Armenian Journal of Physics, 2011, vol. 4, issue 4, pp. 206-210

MANUFACTURE AND INVESTIGATION OF GAS SENSOR MADE OF CNT/SnO_2 TUBE

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Received 25 April, 2011

1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 by S. Iijima [1], they have attracted the attention of many researchers due to the number of their unique properties such as high strength, good deformation elasticity, a wide range of electrical properties, chemical stability, etc. These properties allow using CNTs in many different applications. In particular, CNT is a promising material for gas sensor [2-8]. Active works are carried out today in the field of their fabrication when CNTs are modified with metal oxide semiconductors. The topic of this paper is the synthesis of CNTs grown by Chemical Vapor Deposition (CVD) and the investigation of the sensitivity of sensors made of nanocomposite CNT/SnO_2 to isobutane gas.

2. Manufacture of Carbon Nanotubes

A setup has been mounted for the synthesis of CNTs using the CVD method. Basic components of this setup (Fig. 1.) are a device for production of acetylene and a reactor with substrates placed in a furnace. Carbide of calcium (20 g) was located in a netted vessel of the device for acetylene production. When the water level in the chamber reached the carbide, reaction of acetylene formation takes place:

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2.$$

Acetylene is isolated and passing through a moisture absorber. It is then mixed with a stream of nitrogen which is used as transport gas. The quantity of acetylene and nitrogen in the mix of gases regulated using rotameters is fixed to nitrogen/acetylene equal to 90:10, and the stream of this mixture is equal 100 ml/minute. The mixture passes again and repeatedly through a moisture absorber before being introduced in the reactor for CNTs synthesis. The reactor consists of a furnace preliminary heated at 600°C. An electronic regulator has been mounted to maintain the temperature constant in the limits of ±1°C (Fig. 2). The special feature of this regulator is that the temperature adjustment does not occur at the expense of powering on and off the furnace, but at the expense of smooth changes of power applied to the furnace.

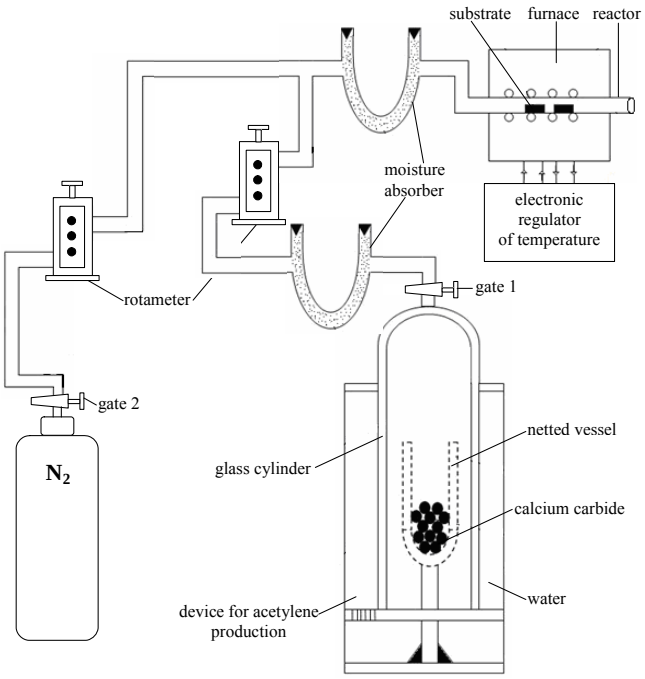

Fig. 1. Setup for the manufacture of CNT.

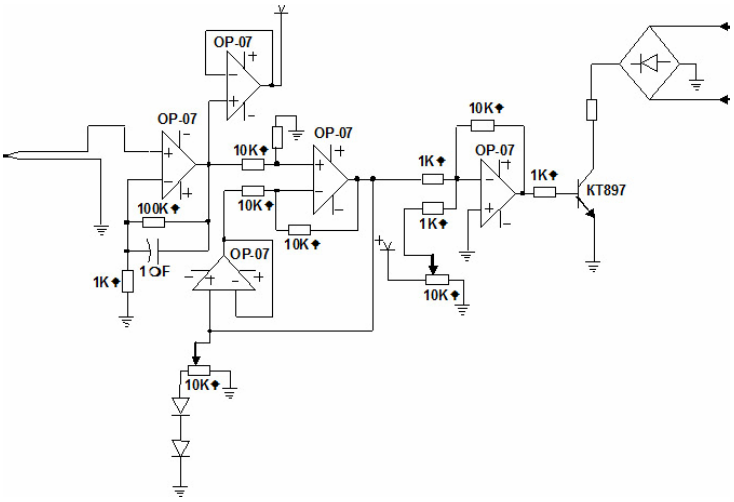

Fig. 2. Electronic circuit for regulator of temperature.

