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 and Pd nanoparticles both by direct reduction of metal salts in water solutions and by reverse micelle technique were prepared. Layers of the nanoparticles on InP and GaN substrates using electrophoretic deposition were prepared. Metal nanoparticles in the colloid and deposited metal nanoparticles on semiconductor surface were characterised by SEM. Schottky diodes were fabricated by application of colloidal graphite or silver paste on nanoparticle layer. Diodes exhibited excellent current–voltage rectifying characteristics. Schottky barier 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 H2/N2 was observed and measured for different hydrogen concentration and voltage applied on diode.

Metal nanoparticles in water solutions

Reduction of **H_2PtCl_6** and **$PdCl_2$** by hydrazine, boronhydrate or methanol

Reaction with methanol

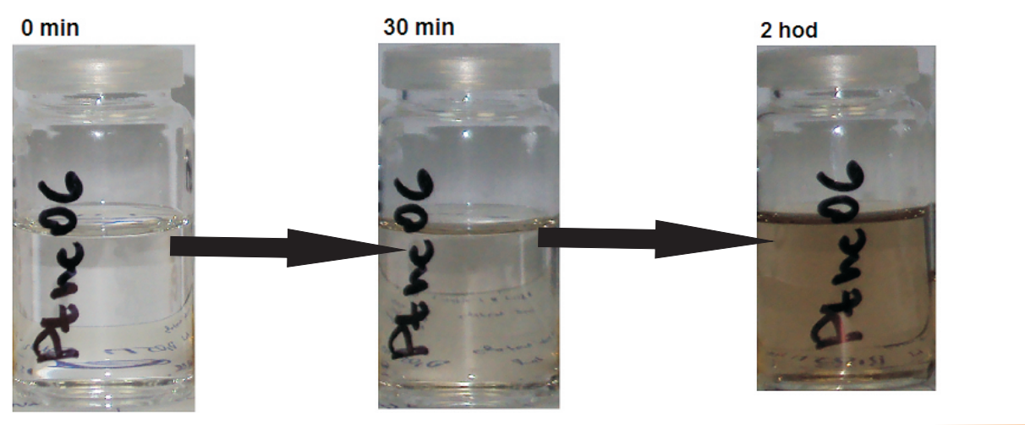
$PtCl_6^{2-} + CH_3OH \rightarrow PtCl_4^{2-} + HCHO + 2H^+ + 2Cl^-$

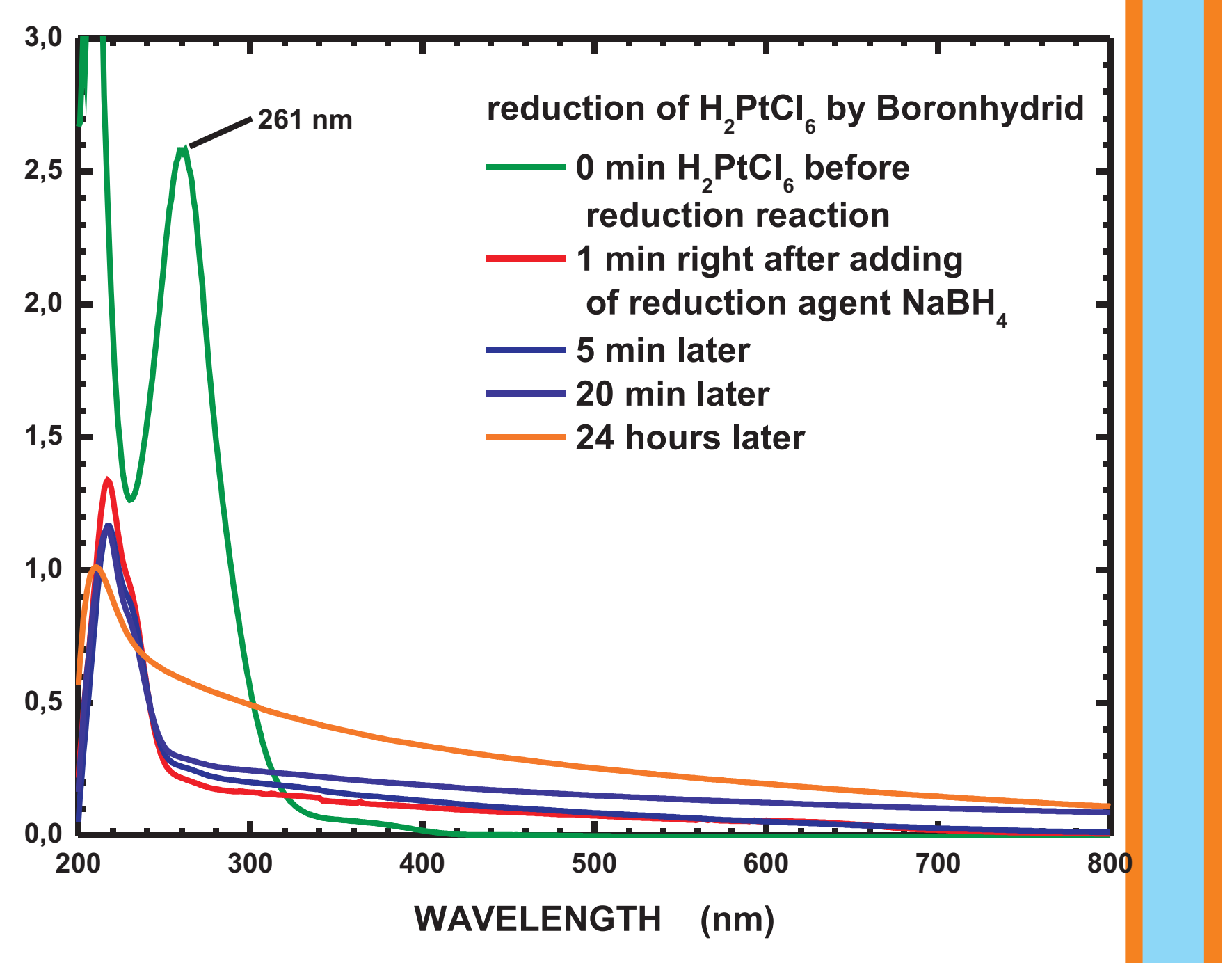
$PtCl_4^{2-} + 2CH_3OH \rightarrow Pt^0 + HCHO + 4H^+ + 4Cl^-$

