DEPOSITION OF PVP-PROTECTED PLATINUM NANOPARTICLES ON SEMICONDUCTOR SUBSTRATES FOR HYDROGEN SENSING

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Abstract

High quality Schottky diode hydrogen sensors were prepared by the deposition of colloidal graphite on n-type InP substrates partly covered with PVP-protected Pt nanoparticles (NPs). A sub-monolayer of the Pt NPs was created by simple evaporation of the solvent in which Pt NPs were dispersed. The Pt NPs serve to dissociate hydrogen molecules into atomic hydrogen, which is absorbed at the metal-semiconductor interface. Hydrogen absorption leads to the formation of the dipole layer, which changes the Schottky barrier height and results in the increase of both forward and reverse current. The proposed hydrogen sensor showed high sensitivity response of ~10^6 to 1000 ppm H_2 in N_2 at room temperature.

Keywords: Hydrogen sensors, PVP-protected Pt nanoparticles, Graphite based Schottky junction

1. INTRODUCTION

Hydrogen gas has been widely used in research and industry. However, hydrogen is 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 [1].

Pt is transient metal with superior catalytic properties and is thus convenient for preparation of highly sensitive hydrogen sensors. Pt ability to dissociate hydrogen molecules to single atoms is very well described in the literature [2]. When Pt is in nanoparticle form, its catalytic properties are further improved due to the enhanced active surface, sharp edges and corners and is strongly dependent on surface saturation [3]. In our previous works we presented high-sensitivity Schottky diode hydrogen sensors, which were created by electrophoretic deposition of Pt NPs onto an n-type InP substrate [4], or by inserting Pt NPs between graphite contact and n-type InP substrate [5]. In both cases we used solution of the Pt NPs with sodium di-2-ethylhexylsulfosuccinate (AOT) as protective agent. To verify whether the protective agent influences the sensing properties, we prepared Pt nanoparticles in suspension with polyvinylpyrrolidone (PVP) as protective agent. PVP surfactant is commonly used polymer in many branches of industry mainly for its good solubility in water and organic solvents, chemical stability, and nontoxic character [6]. The sensor structures were created in two steps. First, sub-monolayer of the PVP-protected Pt NPs was deposited by simple evaporation technique. Next, a drop of colloidal graphite was deposited and a Schottky contact with the diameter of about 1 mm was created. Graphite-Pt NPs/InP junctions were investigated by the measurement of current-voltage characteristics and tested for their sensitivity to hydrogen.

2. EXPERIMENTAL AND RESULT

2.1 Preparation of Pt nanoparticles

Preparation of the PVP-protected Pt NPs was carried out following the procedure developed by Teranishi [6]. Two solutions were prepared. First, 5 ml of 6 mM solution of $H_2PtCl_6 \times 6H_2O$ in water, second, 45 ml of 18 M of PVP solution in methanol. Then, these two solutions were mixed and boiled and refluxed for 30 min. After 30 min, temperature of solution reached 79 °C, the solution boiled, and suddenly turned color from pale yellow to dark brown. Before synthesis, the absorption peak at 260 nm could be seen in UV-Vis spectra. This peak vanished after color change, which indicates the Pt nanoparticle formation in correspondence with literature [6,7]. The morphological properties of the Pt NPs were studied by transmission electron microscopy (Fig. 1a) and scanning electron microscopy (Fig. 1b). It is seen that the NPs exhibit a fairly uniform size distribution. The average NPs diameter was about 4.5 nm.

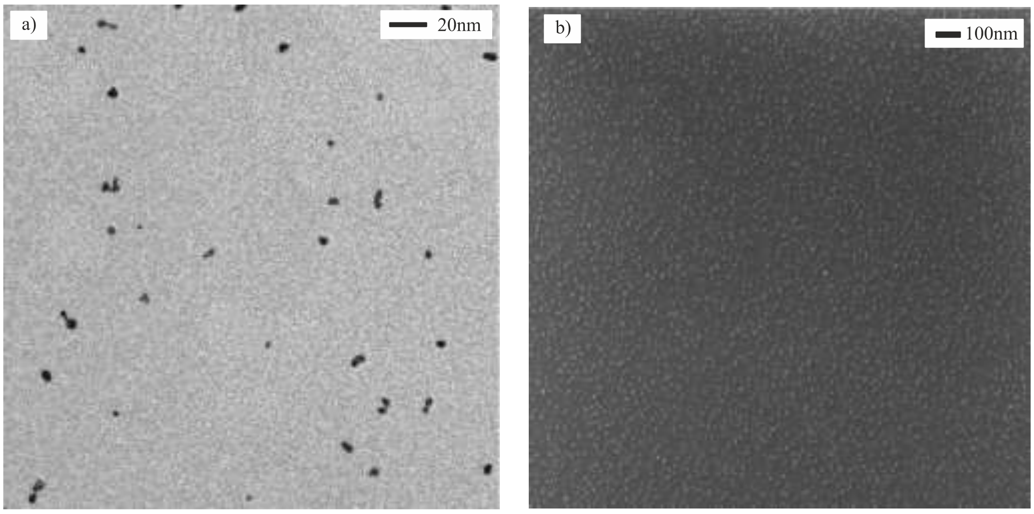

Fig. 1 (a) TEM image of the Pt NPs. (b) SEM image of the Pt NPs deposited on InP substrate by solvent evaporation

