Journal of Physics: Conference Series **450** (2013) 012020 doi:10.1088/1742-6596/450/1/012020

Hydrogen sensing using reduced graphene oxide sheets supported by Pd nanoparticles

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Abstract. We investigated Schottky diode hydrogen sensors prepared by the deposition of reduced graphene oxide functionalized by nanocrystals of Pd on InP substrate. Schottky diodes were investigated by the measurement of current voltage characteristics and further tested for their sensitivity to hydrogen in a cell with a through-flow gas system. Pd nanocrystals which are in direct contact with the semiconductor substrate serve to dissociate hydrogen molecules into atomic hydrogen, lowering the work function of Pd, and resulting in the decreased Schottky barrier height.

1. Introduction

Hydrogen gas has been widely used in chemical industry, medicine, or hydrogen-fuelled vehicles. However, hydrogen is very volatile and extremely flammable. A small leakage of high concentration of hydrogen-containing gases can cause explosion. Thus, development of hydrogen sensors with high sensitivity, short response time, small size and low cost is in great demand. One of the promising sensing materials is graphene because of its unique and outstanding mechanical, thermal and electrical properties [1]. Graphene can be extracted by various chemical and physical methods. Mechanical cleavage of graphite was the initial method to produce single-layer grapheme sheets [2]. Unfortunately it is underproductive process that is not suitable for large scale production. An alternative method is growth of graphene on silicon carbide [3], which allows to prepare high quality mono and multilayers of graphene, however, the ultrahigh vacuum requirement limits its technological applicability. Another suitable methods for production of large area graphene films is chemical vapor deposition [4], but the sheets obtained in this manner suffer from bad structural homogeneity over larger areas. A potentional low-cost method is to first produce graphene oxide and then reduce it to obtain graphene for device applications [5].

Recently, mechanically exfoliated graphene sheet and reduced graphene oxide have been shown to exhibit sensitivity for different sensing gas molecules [6,7]. The gas sensing mechanism is based on the change in the electrical conductivity of graphene due the charge transfer from molecules absorbed on its surface. Unfortunately pristine graphene layers do not show much sensitivity towards hydrogen. Therefore, functionalization of graphene with catalytically active metals such as Pd or Pt can be used to enhance its hydrogen sensitivity.

Lately, it has been demonstrated that highly oriented graphite or graphene form high-quality Schottky diodes (SD) on various n-doped semiconductor such as Si, Ge, InP, SiC, GaN and ZnO [8-10]. A high quality SD formed by colloidal graphite is a good starting point for the fabrication of high sensitivity hydrogen sensor. In our previous works [11-13] we presented high sensitivity hydrogen sensor, which was created by inserting Pd or Pt nanoparticles between graphite Schottky contact and the semiconductor substrate. The sensor elements prepared in this way are capable of detection of low concentration (about 1 ppm) of hydrogen at room temperature.

In this work we propose using the reduced graphene oxide supported by Pd nanocrystals for the fabrication of SD hydrogen sensors.

2. Experiment and results

For our experiment we used commercially available reduced graphene oxide functionalized by nano Palladium (rGO@Pd was supplied by NanoInnova Technologies [14]). The rGO@Pd powder was sonicated in ethanol to produce a uniform suspension. This suspension was deposited on n-type InP substrate by microcapillary tube and let dry. The contact area was checked by optical microscope to maintain the diameter close to 1mm. Prior to the to the rGO@Pd deposition, the InP surface was cleaned in boiled methanol for 5 min. An ohmic contact on the back side was formed by rubbing liquid gallium with a tin rod. The diodes were characterized by current-voltage (I-V) characteristic and further tested for their sensitivity to hydrogen in a cell with through-flow gas system. The measuring system consisted of a test chamber, a sensor holder, a Keithley current/voltage source measure unit, mass flow controllers (Bronkhorst High-Tech B.V.) and of a data acquisition system (LabView, National Instruments).

