STUDY OF LAYERS OF METAL NANOPARTICLES ON SEMICONDUCTOR WAFERS FOR HYDROGEN DETECTION

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Abstract

In this work, colloid solutions of metal Pt, Pd and Pt/Pd alloy nanoparticles by reverse micelle technique in isooctane were prepared. Layers of the nanoparticles on InP and GaN substrates using electrophoretic deposition were prepared. Different coating of semiconductor surface under different polarity of electrical field during electrophoretic deposition was investigated. Metal nanoparticles in the colloid and deposited metal nanoparticles were characterised by SEM. Schottky diodes were fabricated by application of colloidal graphite on nanoparticle layer. Diodes made with colloidal graphite exhibited better characteristics, than diodes with contacts made by other methods (evaporating, electrolysis). Diodes exhibited excellent current–voltage rectifying characteristics, the difference between forward and reverse current at 1 V was greater than 5 orders of magnitude. Schottky barrier height of 1.03 eV was calculated for GaN–Pd structure and 0.78 eV for InP–Pd structure. A rapid increase in current under the flow of mixture of hydrogen in nitrogen was observed and measured for different hydrogen concentration range between 5 ppm and 1000 ppm.

Keywords: metal nanoparticles, reverse micelle, electrophoretic deposition, Schottky diodes, hydrogen detection

1. INTRODUCTION

Nanoparticles have many applications today. One of them is utilization layers of palladium or platinum on semiconductors surfaces as sensors of hydrogen, which were reported in [1]. These nanostructures have attributes similar to Schottky diodes, it means there exists a Schottky barrier between metal nanoparticle and semiconductor. Presence of higher concentration of hydrogen leads to dissociation of molecular hydrogen on the catalytic surface of nanoparticles. Hydrogen ions form an electric dipole layer on the interface between metal nanoparticle and semiconductor surface which leads to changes of effective work function of the metal. This change leads to decrease in Schottky barrier height which can be measured as an increase in current of diode.

In this work, the layers of palladium (Pd), platinum (Pt) and bimetallic alloys of platinum and palladium (Pt/Pd) nanoparticles on InP and GaN are made and the measurements in hydrogen containing atmosphere are showed. The obtained results should be useful for finding new efficient hydrogen sensors.

2. EXPERIMENT

2.1 Preparation of metal nanoparticles

The metal nanoparticles were prepared by the reverse micelle technique [2]. 0.1 M solution AOT in isooctane was prepared and divided into two half. To one half was added water solution of metal salt, to other half was added 1.1 M water solution of hydrazine as a reducing agent. These two solutions of reverse micelles were mixed and the micelles due to mutual collisions were exchanging their contents. The seeds of the metal
particles were created and particle grew to assize of reverse micelle. In the case of platinum nanoparticles 0.1 M hexachloroplatinic acid (H₂PtCl₆) was used as a dilution of metal salt and the growth of nanoparticles was linked with turning to brown colour. This colour change took about half an hour. In case of palladium nanoparticles 0.05 M palladium chloride (PdCl₂) was used and colour change representing nanoparticle growth took just several minutes. For a nanoparticles composed of both metals a dilution containing 0.05 M PdCl₂ a 0.025 M H₂PtCl₆ was used. The chemicals PdCl₂, H₂PtCl₆, hydrazine, AOT and isooctane were purchased from Sigma–Aldridge Company, USA.

2.2 Fabrication of layers of nanoparticles

InP wafers were purchased from Wafer Technology, UK, GaN wafers were purchased from Kyma Technologies, USA. The wafers were provided with a whole area ohmic contact on one side by spotting molten gallium with a tin rod and chafing it with a piece of cotton wool. The contacted side was affixed to one electrode in the cell for electrophoretic deposition (EPD). Second electrode was placed 1 mm above the surface of semiconductor wafer. The EPD cell was filled with colloid solution of metal nanoparticles in isooctane. A DC voltage 100 V keyed at 10 Hz with 50 % duty cycle, as described in Ref. 3, was applied via 5 MΩ serious resistance. The EPD cell with the wafer was washed by isopropanol after deposition. Isopropanol removed the remains of the isooctane colloid solution.

Different duration of EPD and application of both positive and negative potential on semiconductor wafer during EPD were studied. The layers of nanoparticles were characterised by scanning electron microscope JEOL JSM–7500F, electrical measurements were made by Keithley Source–Measure–Unit 236.

3. RESULTS AND DISCUSSION

The SEM image of Pt nanoparticles in the film prepared on a InP substrate by electrophoretic deposition from colloid solution is seen in Fig. 1(a-d). Duration of deposition was one hour on samples showed on Fig. 1(a) and Fig. 1(b). Duration of deposition was 15 hours and eight hours on samples showed on Fig. 1(c) and Fig. 1(d), respectively. Samples showed on Fig. 1(a) and Fig. 1(c) were prepared by EPD with positive electric potential placed on the electrode with InP wafer. On the contrary, samples showed on Fig. 1(b) and Fig. 1(d) were prepared by EPD with negative electric potential placed on the electrode with InP wafer. Positive potential on InP wafer leads to only a finite density of nanoparticles on the surface of wafer practically independent on duration of deposition whereas negative potential leads to higher density of particles on the surface strongly dependent on duration of deposition. It can be explained by positive charge of nanoparticles prepared by the reverse micelle technique with parameters mentioned above. Using the EPD with positive potential on semiconductor wafer can be prepared a layer of organic material from reverse micelle solution (mostly AOT and reverse micelles with no nanoparticles [3]) with several mutually isolated nanoparticles. Using the EPD with negative potential on InP wafer can be prepared surface partially covered by a layer of metal nanoparticles which were studied further.

