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GRAPHITE/n-InP SCHOTTKY BARRIER WITH ELECTROPHORETICALLY DEPOSITED Pt NANOPARTICLES FOR HYDROGEN AND NITROGEN-MONOXIDE DETECTION

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Abstract

N-type InP single-crystal-wafer was deposited with Pt nanoparticles (NPs) by electrophoresis from a colloid solution The colloid solution of Pt NPs in AOT reverse micelles in isooctane was previously prepared from water solution of a Pt-salt and reducing agent hydrazine. Pt NP spheres of 5 nm diameter in colloids were observed by scanning electron microscopy (SEM) and by optical plasmon extinction spectra in UV-Vis region. Deposited Pt NPs were observed by SEM, atomic force microscopy and scanning tunneling microscopy. Deposit covering was varied from one tenth to several monolayers. Schottky contacts were made by colloidal graphite on InP wafer site with Pt NPs. The diodes with the Schottky and an ohmic contact were measured by current-voltage characteristics with both forward and reverse polarity. For determination of the hydrogen or nitrogen-monoxide detection-performance, the current was measured as a function of time after exposure to detected gases diluted in nitrogen. Maximum current after hydrogen exposure increased and the response time decreased monotonously with Pt NPs coverage. Hydrogen was detected by an increase of current while nitrogen-monoxide was detected by a decrease of current. A change of current is caused by the change of the Schottky barrier height due to adsorbed atoms forming a dipole layer. The dipole layer has been explained by polarization of adsorbed atoms. However, this mechanism leads only to barrier height decreasing which is in contradiction with our result of nitrogen-monoxide measurements. Thus, other mechanism, involving negative charging of hydrogen atoms and positive charging of oxygen atoms, is discussed.

Keywords: platinum nanoparticles, keyed electrophoresis, Schottky diode, hydrogen detection, nitrogen-monoxide detection

1.   INTRODOCTION

Hydrogen sensors are very important to be installed for safety in places where hydrogen is used in any human activity to prevent danger explosions of that colorless, invisible and scentless highly inflammable gas. On the other hand, hydrogen diluted in nitrogen can be used as a safe and cheap tracer gas for leak detection instead of high cost helium when suitable hydrogen detectors are available. It is desirable to have hydrogen detectors of high sensitivity, fast response and recovery, small size, low cost and well compatible with novel miniature electronics. Semiconductor sensors based on Schottky barriers are potentially useful for that purpose.

However, Schottky barrier interfaces of semiconductors are still neither well understood, nor well controlled up to now. There have been already reported a number of palladium (Pd) and platinum (Pt) Schottky diode gas sensors using single crystals of various semiconductors. However, in spite of the basic similarity of the device structure, reported sensing performances are surprisingly different. One of possible reasons for this difference is variations of leakage currents as well as little understanding of the current transport and sensing mechanism.

The paper reports on n-type InP Schottky diode hydrogen sensors with low-leakage currents prepared by printing colloidal graphite and electrophoretic depositions (EPD) of Pd and Pt nanoparticles (NPs), as developed in our lab.

2. EXPERIMENTAL

Colloid solutions of Pt NPs in isooctane were prepared by reducing with hydrazine water solutions of Pt salts, enclosed in reverse micelles formed with the surfactant sodium di-2-ethylhexysulfosuccinate (AOT). Pure chemicals for preparing colloid solutions were purchased from Sigma Aldrich Corporation (St. Louis, MO, USA). The obtained Pt or Pd NPs were imaged by scanning electron microscope (SEM, JSM-7500F, JEOL Ltd. Akishima-shi, Japan). Optical absorption peak due to surface plasmon resonance of Pt or Pd NPs in the colloid solution was observed by split-beam UV-Vis spectrophotometer (SPECORD 210, Analytik Jena, Germany).