SEM investigation of the rGO@Pd layer deposited onto the InP substrate showed that it does not form a solid layer, but it consists of irregular sheets of sizes in the range of few μm (figure 1). Graphite oxide sheets were covered by Pd nanocrystals with size from 10 to 30 nm (figure 1a). The rGO@Pd was characterized by energy dispersive x-ray analysis (EDX), which proved the presence of C and Pd.

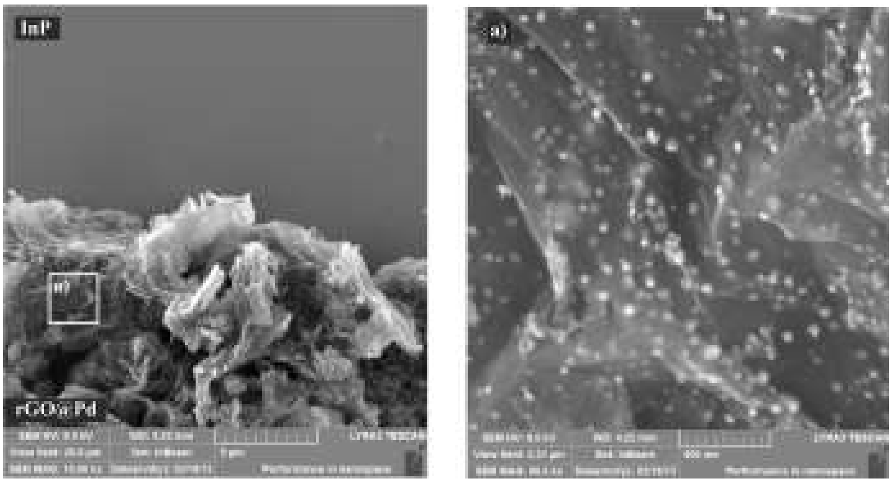

Figure 1 SEM images of rGO@Pd deposited on InP substrate.

The I-V characteristic of the Schottky diodes in a dark chamber at room temperature is presented in figure 2. For metal-semiconductor diodes, according to the thermionic emission (TE) theory, the forward I-V relationship of a Schottky diode at V>3kT/q can be expressed as:

$$I_s = I_0 \exp(\mathrm{qV}/\eta kT) \ , \qquad (1)$$

where

$$I_0 = AA^{**}T^2 exp(q\phi_B/kT). \qquad (2)$$

where A^{**} is the Richardson constant, which has theoretical value of 9.6 for InP [15], A is the contact area, T is the absolute temperature, k is the Boltzmann constant, ϕ_B is the barrier height and η is the ideality factor. By fitting the forward I-V curves, the barrier height and ideality factor were determined. The ideality factor was found to be higher than one for rGO@Pd/InP Schottky diodes. Nonideal behaviour can be attributed to either (i) defect states in the band gap of the semiconductor providing other current transport mechanism such as barrier tunnelling or generation recombination in the space charge region [16], or (ii) laterally inhomogeneous contacts [17]. A summary of the basic electrical parameter calculated from I-V characteristics is given in table 1.

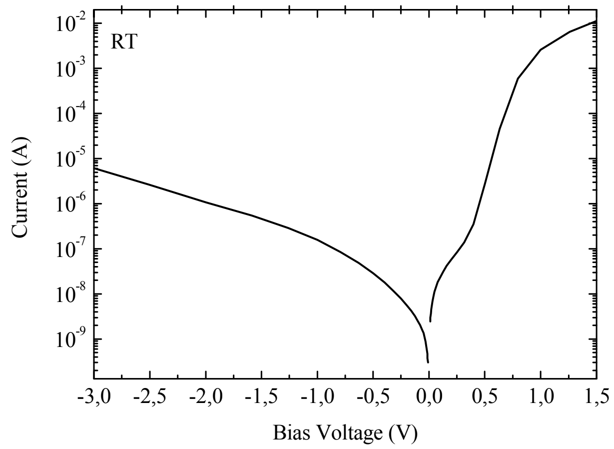

Figure 2 Current-voltage characteristics of the rGO@Pd/InP Schottky diodes.