Passing through the reactor, acetylene under the influence of heat decays and carbon is precipitated on the substrate surface in the form of a mix of nanotubes, particles of graphite and nanowires. The duration of CNT synthesis was ~ 30–50 minutes. Then, the supply of acetylene is cut off in the reactor. When gate 1 is closed, the gas pressure in glass cylinder of the acetylene production chamber increases. Water is forced out to avoid reaction with the carbide and the reaction of acetylene production stops. Then, the furnace is cooled to room temperature. We used different substrates to support the nanocomposites: quartz plate, glassceramic coated with Pd grains, layer of porous Al_2O_3, prepared by anodization of aluminum plate, and also polished silicon plate and porous silicon. CNT membranes, prepared at EPFL (Switzerland), were also employed for this study. Millimeter long CNTs grown by CVD were used to prepare membranes by vacuum filtration

form a suspension in isopropanol [9]. The Institute for Crystal Growth (IKZ) in Berlin gave us the kind opportunity to investigate CNTs samples prepared at YSU (Fig. 3a-d) and recieved from Lausanne (Fig. 3e,f). SEM images were recorded using SEM-EDAX (FEI Nova 600-Dual Bean) interconnected with Focused Ion Beam (FIB).

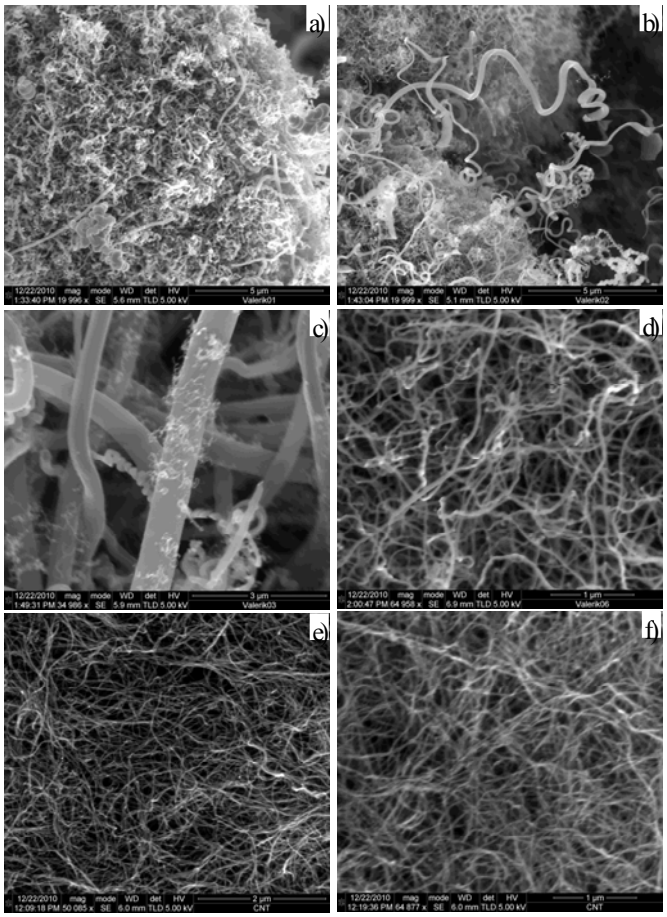

Fig. 3. SEM images of carbon nanotubes on (a) Al_2O_3 substrate, (b) quartz plate substrate, (c) reactor wall, (d) polished silicon plate, and (e,f) from Lausanne, EPFL.

3. Manufacture and investigations of structure made of nanocomposite CNT/SnO_2

A technology for the manufacture of gas sensitive structures made of nanocomposite CNT/SnO_2 was developed. CNT membranes of EPFL (Switzerland) were used for the preparation of nanocrystalline powder CNT/SnO_2 by the sol-gel method.

The functionality of CNT surface was processed by HNO_3/H_2SO_4 acid mixture at 70°C for 2 h. Then the obtained carboxylated powders were dispersed in 5 ml of deionized water by ultrasonication for 5 min. Tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) powder was subsequently added into the suspension of CNTs (the ratio CNT:$SnCl_4 \cdot 5H_2O$ was equal 1:7), the solution was processed by ultrasound again. SnO_2 precipitate on CNT surface after stirring at 140°C for 5h. 0.5M $SnCl_4$ solution was added to CNTs (the ratio CNT: $SnCl_4$ was equal 1:4.5). The resulting solution is treated by ultrasound. Diluted solution of NH_4OH was dropped in the solution CNT to keep a final constant pH of 8.3. After precipitation, the sediment is aged at 80^{o}C for 24 h. It is filtered, rinsed by

the distilled water for removal of chlorine-ions and dried at 120°C for several hours. CNT (0.1% wt) with functionalized surface has been added to the prepared CNT/SnO_2 powder. The mix was grinded and the resulting powder was annealed in the air at 400°C for 1 h. After calcinations tablets are pressed. Part of tablets were sensibilized at the 0.01M and 0.03M $Ru(OH)Cl_3$ water solution and in $Mg(NO_3)_2$ solution. Then tablets were exposed to heat treatment in air at 400°C for 10 h.