Intentionally not-doped, one-side-polished wafers of n-type InP single crystals, with donor density 10^{16} cm^{-3} were purchased from Wafer Technology (Milton Keynes, UK) . The not polished side was provided with an ohmic contact. The polished surface was masked with a grid leaving 0.3 mm^2 separated free places on the surface for EPD of Pt NPs. The deposits were observed by SEM, atomic force microscopy and tunneling electron microscopy (AFM and TEM, Veeco Multimode). The EPD was performed with a negative voltage of 100 V applied on the wafer for various time of deposition. The voltage was keyed with 10 Hz of frequency and 1:1 duty cycle. Four deposition times were used, ¼ h, 1 h, 4 h, and 27 h.. Schottky contacts were printed by colloidal graphite on places deposited with Pt NPs. Water solution of colloidal graphite for printing Schottky contacts was obtained from Agar Scientific. Each diode consisting of the graphite Schottky contact and the ohmic contact on the other side was studied by measuring current-voltage characteristics (I-V, 236 Source-Measure Unit, Keithley, Cleveland, OH, USA) and their change by exposition to hydrogen (H$_2$) or nitrogen monoxide (NO) ambient. The sensitivity to H$_2$ or to NO was assessed by measuring current at constant voltage as a function of time alternatively in the flow of 0.1 % H$_2$ or 0.1 % NO mixed in nitrogen (N$_2$) carrier gas and in the flow of air. Pure N$_2$ and calibrated mixture H$_2$/N$_2$ or NO/N$_2$ were mixed using gas flow meters and controllers (Bronkhorst High-Tech, Ruurlo, Netherlands) to get flows of defined hydrogen-nitrogen mixtures.

3. RESULTS AND DISCUSSION

The SEM image of Pd NPs in colloid solution is seen in Fig.1 and the SEM image of Pt NPs is seen in Fig. 2. In both cases the NPs are spherical and not aggregated. The diameter is about 10 nm and 5 nm of Pd and Pt NPs, respectively. Colloid solutions were diluted with pure isooctane before samples for measurements on microscopic grids were prepared.

Optical absorption spectrum in UV-Vis region of the colloid solution with Pd NPs is seen in Fig. 3. and the one with Pt NPs in Fig. 4, respectively. The peak at 282 nm in Fig. 3 or the peak at 266 nm in Fig. 4 is induced by extinction in surface plasmon resonance in Pd and Pt NPs, respectively. The band consisting of two peaks, at 213 nm and 236 nm, seen in both Figs 3 and 4, is caused by the absorption in the organic compound AOT, which is added in surplus to colloid solutions as a surfactant. It is seen that a reasonably good fit was achieved for spectra decomposition into two Lorentz curves for the AOT band and a Gauss curve for a plasmon resonance extinction in Pd or Pt NPs.

The EPD keyed with frequency 10 Hz and 50 % duty cycle was provided on four InP wafers cut from the same plate, with four various deposition times, ¼ h, 1 h, 4 h and 27 h. The SEM, AFM and STM images of deposits obtained after 1 h EPD are shown in Figs 5, 6 and 7, respectively. Bright spots in the SEM image in
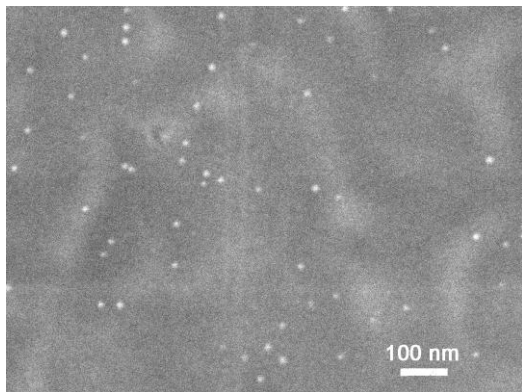
Fig. 1. SEM image of Pd nanoparticles (NPs) in diluted colloid solution represented by round light spots of 10 nm diameter
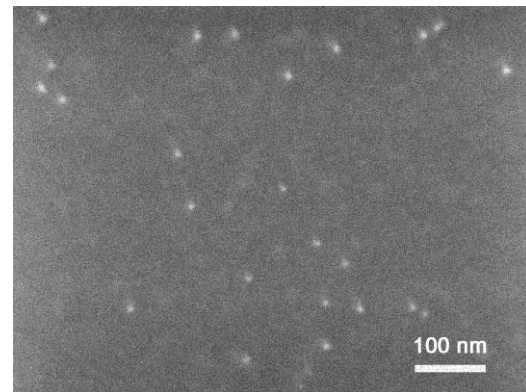

Fig. 2. SEM image of Pt nanoparticles (NPs) in diluted colloid solution represented by round light spots of 5 nm diameter