Reaction with hydrazine

$PtCl_6^{2-} + N_2H_5OH \rightarrow Pt^0 + 4HCl + N_2 + H_2O + 2Cl^-$

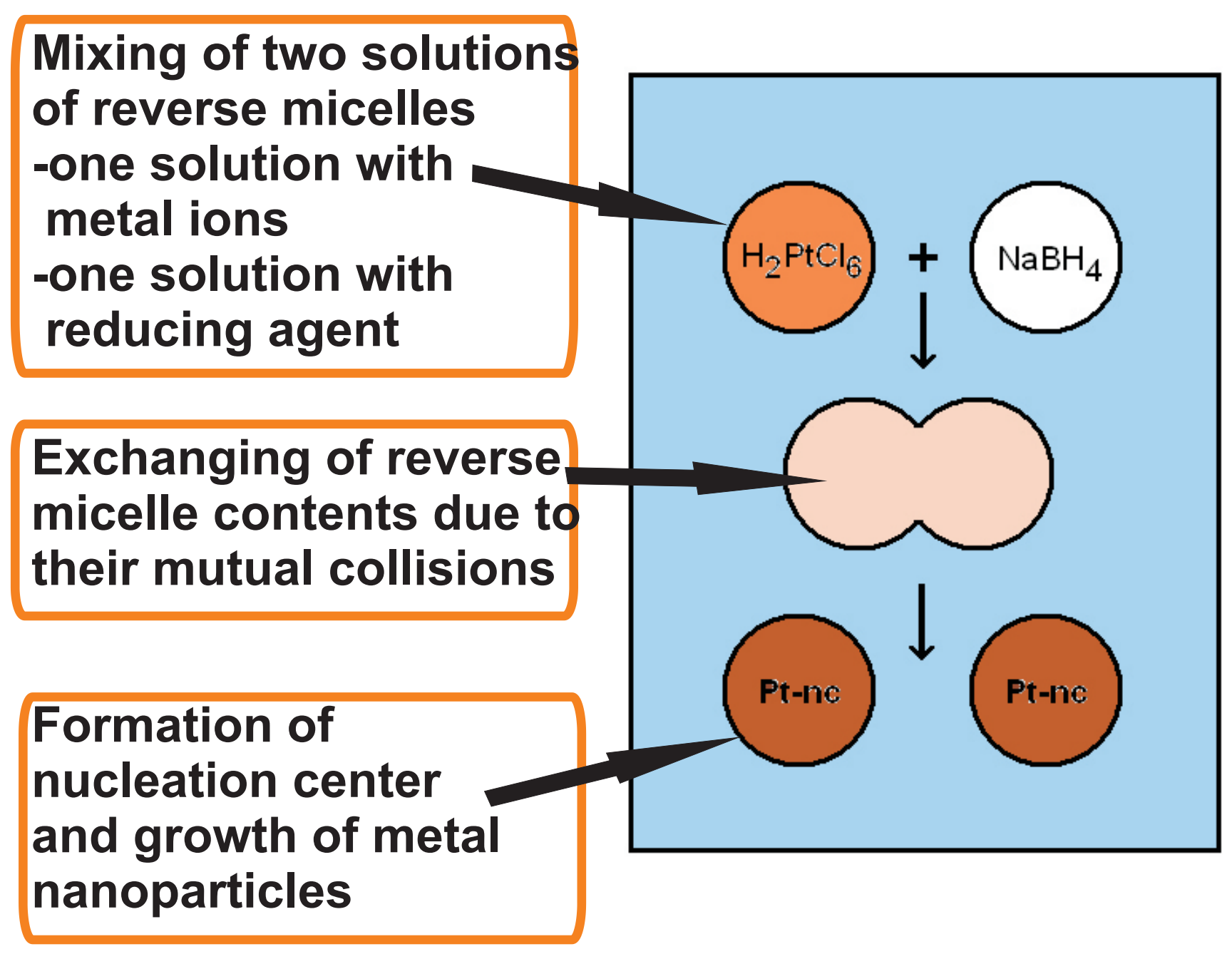
Reduction reaction is very fast, followed by nucleation and growth of nanoparticles. Stabilisation of colloidal solution is provided by citrate ions. Growth of palladium and platinum nanoparticles is connected with change of color of solution from colourless into brown.





