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STUDY OF LAYERS OF Pd ON InP

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Abstract

Layers of Pd nanoparticles on n-InP seem to be good structure for monitoring hydrogen concentration in the air. Generally, energetic barrier, called Schottky barrier, is formed on the interface between metal and semiconductor. This barrier is lowered by the presence of hydrogen and this influences the amount of current which flows through the structure. Pd was chosen for its ability to dissociate hydrogen molecules to single atoms. This fact is further enhanced by nanoparticle form of this metal because of its high surface-to-volume ratio. Pd nanoparticles were prepared in colloid solution stabilized by AOT. The layers were prepared by electrophoretic deposition through the mask of polystyrene spheres. Electrophoretic deposition lies in acceleration of particles in electric field in the direction towards the InP wafer. SEM measurement showed that particles in colloid solution are separated and after deposition they form small aggregates on InP. The size of these aggregates depends on the time of deposition. The I-V characteristics were measured and from these data Schottky barrier height and ideality factor were calculated. The morphology of layers was monitored by SEM.

Keywords: Palladium, InP, nanoparticles

1. INTRODUCTION

The interface of n-type InP and Pd nanoparticles has very good rectifying characteristics with high Schottky barrier and ideality factor close to 1. Because of high catalytic activity of Pd which is further enhanced by nanoparticle form of Pd (high surface-to-volume ratio), this structure can be used as hydrogen sensor [1]. Hydrogen is dissociated on Pd nanoparticles and single hydrogen atoms are adsorbed on InP surface where they create dipole layer which lowers Schottky barrier.

Method of interface preparation is very important in the sense of quality of rectifying properties of structure and height of Schottky barrier which is theoretically given by the difference of metal work function and electronic affinity of semiconductor. In practice, the Schottky barrier is lower than this difference because of Fermi level pinning which is explained by electronic states in band gap induced by disorder of atoms on the interface [2]. We can partly eliminate these unwanted states by method of preparation. It was proved that Schottky barrier is lower when the structure is prepared by high energetic means of deposition (e.g. thermal evaporation) [3]. Preferable method of interface fabrication is electrophoretic deposition with measured Schottky barrier height of 0.85 eV [1] what is higher when compared to 0.55 eV obtained by using thermal evaporation [3].

We tried to prepare Pd nanoparticles on InP by electrophoretic deposition through the mask of polystyrene spheres to obtain periodic arrangement and we wanted to investigate the properties of these structures. This paper refers about preparation of these layers and their morphological characterization by SEM. Current-voltage characteristics were also measured.

2. MATERIALS & METHODS

2.1 Preparation of Pd nanoparticles

Pd nanoparticles are prepared in colloid solution. This solution is formed by reverse micelles with water inside in isooctane environment. In these micelles reduction of palladium(II) chloride by hydrazine occurs [4]. 0.05M palladium(II) chloride and 1M hydrazine water solutions were prepared. Equal amounts ruled by parameter ω_0, defined as a ratio of molar concentration of H_2O and AOT in final isooctane solution, $\omega_0=[H_2O]/[AOT]$, were added to two equal amounts of 0.1M AOT/isooctane solution. AOT (sodium 1,4-bis(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate) plays a role of surfactant here. Parameter ω_0 controls the size of the nanoparticles. Here, $\omega_0=5$. Chemicals were purchased from Sigma-Aldrich.

In the end, these AOT/isooctane solutions, the first with palladium salt, the second with hydrazine, were mixed. SEM (JEOL-JSM7500f) observation of solution deposited on TEM grid showed that nanoparticles are separated and about 10 nm size with less than 10% dispersion.

2.2 Preparation of monolayers of polystyrene microspheres

Layers of polystyrene spheres (100 nm and 500 nm in diameter) were prepared from their solution [5]. This solution was spread on water surface where the spheres created a monolayer. Then InP wafer (Wafer Technology LTD., crystallographic orientation 100, carrier concentration $\leq 10^{16}$ cm^{-3}) was gripped in a tweezer, immersed in water, and by pulling the wafer out of water the layer of polystyrene spheres sticked on the wafer surface. Layers of spheres 100 nm and 500 nm diameter were prepared and observed in SEM.