Fig.5 represent bare Pt NPs. They appear either separated or joined in small groups of two or three. The total number of Pt NPs per unit area in 1 h EPD sample was approximately four times larger than in ¼ h EPD sample (not shown). Likewise, the total number of Pt NPs per unit area in 4 h EPD sample (not shown) was approximately four times larger than in 1 h EPD sample, which proved that the sheet average density of deposited particles depended linearly on the deposition time. The bright spots in Fig. 6 are caused by Pt NPs enclosed in shells of organic compound AOT which formed reverse micelles in the colloid solution before EPD. Due to those shells, the size of NPs with Pt observed in the AFM image is larger (about 15 nm) than the size of bare Pt NPs observed in the SEM image (about 5 nm). The STM image seen in Fig. 7 is similar to the AFM image, except of the background. In the background in the STM image are seen round spots due to grains of the gold layer deposited on the sample with EPD of Pt NPs. Similar grains were seen also on gold layers made on bare InP wafers, without any EPD.
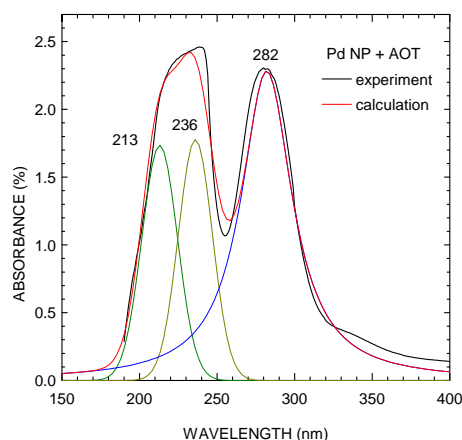

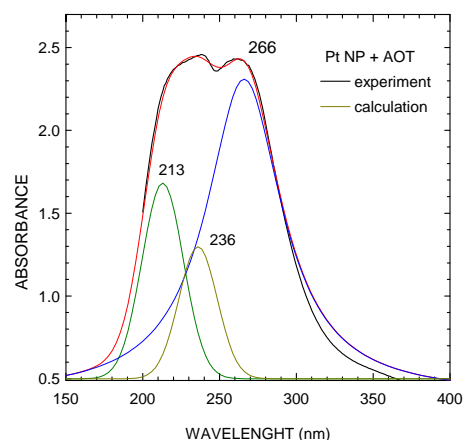**Fig. 3.** Optical absorption spectrum of the colloid solution with Pd NPs

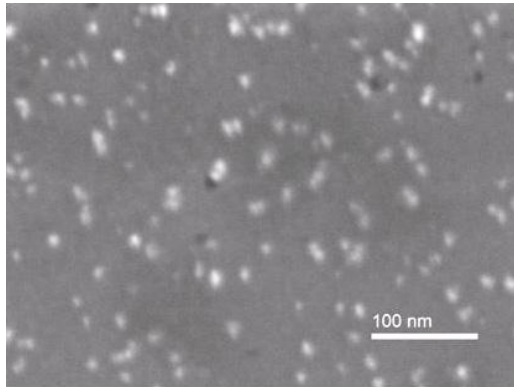**Fig. 4.** Optical absorption spectrum of the colloid solution with Pt NPs

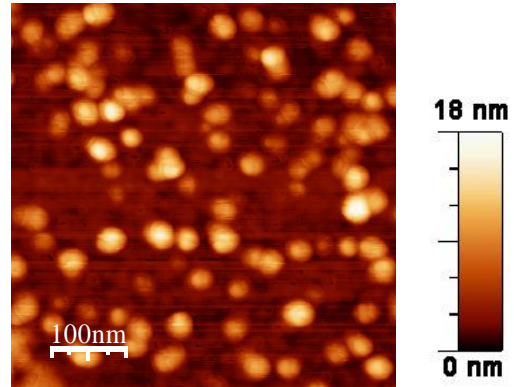**Fig. 5**. SEM image of InP surface with Pt NPs after 1 h of EPD

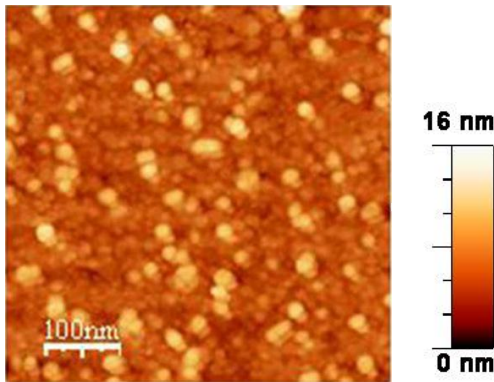**Fig. 6.** AFM image of InP surface with Pt NPs after 1 h of EPD