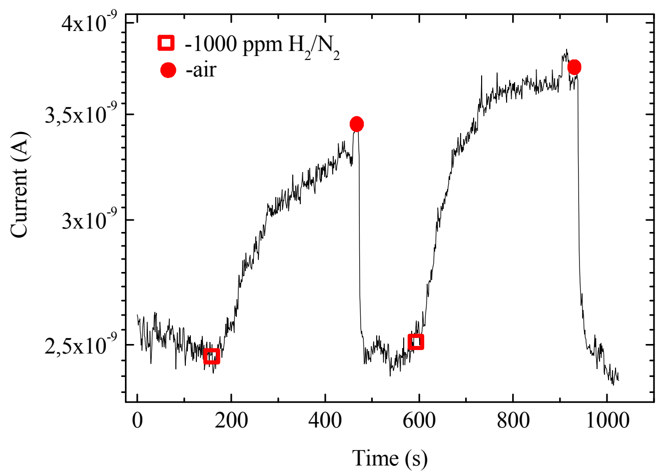

Figure 3 Current-transient characteristics of the rGO@Pd/InP Schottky diodes hydrogen sensor measured at -0.1 V at room temperature.

The rGO@Pd/InP Schottky diodes were tested for their sensitivity to hydrogen in a cell with a through-flow gas system. Our experiments were performed with a mixture of H_2/N_2 containing 1000 ppm of hydrogen in nitrogen (figure 3). The current increase characterized by the sensing response S = 1.6 was observed.

$$S = \{J_H - J_{air}\}/J_{air}, \quad (3)$$

where J_H is the saturation current density under exposure to hydrogen and J_{air} is the same for air. The mechanism of sensing can be explained by the dissolution and dissociation of hydrogen molecules into atomic hydrogen at the Pd nanocrystals, lowering the work function of Pd (palladium hydride [PdH_x] is formed), and resulting in the decreased Schottky barrier height of the rGO@Pd/InP Schottky diodes. The rGO@Pd/InP Schottky diodes sensor has lower sensitivity in comparison with the result obtained in our previous work, where Pd or Pt nanoparticles were inserted by electrophoretic techniques between the graphite contact and the semiconductor substrate [11]. This result indicates that a key role in the dissociation of hydrogen and consequently in the change of the Schottky barrier height is played by Pd nanocrystals which are in close contact with a semiconductor substrate. The rGO@Pd had layered structure and only small amount of Pd nanocrystals are in direct contact with the semiconductor substrate resulting in relatively low sensitivity response.

Table 1 Electrical parameters calculated from I-V and I-t characteristics for the rGO@Pd/InP Schottky diodes. R-rectification ratio at 1.5V, η-Ideality factor, ϕ_β-Schottky barrier height, S-sensing response at -0.1V (in 0.1% H2/air).

	R	**η**	**$\phi_{b,}$ (eV)**	**S**
rGO@Pd/InP	2.1×10^4	2.07	0.87	1.6

3. Conclusion

We have demonstrated the fabrication of Schottky diode hydrogen sensors by the deposition of reduced graphene oxide decorated with Pd nanocrystals on n-type InP substrates. These Schottky diodes are capable of the detection of 1000 ppm hydrogen at room temperature. The sensing mechanism can be explained by the dissolution and dissociation of hydrogen molecules into atomic hydrogen at the Pd nanocrystals which are in direct contact with semiconductor substrate, lowering the work function of Pd, and resulting in the decreased Schottky barrier height of the rGO@Pd/InP Schottky diodes.

Acknowledgments

This work has been supported by the project COST LD12014 of the Ministry of Education CR and by the international collaboration project M100671201 of the ASCR.

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