2.3 Electrophoretic deposition

The full-area ohmic contact on one side of the wafer was made by obtrusion of molten Gallium and then by application of conductive silver colloid paint. Electrophoretic deposition was performed in a teflon cell with two electrodes (**Fig.1.**). On the bottom electrode the InP wafer with polystyrene spheres is mounted (on the side with full-area ohmic contact). The colloid solution of Pd nanoparticles is placed between electrodes. The polarity on the sample was negative, because it was found that the quality of layers is better in the sense of Schottky barrier height and sensitivity to the presence of hydrogen [6] The applied voltage was 50 V for 30 min with 1:1 stop-go voltage interrupter at 10 Hz frequency.

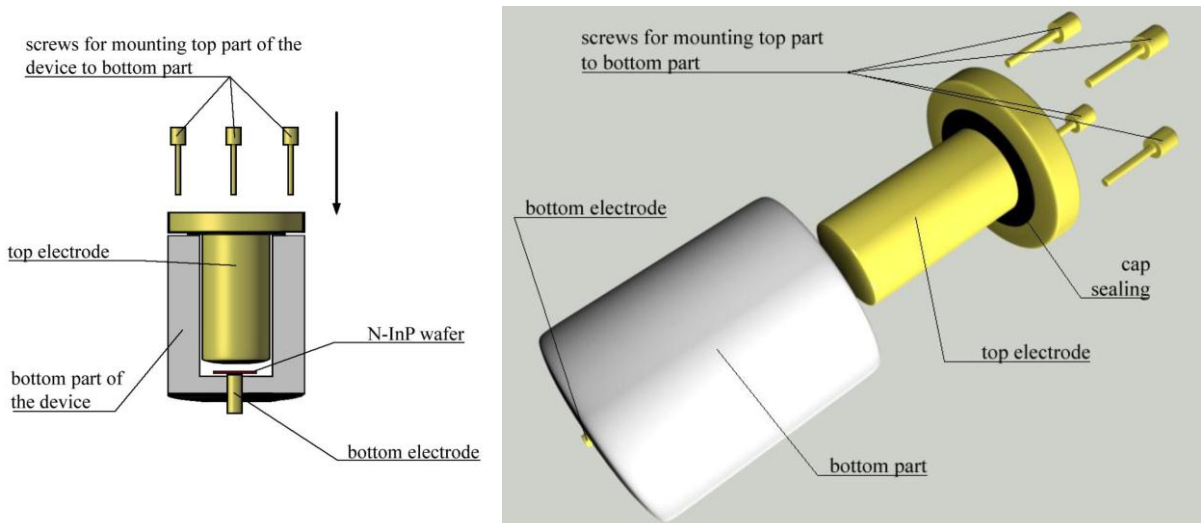

Fig.1 Schematic drawing of the cell for electrophretic deposition

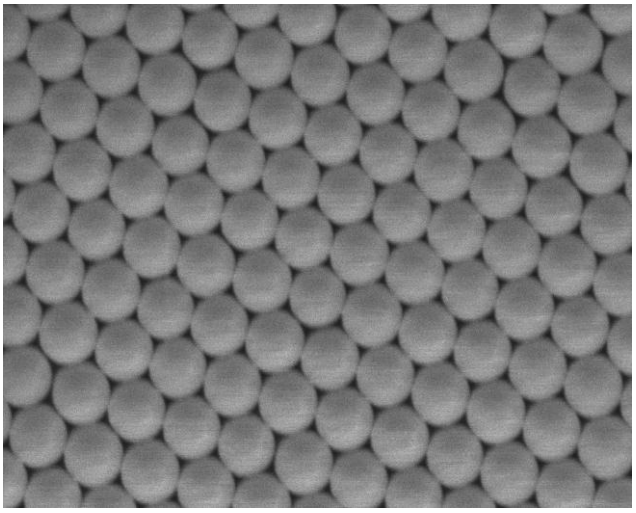

Fig. 2 SEM image of monolayer of polystyrene spheres with hexagonal arrangement. White bar correspond to 1 μm.

