Catalytic activity of metallic nanoisland coatings.  
The influence of size effects on the recombination properties

O A Tomilina, V N Berzhansky, S V Tomilin, A N Shaposhnikov

1Research Centre of Functional Materials and Nanotechnologies, Physical-Technical Institute, Vernadsky Crimean Federal University, Crimea, Simferopol 295007, Russian Federation
2Experimental Physics Department, Physical-Technical Institute, Vernadsky Crimean Federal University, Crimea, Simferopol 295007, Russian Federation

Abstract. The results of investigations of the quantum-size effects influence on selective properties of heterogeneous nanocatalysts are presents. As etalon exothermic reaction was used the reaction of atomic hydrogen recombination. The nanostructured Pd and Pt films on Teflon substrate were used as a samples of heterogeneous nanocatalysts. It was shown that for nanoparticles with various sizes the catalytic activity has the periodic dependence. It has been found that for certain sizes of nanoparticles their catalytic activity is less than that of Teflon substrate.

1. Introduction
In ultra-small nanoparticles (< 10 nm) the structure of the electron and phonon spectrum is discrete due to the small number of atoms and the effect of spatial quantization of energy levels. These nanoparticles can’t be clearly identified as metals or semiconductors. They are called quantum dots [1,2]. For these nanoobjects the energy absorption for the excitation of new phonons or electron transitions occurs not in continuous range, but discrete – with certain portions (quants). In the case of optical radiation absorption this effect appeared in the form of the depression and peaks in the transmission (absorption) spectra. In the study of heterogeneous catalysis, this effect leads to a selectivity properties of the solid state catalysts in relation to reactions with various releases of energy. The goal of this work was to make comparative researches of catalytic properties of nanostructured metal films with different effective thicknesses which have obtained by thermal deposition.

2. Experimental technique
The samples were produced in the form of Pt and Pd nanostructured films, deposited on a teflon (poly-tetra-fluor-ethylene, PTFE) substrate. Before the deposition of the catalytically active coating, the substrates were treated with acetone, ethanol and were sustained at least a day in a vacuum (pressure of 10^-5 Torr). Samples were obtained by method of thermal vacuum deposition of metals. To make the nanostructured coatings the original deposition technique of the films with a gradient of thickness along its surface was used. Conditions and parameters of deposition are chosen in such a way to deliberately get the nanoislet coating (ultrasmall thickness of film, low deposition rate, non-wetting substrate). This technique allows one to obtain and research films with different effective thicknesses $h_{\text{eff}}$ (and structure) in a single technological cycle [3].
After deposition the sample in the area of thickness gradient was cut into 6 pieces of \(20 \times 6\) mm. The catalytic activity of nanostructured metallic films to the reaction of atomic hydrogen recombination was determined using a method of recombination sensor (figure 1). In this method the atomic hydrogen, which is produced by HF glow discharge, flows in the PTFE atom-pipes through catalyst into recombination sensor. As sensor a serial thermo-manometer transducer PMT-2 was used, in which the concentration of free H-radicals was determined calorimetrically.

![Figure 1](image)

**Figure 1.** Scheme of catalytic properties experimental investigation by method of recombination sensor. 1 – discharge tube, 2 – PTFE atom-pipe, 3 – thermo-manometer transducer PMT-2 (recombination sensor), 4 – etalon sensor, 5 – sample of bulk catalyst, 6 – sample of investigated nanocatalyst.

### 3. Results and discussion

Since the catalytic activity of nanostructured coating determines as the number of free radicals, entering to the sensor, should consider how the output data of sensor are associated with radicals concentration. Based on the experiment methodology, we can assume that the system at the moment of maximum heating of the sensors catalytically active Pt wire at small but finite times was in quasi-equilibrium thermodynamic state. On the basis of this assumption consider the following model.

The output data of the sensor is electromotive force (EMF) of thermocouple, which is connected to a platinum wire. Therefore, when the temperature of the wire is changed the changing of thermal electromotive force can be written as

\[
dU = \gamma(T) dT,
\]

where \(\gamma(T)\) – the proportionality factor of a specific sensor (not confused with thermal EMF coefficient), \(T\) – the temperature.

Then the total potential difference can be found by integrating the equation (1). The heat flow radiated from the heated wire is determined by the equation of heat transfer

\[
\dot{q} = -\vartheta(T) \cdot \text{grad}T,
\]

where \(\vartheta(T)\)– the coefficient of thermal conductivity.
At equilibrium conditions the heat flow from wire equals to the heat flow transferred to it. So accounted that the heat is transferred to wire by portions from radical recombination we can write

\[ q' = N_r E_0 \mu(T), \]  

where \( N_r \) – number of the recombination acts on unit of surface area per one unit time, \( E_0 \) – reaction energy in one recombination act, \( \mu(T) \)– coefficient of energy accommodation.