Fig. 7. STM image of InP surface with Pt NPs after 1 h of EPD
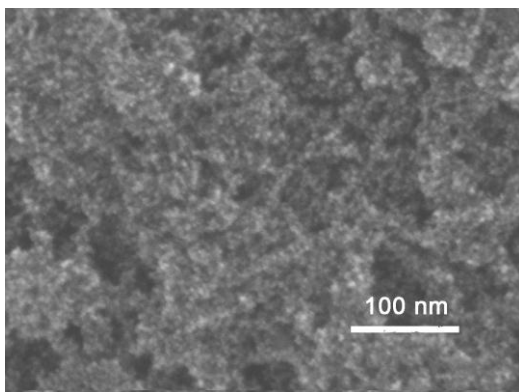

Fig. 8. Top view SEM image of InP with Pt NPs after 27 h EPD

Top and side view SEM images of InP with Pt NPs after 27 h EPD are shown in Fig. 8 and Fig. 9, respectively. It is seen in Fig. 8 that the whole surface was covered with a continuous layer of Pt NPs. The width of the Pt NPs layer, greater than 100 nm, can be estimated from Fig. 9, as it is imaged by the strip 3. The cleavage edge is highlighted by the white line between parts 1 and 2. The part 1 represents the bare InP surface of the cleavage plane and the part 2 is the bare top plane of InP. The part 4 is the top plane of the Pt NPs layer. During the cleavage, the Pt NPs layer was broken further apart from the cleavage edge of InP and peeled off of the InP in part 2.

Forward and reverse current-voltage characteristics of four types Schottky diodes with ¼ h, 1 h, 4 h and 27 h EPD Pt NPs are seen in Fig. 10. All diodes possess high rectification ratio and low reverse current. Linear parts of their forward characteristics show on two electron transport mechanisms, thermionic emission and generation-recombination. Their barrier heights are close to the level alignment of Pt and n-InP (Schottky-Mott limit) 1.27 eV [1], showing on small Fermi level pinning – precondition for sensitive detection of hydrogen or other gases.

Response of the diodes to the exposure of 0.1 % hydrogen in nitrogen and recovery after switching to air exposure can be seen in Fig. 11, where dependences of the current as a function of time of 0.1 V forward biased diodes are plotted in semi-log
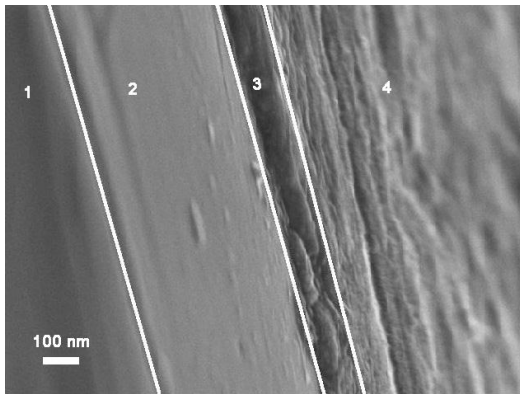
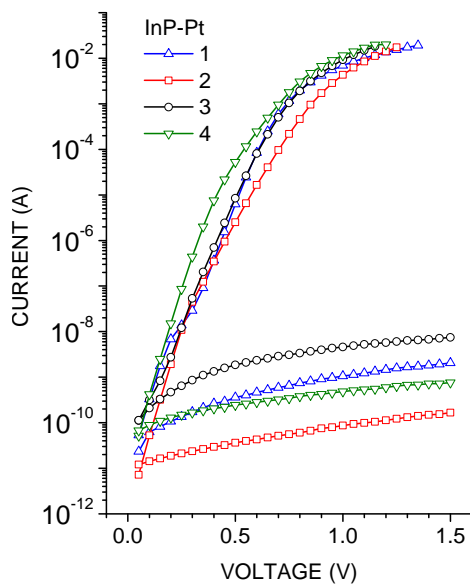**Fig. 9.** Side view SEM image of InP with Pt NPs after 27 h EPD

scale. Each current increases from its value in air I_0, approaches its maximum I_m in hydrogen and returns to back to I_0 in air. The sensitivity $\Delta I = \log(I_m/I_0)$ of each diode is shown in the legend in Fig. 11, it increases from the value 4.82 for the diode 1, with ¼ h EPD of Pt NPs, to the value 7.19 for the diode 4, with 27 h EPD of Pt NPs. There is a negligible difference between the sensitivity 7.18 of the diode 3, with 4 h EPD of Pt NPs and the diode 4. However, there is still a considerable difference between response times Δt of these two diodes, 58 s and 10 s for the diode 3 and 4, respectively. The response time of each diode is also shown in the
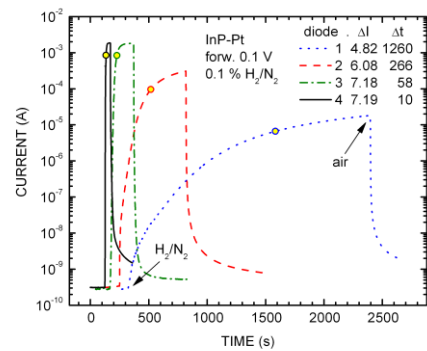