The deposited layers were observed in SEM and then the layer of polystyrene spheres was peeled off by a Scotch tape. Then the layers with only Pd nanoparticles were observed in SEM again. I-V characteristics were measured using Keithley Source-Measure Unit 236.

3. RESULTS AND DISCUSSION

In **Fig. 2** we can see InP wafer with deposited polystyrene spheres of size 500 nm. Monolayer of this spheres made hexagonal arrangement. Calculated area of holes among the spheres is 0.003 μm^2 for 100 nm spheres and 0.075 μm^2 for 500 nm spheres. These holes are large enought to let the particles get through and settle on the wafer. In the solution, there is approximately 10^{16} Pd particles.

After the electrophoretic deposition, SEM observations revealed that the particles settled on the InP wafer and also on the polystyrene spheres which were non-conductive and that was the reason we supposed that no particles would be localized on the spheres. Sample in SEM showed less charging than the sample with plain polystyrene spheres what indicated that the surface is conductive. On **Fig.2.** we can see 100 nm resp. 500 nm polystyrene spheres and deposited Pd nanoparticles over them and in the holes between polystyrene spheres.

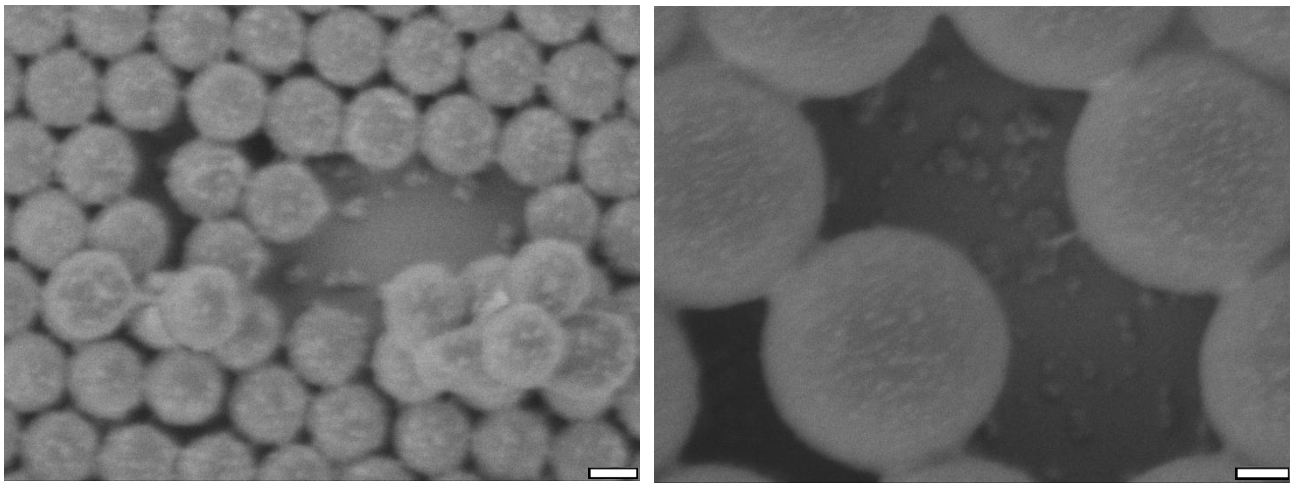

Fig. 3 SEM image of Pd nanoparticles deposited on polystyren spheres of size 100 nm (left image) and 500 nm (right image). White bars correspond to 100 nm.