Metal nanoparticles in water-in-oil microemulsiuons

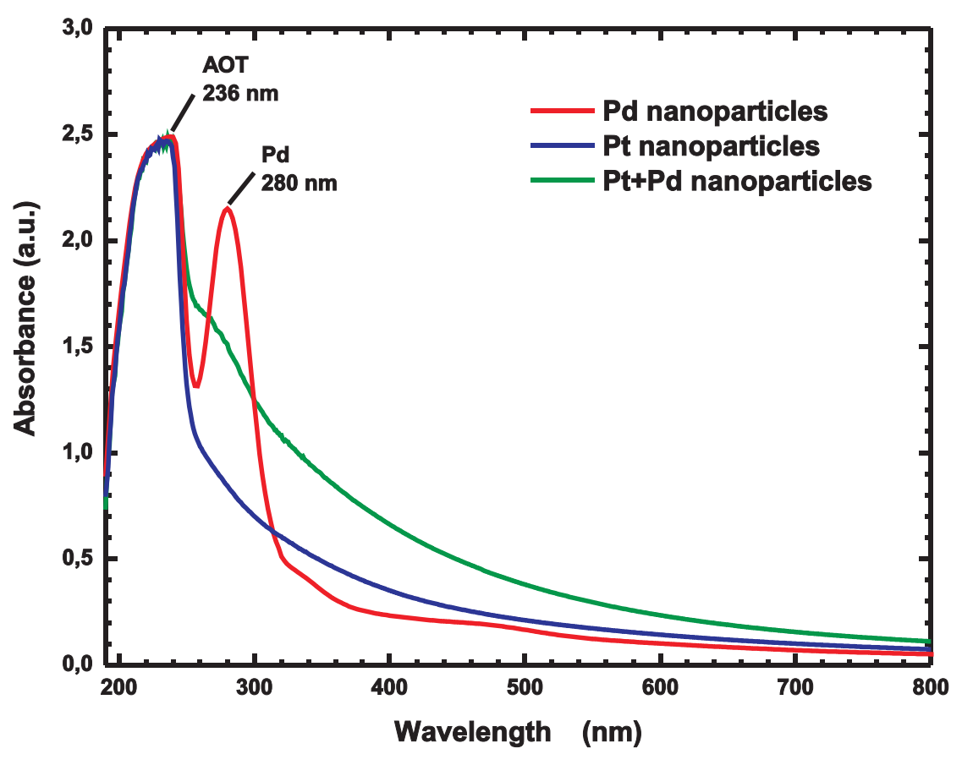
Reverse micelles: **surfactant AOT in isooctane** → diameter controlled and monodisperse metal nanoparticles

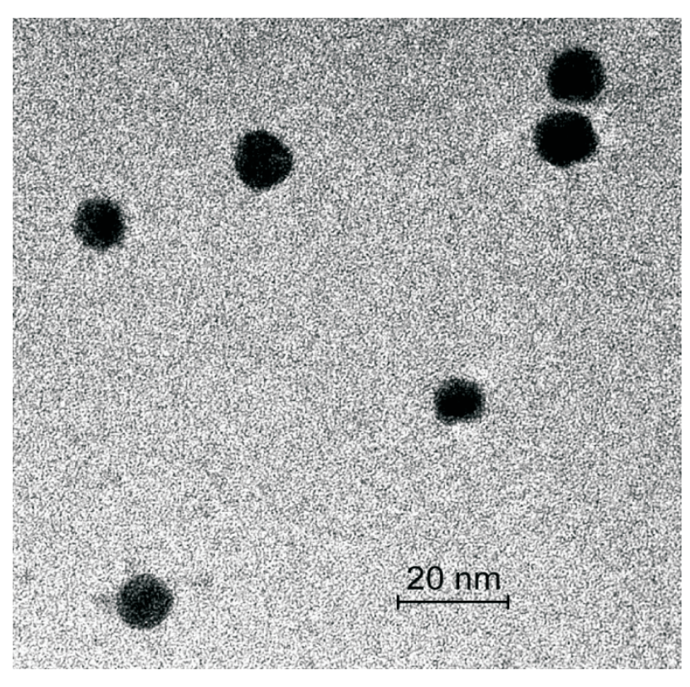


Mixing of two solutions of reverse micelles
-one solution with metal ions
-one solution with reducing agent