2.2 Preparation of the Schottky diode hydrogen sensors

Schottky diodes were fabricated on n-type InP substrate with the free electron concentration 6.7×10^{15} cm^{-3}. The sub-monolayer of the PVP-protected Pt NPs was deposited on InP substrates by simple evaporation technique. A drop of colloidal graphite suspension was deposited on the sub-monolayer Pt NPs (for more details see our previous publications [8,9]). An ohmic contact on the backside was formed by rubbing liquid Ga-In alloy with the tin rod. Prior to the deposition of both ohmic and Schottky contacts, the InP substrate was cleaned in boiling methanol for 5 min.

2.3 Hydrogen sensor performance

Fig. 2b shows I-V characteristics of the graphite-Pt NPs (PVP)/InP Schottky diode measured at room temperature. 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 [10]:

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

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 [11], 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 (Table 1). The ideality factor η was found to be higher than one. 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 [12], or (ii) laterally inhomogeneous contacts [13]. The deviation from linearity at higher voltage in the semi-logarithmic I-V characteristics is due to the series resistance of the structure.

The graphite-Pt NPs(PVP)/InP structures were tested for their sensitivity to hydrogen in a cell with a through-flow gas system. First experiments were performed with a mixture of H_2/N_2 containing 1000 ppm of hydrogen (Fig. 1a). Rapid current increase characterized by the sensing response S=0.8*10^6 (S=[J_H-J_{air}]/J_{air}, where J_H is the saturation current density under exposure to hydrogen and J_{air} is the same for air). This value is in good agreement with S=1.8*10^6 for graphite-Pt NPs(AOT)/InP[14] Schottky diode hydrogen sensor. These results confirm that the protective agent does not significantly affect the sensing properties.

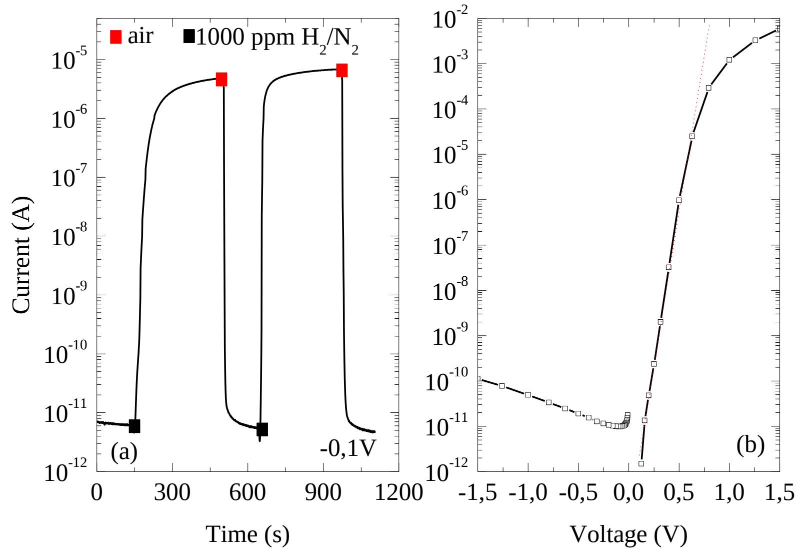

Fig. 2 Current transient (a) and current-voltage (b) characteristics of the graphite-Pt PVP NPs/InP Schottky diode sensor structure measured at room temperature

Table 1 Electrical parameters calculated from I-V characteristics for the graphite based Schottky diodes.

Samples	Rectification ration at 1.5V	Ideality factor, η	Schottky barrier high, ϕ_B (eV)	Sensitive response at -0.1V S, (in 0.1% H_2/air)
Graphite-Pt NPs(PVP) NP/InP	5.0E8	1.20	1.0	0.8E6

3 CONCLUSION

In conclusion, we showed that simple evaporation of PVP-protected Pt NPs followed by the deposition of graphite contact allows us to fabricate high quality Schottky barrier hydrogen sensor. The proposed hydrogen sensor showed high sensitivity response (of ~10^6 to 1000 ppm of H_2 in N_2), and a large degree of reproducibility at room temperature. We also presented that different protective agents (PVP, AOT) do not significantly affect the sensing properties.

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