Pd nanoparticles created small aggregates when deposited on InP surface. Size of these aggregates grows with the time of deposition. The Pd particles settle probably selectively to the nearness of previously settled Pd particles because lines of force of electric field are denser at surfaces with high curvature. In these areas is higher gradient of field a therefore higher force which drives the particles toward surface. In **Fig.4.** we can see aggregates made of Pd nanoparticles.

When we removed a layer of polystyrene spheres, we observed in SEM that Pd nanoparticles remained on the wafer and they created a net structure ruled by the previous presence of polystyrene spheres (**Fig.5.**). On these structures, contact from graphite colloid paint was made for I-V measurement. In **Fig.5.**, we can see I-V curve of this structure. Very poor diode characteristics with high ideality factor about 2.8 were

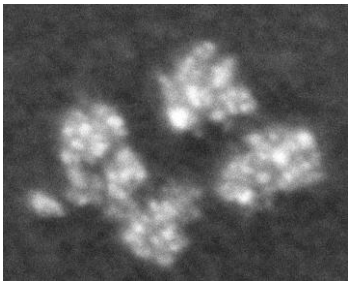

Fig. 4 SEM image of a small cluster of Pd nanoparticles. White bar corresponds to 10 nm

observed. It indicates that other mechanism than thermionic emission occurs here. It is well known that Pd nanoparticles deposited by electrophoretic deposition shows very good rectifying characteristics [6] and from this point of view the different behavior of structures deposited through mask of polystyrene spheres suggests that probably the surface of InP was disturbed during the process of deposition.

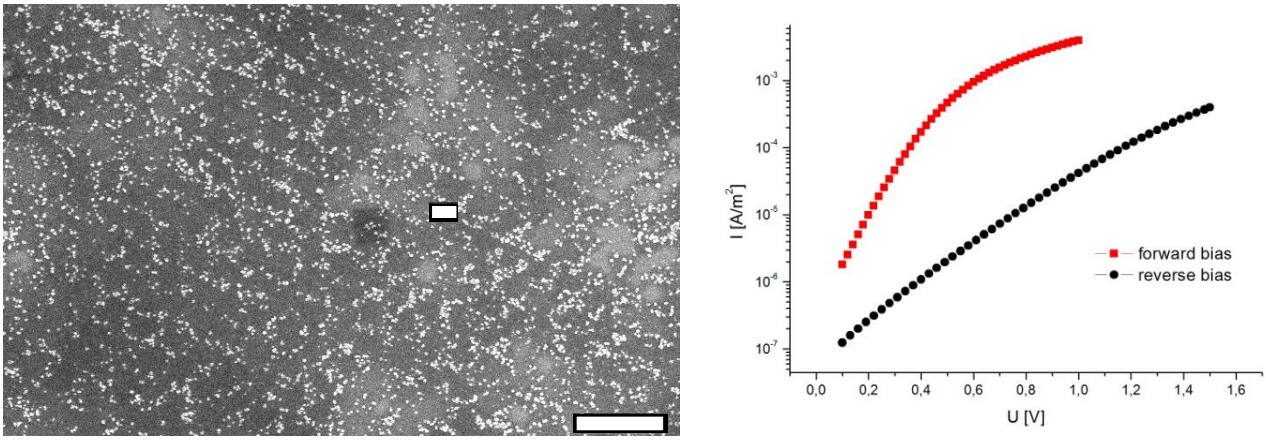

Fig. 5 SEM image of Pd nanoparticles deposited through polystyrene mask. White bar corresponds to 1 μm (on the left). I-V characteristics of these structures (on the right).

CONCLUSIONS

The structures of Pd nanoparticles were prepared by electrophoretic deposition through the mask of polystyrene spheres of diameters 100 nm and 500 nm. Pd nanoparticles were prepared by reverse micelle technique. Current-voltage measurement showed that the Schottky barrier was poor and the ideality factor suggested that another carrier transport than thermionic emission occurred in this structure.

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