Synthesis of the ‘carbon nanotubes-porous silicon’ hybrid material for gas sensors

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Abstract

The present work represents the approach to develop the novel functional material for gas micro- and nanosensors. The isolated porous silicon arrays have been synthesized using the electrostatic mask method in the electro-chemical chamber. The hybrid material ‘carbon nanotubes-porous silicon’ has been synthesized on the isolated porous silicon arrays with the CVD process. The nanocomposite structure has been synthesized by tin sputtering on the hybrid material ‘carbon nanotubes-porous silicon’. The morphology and electro-physical properties of the nanocomposite structures have been investigated. The test gas sensor based on the nanocomposite structures showed high sensitivity to NO2 molecule absorption at room temperature.

Keywords: hybrid material; carbon nanotube; porous silicon; electron microscopy; gas sensors; developed surface

1. Introduction

The unique properties of multi-walled carbon nanotubes (MWCNT) make them a lot of perspectives for use in many fields, such as gas concentrators, energy, materials engineering, chemical, electromechanical and bio sensors, etc. One of the ways to improve the sensory properties of MWCNTs is creation of a nanocomposites based on nanotubes and semiconducting metal oxides [1].

The MWCNT layers grown by catalytic vapor deposition (CVD) method are applicable for modern silicon technology. Design of the MWCNT-based microelectronic devices demands to create the specified topology of the nanotube layers. The most of the studies devoted to synthesis and investigation of the MWCNT-based gas sensors
utilize dispersed and individual nanotubes (see, for example, [2]). It makes very difficult the practical production and usage of such structures.

Consequently, we need to develop the basis for controllable synthesis of MWCNT arrays with desired topology and properties adoptable for silicon technology [3]. At the present work we have grown the isolated nanocomposite arrays based on ‘carbon nanotubes-macroporous silicon’ hybrid structure and tin oxide. The structure of the obtained nanocomposite arrays has been studied by means of scanning electron microscopy and electro-physical properties have been investigated.

2. Experimental

The macroporous silicon (macroPS) layers were synthesized in the specialized electro-chemical chamber. The p-type monocrystalline silicon wafers (12 Ohm cm, orientation (100)) with a thickness 380 μm were used as a substrate.

The MWCNTs for hybrid structures were synthesized by CVD method in ‘CVD-4’ reactor (designed in Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, reaction temperature – 800-900 °C, carbon source – acetonitrile). The nickel catalyst nanoparticles were obtained via thermal sputtering on the macroporous silicon arrays. The as-grown hybrid structures were subjected to thermal annealing in order to remove the amorphous carbon contaminants.

The nanocomposite structures were synthesized by magnetron sputtering of tin on the hybrid structures ‘MWCNT-macroPS’ followed by oxidation at a temperature of 400 °C. For the electrical insulation of the nanocomposite structures with a silicon substrate, a macroPS arrays prior to the synthesis of the hybrid structures ‘MWCNT-macroPS’ were subjected to thermal oxidation at 1000 ºC during 12 hours in oxygen atmosphere. As the result, the 200 nm-thick silicon oxide layers were obtained on the macroporous surface.

The morphology of the hybrid structures and nanocompounds was studied by means of scanning electron microscope (SEM) Jeol JSM-6610 LV. The electro-physical investigations were carried out with LCR-meter Agilent E4980A.

3. Results and discussion

For the synthesis of the isolated macroPS arrays, we have developed and applied a method of electrostatic mask (Fig. 1). The mask was created by magnetron sputtering of 20 nm-thick platinum layers with the desired topology. During the synthesis of macroPS arrays the metallic mask was electrically connected with anode. Hence, the metallic layer acted as the electrostatic mask and blocked the electrochemical etching of the protected area.

![Fig. 1. The scheme of the electrochemical chamber for synthesis of the isolated macroPS arrays by means of electrostatic mask.](image)

As the result, we obtained the different surface morphology (Fig. 2). In the un-protected area we obtained the ordinary macroPS layer. Its structure was given by the applied growth parameters. In the protected area (under the
mask) we found the shallow etching holes (1 to 2 μm deep) but there were no penetrated pores. The morphology of the protected surface greatly differed from the un-protected one. It allows one to create the isolated porous arrays on the silicon substrates. The observed etching holes in the protected area probably caused by imperfection of the mask layer.

![Fig. 2. SEM-image of the macroporous silicon surface: un-protected area (left) and under the electrostatic mask (right).](image)

The obtained macroPS arrays provided the ground for synthesis of the hybrid material ‘MWCNT-macroPS’ by CVD growth method. Before the CVD-process we subjected the macroPS layers to thermal oxidation in order to obtain the electrical isolation of the future structures with substrate. The SEM images showed that MWCNTs in the hybrid material occurs predominantly on the outer surface of the porous layer, with the bases between the pores (Fig. 3). Also we obtained the MWCNTs inside the pores, but their concentration is neglecting. The average MWCNT diameter is 50 nm, but there are a little of thin MWCNTs with 5 to 10 nm outer diameter.

![Fig. 3. SEM images of the hybrid material ‘MWCNT-macroPS’.](image)

The nanocomposite structures were grown on the surface of hybrid material ‘MWCNT-macroPS’ by means of magnetron tin sputtering. After the tin sputtering and subsequent oxidation we predominantly obtained the cylindrical objects with the average outer diameters of 100 nm (Fig. 4) on the surface of nanocomposites. These objects are the result of decoration of MWCNT’s surface by dense tin oxide layer [1].

The resulting nanocomposite material possesses a large effective area of the gas sensing component (tin oxide); it is electrically insulated with the substrate and has a sufficient mechanical strength. Consequently, it is suitable as the basis for gas-sensitive chemo-resistive structures. Also the free space between the nanotubes serves as the concentrator for chemical reagents to be detected.
The electrophysical investigations showed the non-linear behavior of the volt-ampere characteristics for nanocomposite structures (Fig. 5). The hybrid material showed the linear volt-ampere characteristics and conductivity 25 times higher as compared to the nanocomposite structures. The obtained result evidences that nanocomposite conductivity is determined by the metal-oxide component; the nanotubes serve as the spatial frame for gas-sensing component with the developed surface.

The test sensor structures were created using the nanocomposite structures as the functional media. The dependence of test sensor resistance on the NO₂ molecule absorption was studied (Fig. 6). Our sensors showed the sensitivity to NO₂ molecule in concentration of 3 ppm at room temperature. At the same time, the most of metal oxide-based gas sensors demand high operating temperature (~ 300 °C). The obtained data showed the perspectives of the nanocomposite structures based on hybrid material ‘MWCNT-macroPS’ and semiconducting tin oxide for high-sensitivity and energy-effective gas sensors.
4. Conclusion

The hybrid materials based on MWCNT and macroporous silicon arrays have been synthesized. It is shown that the use of electrostatic masks lets us to obtain the isolated macroporous silicon arrays suitable for integrated micro- and nanosensor structures.

The nanocomposite structures based on ‘MWCNT-macroPS’ hybrid material and semiconducting tin oxide have been obtained. The electrophysical and gas sensing properties of the obtained test sensor structures have been investigated. The test sensor structures showed sensitivity to NO₂ molecule in concentration of 3 ppm at room temperature. The nanocomposite structures have a perspectives as a functional media for the gas sensors and integrated gas-analytical complexes.

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References

