400 °C for 1 h (powder ECS with the weight ratio of the MWCNTs and SnO_2 components was about 1:50, respectively).

The thick films were obtained on the base of ECS (1:50) MWCNTs/SnO_2 composite powder (ECS7 and ECS7Ru samples). The paste for thick film deposition was obtained by mixing with α-terpineol ("Sigma Aldrich"), and then printed on chemically treated surface of the substrate over the ready-made Pt interdigitated electrodes. Thin-film heater was formed on the back side of the substrate. Obtained composite structures were cut into 3 × 3 mm chips. Drying and annealing of the resulting thick films were carried out in two stages: heating up to 220 °C with 4 °C min^{-1} rate of temperature rise, hold this temperature for 3 h and then further temperature increase until 400 °C with 1 °C min^{-1} and hold again for 3 h. After that the samples were impregnated into 0.01 M $RuOHCl_3$ aqueous solution for 20 min, followed by drying and annealing at abovementioned conditions.

For samples preparation by hydrothermal synthesis in both cases $SnCl_2{\cdot}2H_2O$ was chosen as a precursor material. Both water and ethanol were used as solvents. Hydrothermal synthesis was carried out at 150 °C during one day and at 60 °C for 4 h, respectively. The samples were heat treated at 450 °C for 3 h. To improve the adhesion behaviors as well as in order to avoid cracks formation, the mixture of α-terpineol ("Sigma Aldrich") and methanol in the ratio of components 1:4 was used as a binder.

After annealing and cooling the MWCNTs/SnO_2 thick films were surface-ruthenated by dipping them into 0.01 M $RuOHCl_3$ aqueous solution for 20 min whereupon dried at 150 °C for 30 min and then calcination treatment was carried out again at 400 °C for 2 h.

A concise outline of described above technological routes is presented in flow chart of Fig. 1.

3. Results and discussions

3.1. Materials characterization

The morphologies of the prepared SnO_2/MWCNT nanocomposite different powders were studied by scanning electron microscopy (SEM) using Hitachi S-4700 Type II FE-SEM equipped with a cold field emission gun operating in the range of 5–15 kV. The samples were mounted on a conductive carbon tape and sputtered with a thin Au/Pd layer in Ar atmosphere prior to the measurement. X-ray diffraction (XRD) analysis was carried out using Rigaku Miniflex II diffractometer with Cu Kα radiation source.

Energy-dispersive X-ray analysis was carried out using a RÖNTEC XFlash Detector 3001 with a Silicon Drift Detector (SDD)