Exchanging of reverse micelle contents due to their mutual collisions

Formation of nucleation center and growth of metal nanoparticles





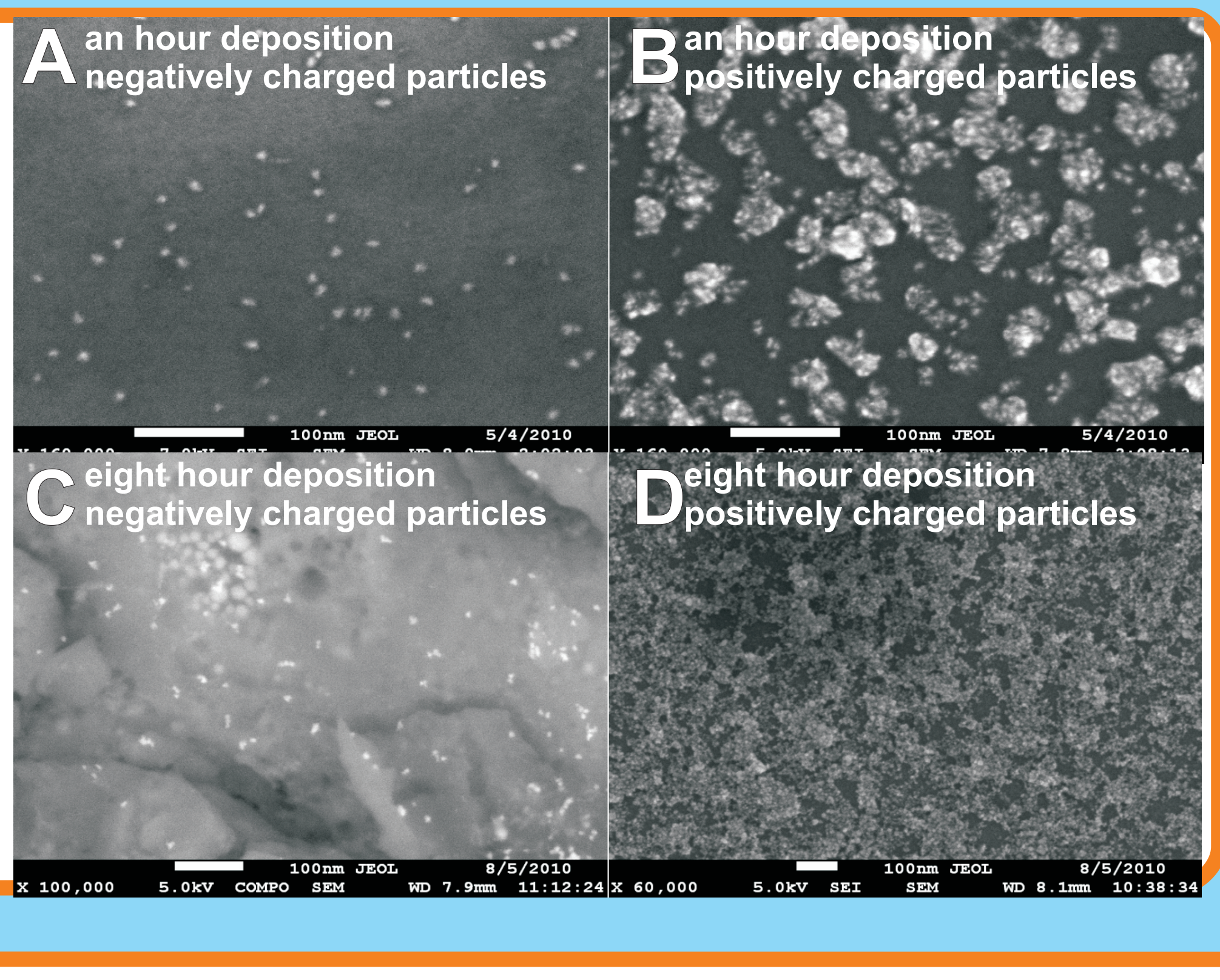
*The diameter of nanoparticles is **10 nm** when the ratio of molar concentrations of AOT and water content is equal to 5.*
*UV–VIS absorbtion spectra shows a peak at **280 nm due to plasmon absorbtion by palladium** particles and a peak at 220–240 nm due to AOT absorbtion.*

Electrophoretic deposition

two–electrode cell: semiconductor wafer is connected to one electrode, the cell is filled by microemulsion of metal nanoparticles in isooctane and the voltage in order of tens of volts is applied.

Pictures A and B show an hour deposition of Pt nanoparticles in AOT reverse micelles. The semiconductor wafer was conected to a positive electrode in the case of the pic. A and to a negative electrode in the case of the pic. B. It is clearly seen, that metal nanoparticles in solution are mostly positively charged.
Pictures C and D show eight hour deposition of Pt nanoparticles under same voltage polarity as pictures above. Longer deposition on negative electrode leads to higher coverage by metal nanoparticles whereas longer deposition on positive electrode leads to higher coverage by organic material from reverse micelle solution.

Situation B gives the best current–voltage characteristics and hydrogen sensitivity.


A an hour deposition negatively charged particles

B an hour deposition positively charged particles

C eight hour deposition negatively charged particles

D eight hour deposition positively charged particles

Current-Voltage characteristics

A potencial barrier arises at the interface of metal nanoparticle and semiconductor wafer. Current–voltage (IV) characteristics is given by thermionic–emission–difusion theory. Current density dependes on temperature, Schottky barrier height and voltage by equation

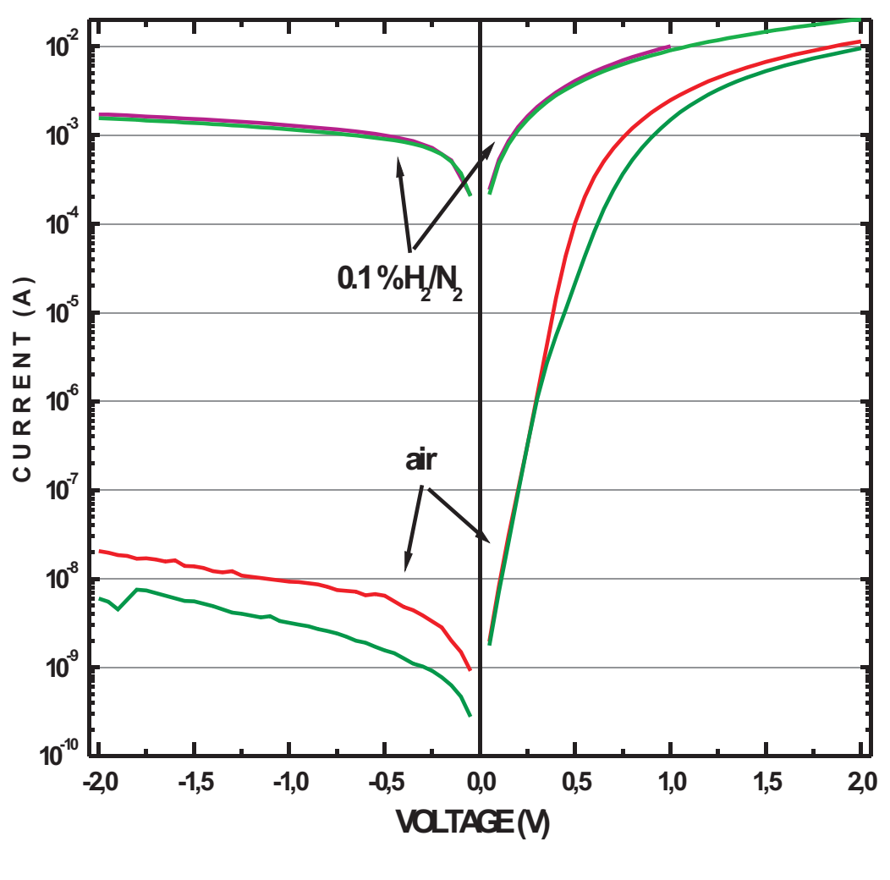
$$j(V) = A^{**}T^2 e^{-\frac{e\phi_B}{kT}}\left(e^{\frac{eV}{kT}} - 1\right)$$