Fig. 10. Forward and reverse current-voltage characteristics of four types Schottky diodes with 1. ¼ h, 2. 1 h, 4 h and 27 h EPD Pt NPs

Fig. 11. Current response of four Schottky diodes with various Pt NP density to alternative exposure on 0.1 % H_2/N_2 and air

legend in Fig. 11. We defined the response time as the difference between the time when the hydrogen exposure starts and the time t_{90} when the log of current reaches 90 % of its maximum value $\log(I_m)$; point on the response curves for t_{90} are marked by small circles in Fig. 11. Reducing of the response time by increasing the amount of Pt NPs in the diode shows that the catalytic dissociation of
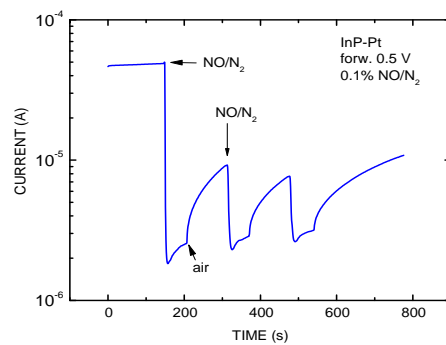

Fig. 12. Current response of Schottky diode 4 to alternative exposure on 0.1 % NO/N_2 and air

hydrogen molecules forms the bottleneck for the speed of hydrogen sensing.

In Fig. 12 is shown the response of the diode 4, with 27 h EPD of Pt NPs, to alternative exposure to 0.1 % nitrogen monoxide (NO) in nitrogen. The sensitivity to NO is obviously much smaller than to H_2 (ΔI about 1 of NO exposure to compare with about 7 of H_2 exposure) and it is of opposite sign (current decreased after NO exposure). A change of current is caused by the change of the Schottky barrier height due to adsorbed atoms forming a dipole layer. The dipole layer has been explained by polarization of adsorbed atoms [2]. However, polarization by the electric field leads only to barrier height decreasing which is in contradiction with our result of nitrogen-monoxide measurements. Obviously, besides atom polarization there is another mechanism which increases the barrier height in the case of oxygen or nitrogen adsorptions on the interface between the metal and the n-type InP. Such mechanism can be in charging of the adsorbed atom by accepting or removing an electron. Then, charged adsorbed atoms on the interface induce opposite charges in the metal and form the dipole layer which can increase the barrier height. In the case of n-type semiconductor, adsorbed atoms have to be positively charged to increase the barrier height. There are two ways leading to charging the adsorbed atoms; 1. chemical bond with atoms on the interface and 2. ionization energy decrease or affinity increase by correlation effects [3]. We suggest that the ionization energy was increased and shifted close to the Fermi level in the case of O or N adsorption which led to their positive charging and increasing of the Schottky barrier height. Simultaneously, the adsorbed atoms are polarized by the electric field of the Schottky barrier which shifts tends to barrier decrease. These two opposite effects lead to much smaller change of the barrier height in the case of NO detection then is the change in the case of H_2 detection, when these two effects support each other.

4.   CONCLUSION

Schottky diodes were prepared on n-type InP with EPD Pt NPs of various coverage from about 0.1 area to about 10 monolayers. All diodes gave current-voltage characteristics of low leakage currents, high rectification ratios showing on thermionic emission and generation-recombination electron transport with the barrier heights close to Schottky-Mott limit for Pt and n-type InP. All diodes were very sensitive to small concentration of 0.1 % hydrogen in nitrogen with whereas the sensitivity was increasing with increasing Pt NPs coverage. The response time reached very short value of 10 s in the case of the diode with the highest coverage. The last diode was also sensitive on 0.1 % NO in N_2 giving a decrease of current in contrast to the decrease of current in the case of H_2. To explain this current decrease, ionization energy decrease of oxygen or nitrogen atoms adsorbed on the semiconductor-metal interface was suggested.

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