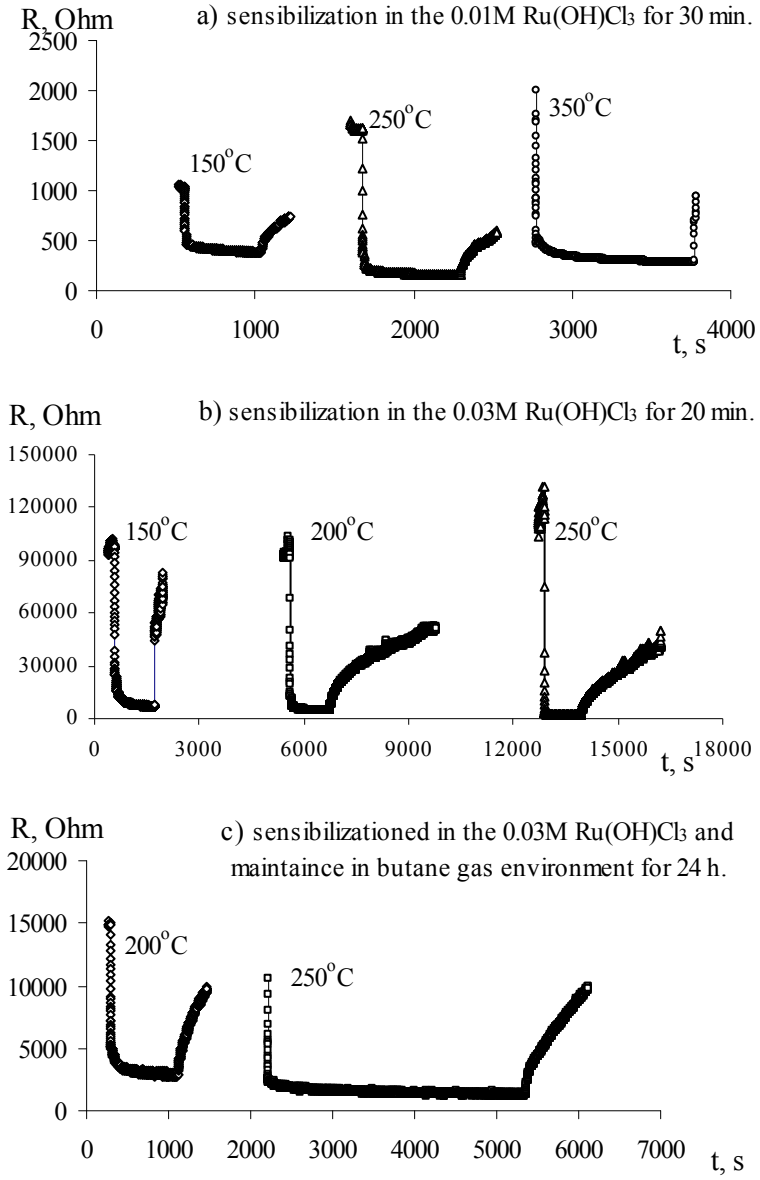

Fig. 4. Change of the resistance of the sensor made of nanocomposite CNT/SnO_2/Pd under influence of isobutane gas at different temperatures.

For the manufacturing of the gas sensor, palladium catalytic nanoparticles and gold digital ohmic contacts have been created on the surface of nanocomposites CNT/SnO_2 using the ion-plasma sputtering method. The subsequent annealing of samples in air is carried out at 300°C for 3 h for an improvement of contacts adhesion and release of possible mechanical stress. The sensitivity of prepared sensors made of the structures nanocomposite CNT/SnO_2/Pd to isobutane was investigated at 5000 ppm concentration. The variation of the sensor resistance is registered at

different temperatures of the working body. All measurements were performed via computer control of the gas concentration, temperature of the working body.

Results of these investigations have shown that the sensitivity to isobutane gas is shown only by sensors, sensibilized in the $Ru(OH)Cl_3$ water solution (Fig. 4.). Note that these sensors show sensitivity already at 120^{o}C. Samples, sensibilized with 0.03M $Ru(OH)Cl_3$ solution, were the most sensitive. For example, the resistance decreases in ~10 times (by heating up to 250^{0}C) and 22 times (by heating up to 200^{0}C) for the sensors, respectively sensibilized with 0.01M and 0.03M $Ru(OH)Cl_3$ solutions,. However, the response time was lower for the samples, sensibilized in the 0.01 M $Ru(OH)Cl_3$ solution. For these sensors, it was equal to ~30-40 s while the response time for samples, sensibilized in 0.03M $Ru(OH)Cl_3$ solution was equal to ~2-3 min. A limitation of the sensor is its slow recovery after the supply of gas is stopped. The prepared sensors were maintained in the environment of isobutane gas for 24 h with the aim of the stabilization of the sensor characteristics. Despite some reduction of sensitivity, it has led to faster sensor recovery (Fig. 4c).

4. Conclusion

A setup had been mounted for the manufacture CNT by CVD method on different substrates. SEM investigations were carried out for both samples prepared at YSU and received from EPFL. Nanocomposites CNT/SnO_2 was prepared by sol-gel methods and gas sensors made of this nanocomposite were manufactured. After sensibilization in $Ru(OH)Cl_3$ solution of the nanocomposite CNT/SnO_2/Pd the sensors are sensitive to isobutane gas at 200^{o}C.

Acknowledgement

This work was supported by a grant from Switzerland through the Swiss National Science Foundation (IZ73Z0_128037/1).

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