Hydrogen detection

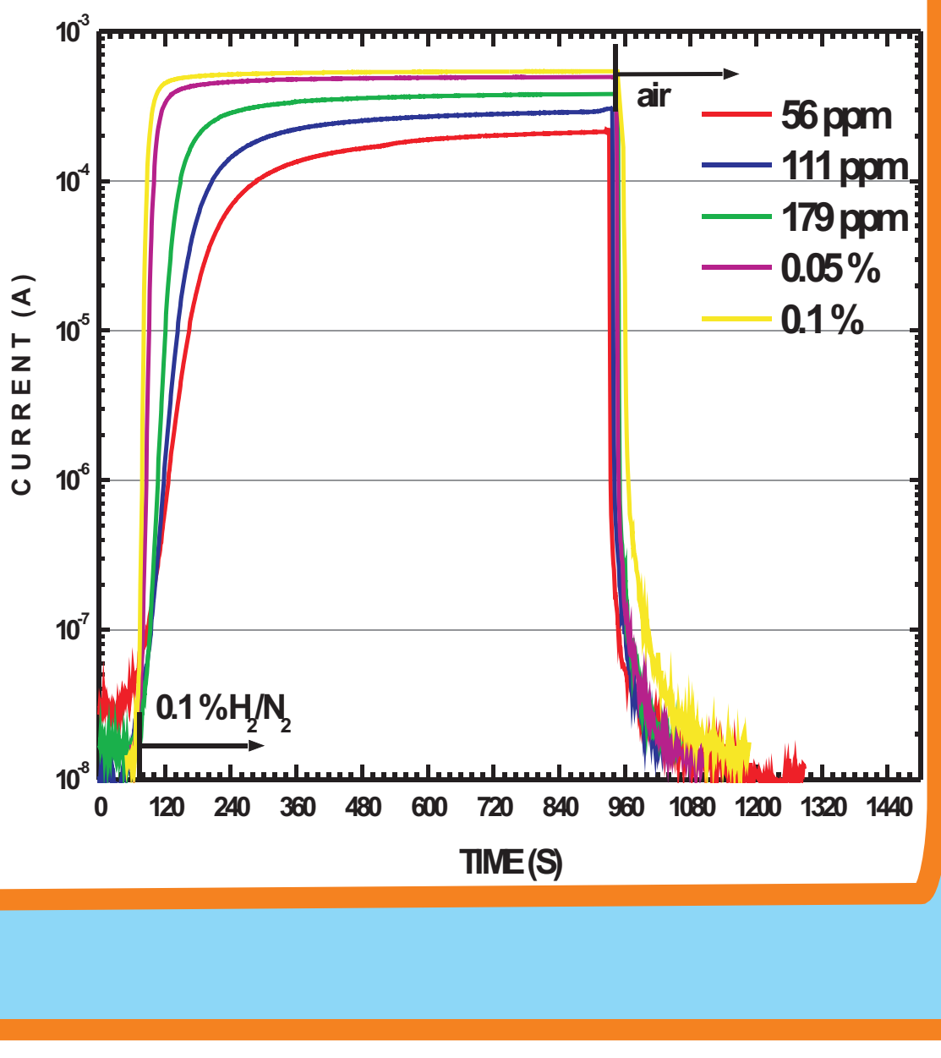
Hydrogen molecule is dissociated by the palladium or platinum nanoparticles, single hydrogen atoms are absorbing by nanoparticles. These hyrogen atoms get into nanoparticle–semiconductor interface and create a dipole layer which decreases the Schottky barrier height. The barrier decrease is measured as an increase in current.