From [4] it is known that the surface recombination can be realized through two mechanisms: shock impact (by Ridil-Ili) and diffusion (by Langmuir-Hinshelwood). Then the total \( N_r \) can be defined as

\[ N_r = \sigma(T) j N + k(T) N^2, \]  

where \( \sigma(t) \) – the effective cross section of the recombination reaction by shock impact, \( j \) – density of free atoms flow, \( k(t) \) – the reaction rate constant by the Langmuir-Hinshelwood mechanism, \( N \) – the concentration of atoms adsorbed on the surface.

Let's take assume about the small changes of wire temperature (the coefficients which depends on the temperature let's considered as constant). Then from (1) - (4) by solving a quadratic equation we can obtain the approximate formula of the surface radicals concentration depending to sensor's EMF

\[ N = -\frac{\sigma j}{2} + \frac{1}{2} \left( \sigma^2 j^2 + 4 \frac{\partial^2 k}{\partial E_0 \partial \mu} \Delta U \right)^{1/2}, \]  

where \( \Delta U \) – the difference of output signals of the recombination and etalon sensors.

The surface concentration of radicals may also be determined from classical Langmuir adsorption theory. Therefore on condition of the thermodynamic equilibrium we have the equation for the partial pressure of radicals

\[ P = \frac{\beta(T) N}{\alpha(T)(N^* - N)}, \]  

where \( N^* \) – the surface concentration of adsorption centers, \( P \) – partial pressure of the radicals, \( \alpha(T) \) – adsorption coefficient, \( \beta(T) \) – desorption probability, and \( N \) described by (5)

Given that at relatively low partial pressure of the radicals \( N \gg N^* \) and concentration \( n \sim P \), it can be shown that

\[ n \sim \Delta U^{1/2}. \]  

Therefore for the possibility of carrying out a comparative analysis of the experimental results obtained for Pd and Pt the dimensionless relative measure of the catalytic activity was introduced

\[ \xi = \frac{n_k}{n} = \frac{n - n_d}{n} = \frac{\sqrt{\Delta U_0} - \sqrt{\Delta U_i}}{\sqrt{\Delta U_0}}, \]  

where \( n_k \) – the concentration of free radicals, which are lost during the recombination on the investigated nanocatalysts; \( n_d \) – the concentration of radicals, which determined by sensor; \( n = n_k + n_d \) – normalizing constant, defined as the concentration of radicals which get to the sensor after recombination on clean PTFE substrate without catalyst; \( \Delta U_0 \) – sensor’s EMF without catalyst; \( \Delta U_i \) – sensor’s EMF for \( i \)-th sample of nanocatalyst.
Figure 1 shows the dependence of the relative index of the catalytic activity from the effective thickness of the nanostructured films of Pd and Pt.

![Graph showing the dependence of the relative index of the catalytic activity from the effective thickness of the Pd and Pt films.](image)

Figure 2. The dependence of the relative index of the catalytic activity from the effective thickness $h_{eff}$ of the Pd and Pt nanostructured films.

As the figure shows the catalytic activity of the investigated coatings for different values of the effective thickness has an oscillation character. This dependence can be explained in the scopes of the band theory and the theory of lattice dynamics in stipulates of discrete type of electrons and phonons energy-spectra in the nanoparticles (quantum dots). Since the size of nanoislands is changing with $h_{eff}$ increase, respectively it energy spectra are changed to. This leads to oscillating changes in catalytic activity. This result is observed in the experiment.

Analysis of the dependencies in Figure 1 reveals the following patterns. Firstly, both graphics have a characteristic minimum, which indicates a low catalytic activity of nanostructured coatings. Secondly, both minima lie lower than the catalytic activity level of pure PTFE. Those catalytic inactive nanoparticles are filling the structural defects on the PTFE surface and it's modified surface with decreasing of its catalytic activity.

Also the figure shows that the essential difference of Pt and Pd catalytic activity observed only at relatively high values of $h_{eff}$ (about 45%). For small $h_{eff}$ the difference of Pt and Pd catalytic activity is decreasing (about 7.5%).

Conclusions
In was shown that the catalytic activity of nanostructured Pd and Pt films has an oscillatory character in depending on the effective thickness of coating (parameters of nanostructures). The catalytic activity of the individual nanostructures in some areas of gradient coatings is lower than the pure PTFE substrate. For large values of $h_{eff}$ the Pt catalytic activity (to the reaction of atomic H recombination) is almost an order of magnitude greater than the Pd catalytic activity. When the effective thickness is reduced the Pt catalytic activity is also significantly reduced and doesn't exceed the activity of Pd more than 50%.

Acknowledgments
This work is supported by the RF Ministry of Education and Science in the framework of the base part of the state task №2015 / 701 (project 3879) and the State Council of Republic Crimea in the framework of the grant for young scientists of the Crimea (resolution № п170-1/16 from 02.02.2016).

References
[1] Dubrovskii V G. 2006 Semiconductors 40 10 1153
[2] Eliseev A A, Lukashin A V. Functional materials / Ed. by Tretyakov Yu.D. Fizmatlit, 2010. 456p.
[3] Tomilin S V, Yanovsky A S. 2013 J. of Nano- and Electronic Physics 5 3 03014.
[4] Kharlamov V F. 1987. J. of Applied Spectroscopy 46 3 273.