The current–voltage (I–V) characteristics between Schottky contact prepared on the deposited layer and the whole area ohmic contact prepared on the opposite side of wafer were measured. Diodes with good rectifying properties were obtained for all six combinations of nanoparticles (Pt, Pd, Pd/Pt) and semiconductor wafer (InP, GaN). The I–V characteristics of diodes made by colloidal graphite contact on the layer of Pt nanoparticles on GaN wafer are shown in Fig. 2. All characteristics were measured at room temperature. Both diodes show very good rectifying character, the difference between forward and reverse current at 1 V was greater than 5 orders of magnitude. The biggest difference between current in air ambience and in the flow of blend hydrogen in nitrogen was observed for small both reverse and forward bias.
Fig. 1 SEM image of InP surface with Pt nanoparticles deposited a) one hour with InP wafer on positive electrode during EPD, b) one hour with InP wafer on negative electrode during EPD, c) 15 hours with InP wafer on positive electrode during EPD, and d) eight hours with InP wafer on negative electrode during EPD. The scale 100 nm is shown with the bright bar at the bottom of each image.

The forward current–voltage characteristic can be expressed as:

$$I_d = A^{*} T^2 e^{-\frac{q\Phi_B}{kT}} \left( e^{\frac{qV}{n kT}} - 1 \right),$$

where $\eta$ is the ideality factor, $\Phi_B$ the Schottky barrier height, $A^{*}$ the Richardson constant (9.24 $A K^2 cm^{-2}$ for InP), $k$ the Boltzmann constant, $e$ the elemental charge and $T$ the absolute temperature. From the straight part of semi–log I–V characteristic can be Schottky barrier height calculated. Table 1. shows Schottky barrier heights for all six combination of nanoparticles and semiconductors. An approximately 0.2 eV difference between barrier heights of diodes on InP and GaN semiconductor is given by the difference between electronic affinities of this two semiconductors.

Table 1. Schottky barrier heights of diodes made on the layer of Pt, Pd and Pt/Pd alloy nanoparticles on InP and GaN wafer.

<table>
<thead>
<tr>
<th>structure</th>
<th>barrier height</th>
<th>structure</th>
<th>barrier height</th>
</tr>
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<tbody>
<tr>
<td>InP-Pd</td>
<td>0.78 eV</td>
<td>GaN-Pd</td>
<td>1.03 eV</td>
</tr>
<tr>
<td>InP-Pt</td>
<td>0.60 eV</td>
<td>GaN-Pt</td>
<td>0.81 eV</td>
</tr>
<tr>
<td>InP-Pt/Pd</td>
<td>0.76 eV</td>
<td>GaN-Pt/Pd</td>
<td>1.09 eV</td>
</tr>
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Current changes of one diode made on Pt nanoparticles on GaN after alternative exposure to the flow of the blend hydrogen in nitrogen at forward bias 0.1 V are shown in Fig. 3. When the ambience changed from air...
to 0.1 % H₂ in N₂ the current increased very fast to a value more than 70000 higher than the original one. By
defining the response time and the recovery time as the times for reaching 50% of the final steady state
current, the response time is equal to about 37 s and the recovery time in the air ambience is equal to about
6 s. Slower recovery development was observed in pure nitrogen ambience and in vacuum. It suggests that
an oxygen from the air is necessary for fast removing of hydrogen from diode surface.

Current changes of the same diode as above after alternative exposure to the flow of hydrogen/nitrogen
mixture at forward bias 0.1 V depending on hydrogen concentration are shown in Fig. 4. Quick response and
high changes in current can be observed for all concentration of hydrogen in the range between 56 ppm and
1000 ppm.

Lower concentration of 6.7 ppm was measured on diode made on the layer of Pd/Pt alloy nanoparticles on
surface of InP wafer as it is shown on Fig. 5. The change of current was slow but still measurable.
SUMMARY

Colloid solutions of Pd, Pt and Pd/Pt alloy nanoparticles in reverse micelles in isooctane were prepared. The layers of these nanoparticles on surfaces of n–type InP and n–type GaN single crystalline wafers were prepared by electrophoretic deposition. Nanoparticles on the surface were coalesced in small clusters when the semiconductor wafer was connected to a negatively charged electrode during EPD. Diodes prepared by colloidal graphite contacts were made on the nanoparticle layer. Diodes showed excellent rectifying character with high Schottky barrier heights and they were very sensitive to presence of hydrogen in ambience. Measurable changes of current were observed when diodes were placed to several ppm of hydrogen in nitrogen ambience.

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LITERATURE