Pt nanoparticles based structures

*Forward and reverse IV characteristics of two diodes on **GaN substrate** with a layer of platinum nanoparticles in air and hydrogen environment. Both diodes show good rectifying character in air ambience. The height of Schottky barier calculated from the forward current is **0.81 eV**.*

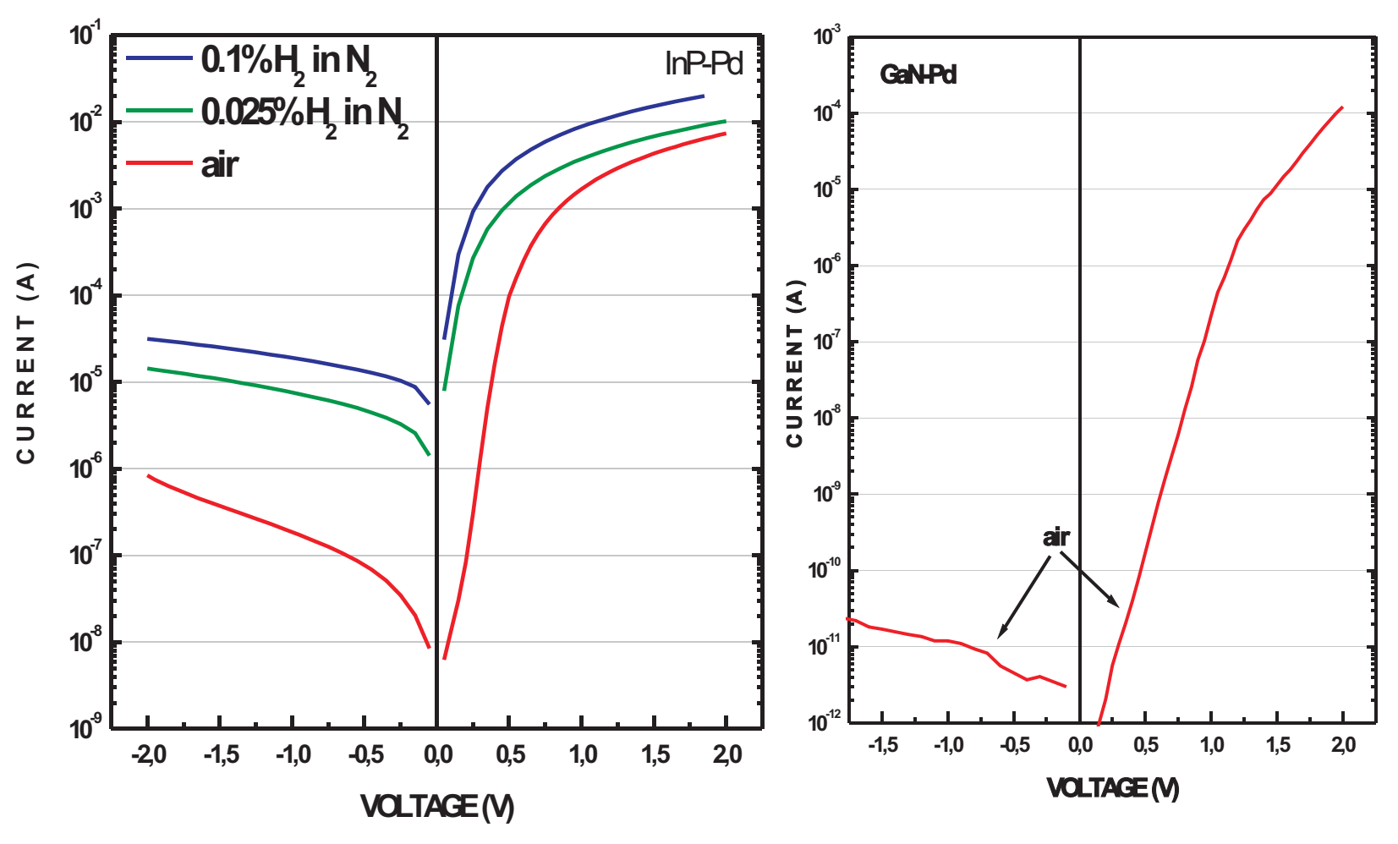


Current of a diode made on GaN with a layer of platinum nanoparticles as a function of time after opening and closing the flow of H_2/N_2 gas and air. The diode was forward biased with constant voltage 0.1 V. The current changed from 7.4 nA in the air ambient to 540 μA in the flow of 0.1 % of H_2 in N_2. The 50 % response time is equal to 37 s.

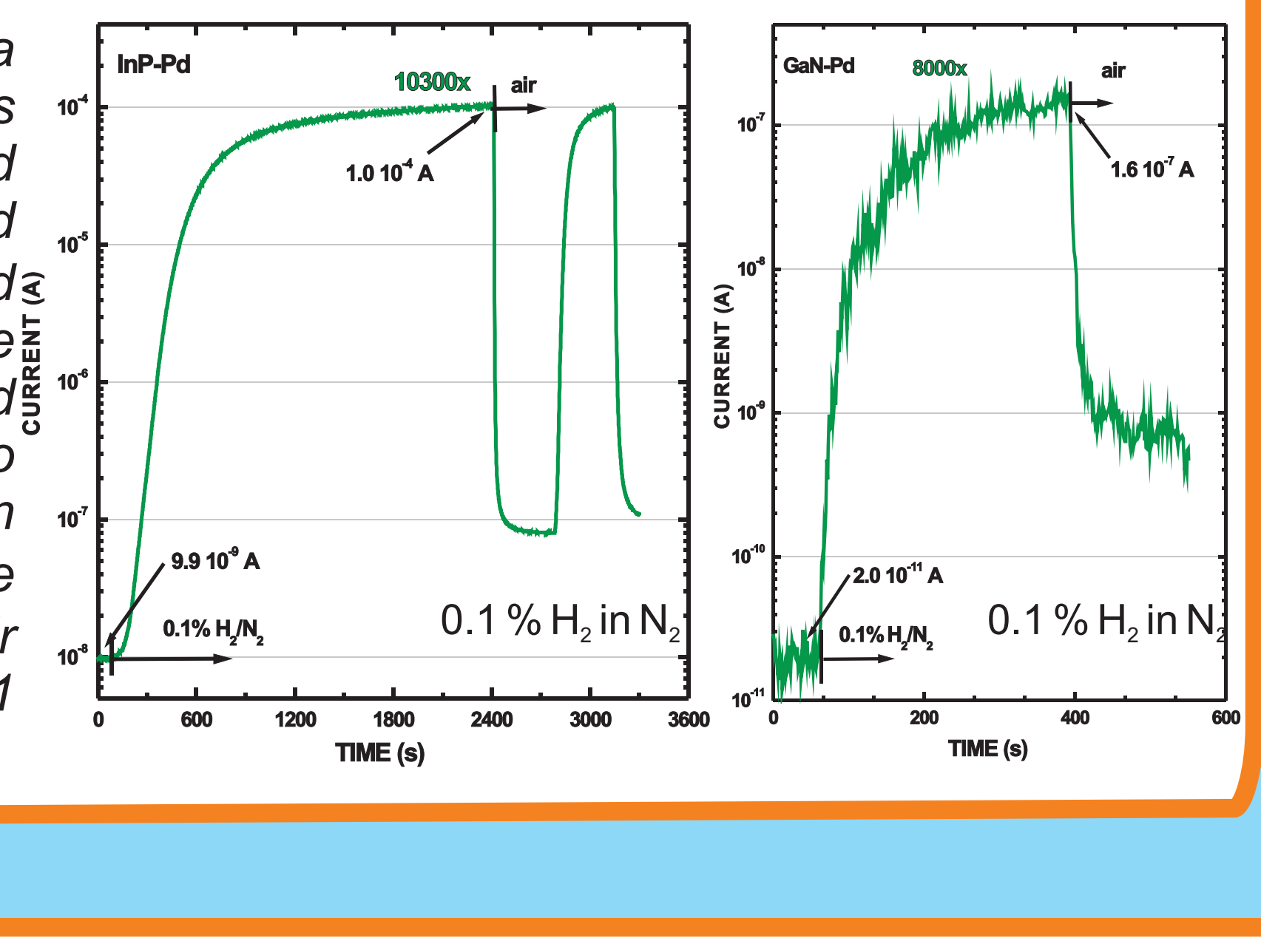


Pd nanoparticles based structures

*Forward and reverse IV characteristics of a diode fabricated on **InP** substrate (left diagram) and on **GaN** (right diagram) with a layer of palladium nanoparticles in air and hydrogen environment. Both diodes show good rectifying character both in air ambience and in hydrogen presence. The height of Schottky barier calculated from the forward current is **0.78 eV for InP–Pd** structure and **1.03 eV for GaN–Pd** structure.*

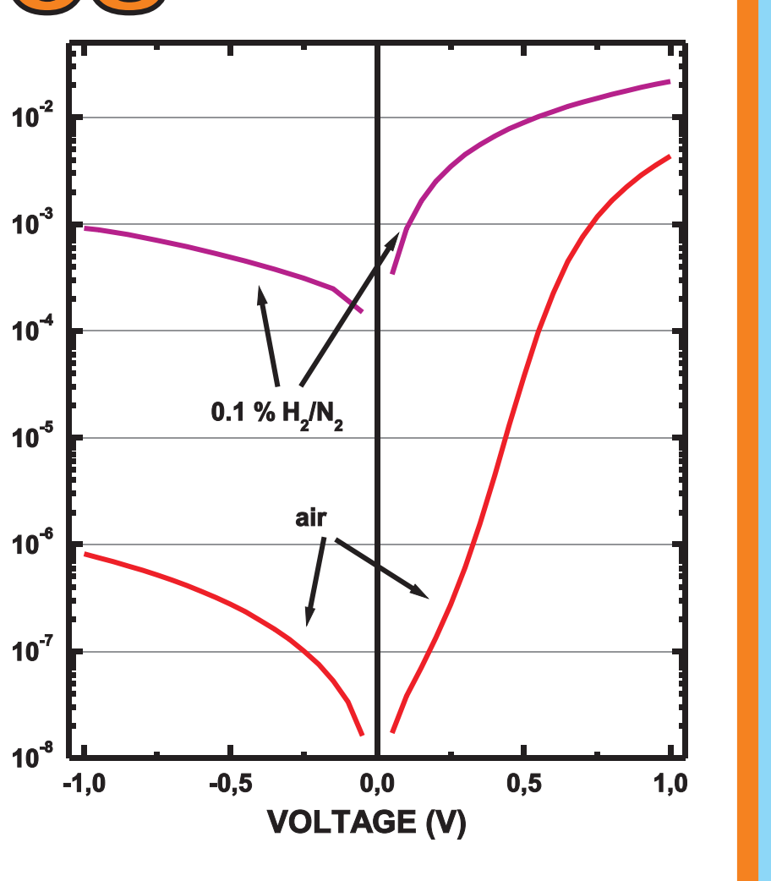


Current of a diode made on InP (left) and on GaN (right) with a layer of palladium nanoparticles as a function of time after opening and closing the flow of H_2/N_2 gas and air. Diodes were forward biased with constant voltage 0.1 V. The current of InP–Pd diode changed from 9.9 nA in the air ambient to 100 μA in the flow of 0.1 % of H_2 in N_2. The current of GaN–Pd diode changed from 20 pA in the air ambient to 160 nA in the flow of 0.1 % of H_2 in N_2.

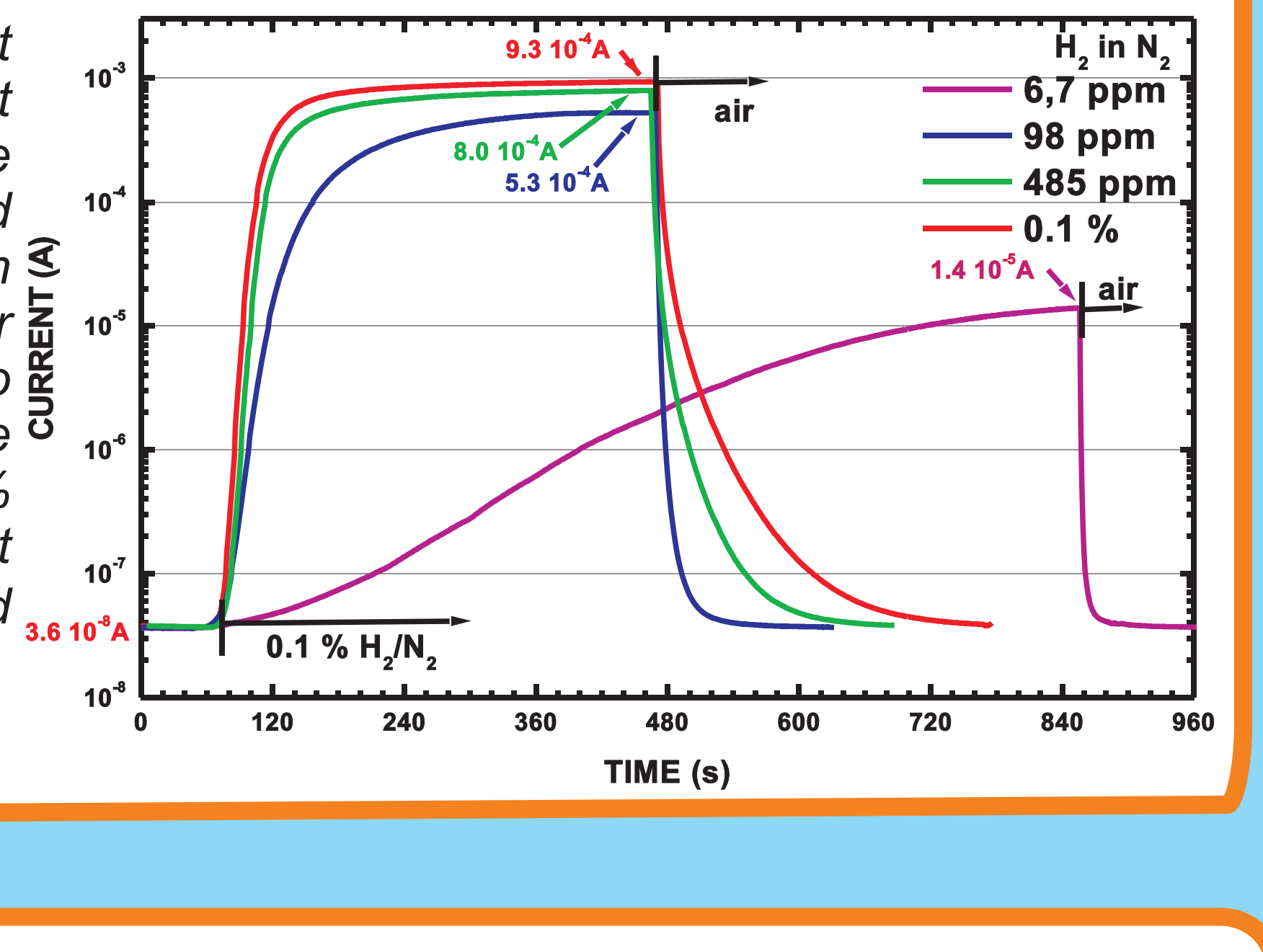


Pt/Pd nanoparticles based structures

*Forward and reverse IV characteristics of a diode fabricated on **InP** substrate with a layer of mixture of platinum and palladium nanoparticles in air and hydrogen environment. Diode shows good rectifying character in air ambience and low rectifying character in hydrogen presence. The height of Schottky barier calculated from the forward current in air is **0.76 eV**. Schottky barier height on the same type of diodeon **GaN** is **1.09 eV**.*



The current of InP–Pt diode changed from 36 nA in the air ambient to 930 μA in the flow of 0.1 % of H_2 in N_2 at 0.1 V forward bias.



Conclusions

- **Schottky diode structure based on layers of platinum and palladium nanoparticles deposited on InP and GaN semiconductor wafers were demonstrated**
- **Good rectyfying character of all structures, Schottky barrier heigher than 1.0 eV for GaN–Pd and GaN–PtPd structures**
- **Fast response time and big changes in current under the flow of 0.1 % H_2 in N_2**

Acknowledgement

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References

[1]H. I. Chen, Y. I. Chou and C. Y. Chu, Sens. Actuat. B85(2002) 10-18.
[2]Y. I. Chou, C. M. Chen, W. C. Liu and H. I. Chen, IEEE Electron Device Letters 26(2005) 62-65.
[3]K. Zdansky, P. Kacerovsky, J. Zavadil, J. Lorincik and A.Fojtik, Nanoscale Res.Lett. 2(2007) 450-455.