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Size dependence of thermoelectric power of Au nanoclusters with rough and smooth surface deposited onto highly oriented pyrolytic graphite

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ABSTRACT

The paper presents the analysis of tunnel current–voltage characteristics of gold nanoclusters deposited onto the highly oriented pyrolytic graphite (HOPG) surface by pulsed laser deposition. An original technique is suggested which allows recovering of the thermoelectric power value of nanoclusters by analyzing their differential tunneling current–voltage characteristics. It was found that the value of the thermoelectric power of pulsed laser deposited Au nanoclusters decreases with decreasing of their size down to −60 μV/K for cluster's volume of 0.1 nm^3. At the same time the thermoelectric power value of thermal evaporated Au nanoclusters which have smooth surface does not reveal the size dependence for clusters with volume down to 0.5 nm^3. The analysis of the results and the possible causes of this behavior are discussed.

1. Introduction

The temperature gradient in solids causes diffusion of charge carriers from hot regions to cold ones. That leads to the formation of an electrical potential difference. The effect allows direct conversion of thermal energy into electrical one and vice versa. It is the perfect way to create quiet and environmentally friendly power generation technologies with no need of mechanical components. However, the main problem in developing thermoelectric generators is low thermoelectric efficiency of materials they are composed of [1,2]. Some attempts aimed to solve the problems resulted in sufficient improvement of thermoelectric figure of merit of bulk materials though were not good enough for practical purposes [1–4].

An advanced approach of creating high efficiency thermoelectric materials was the use of quantum effects in low-dimensional nanostructures [5,6]. The thermoelectric transport in atomic and molecular conductors and metal nanofilms has been extensively studied recently [7,5,8]. However, the main difficulty while caring out an experiments on measuring the thermoelectric properties of systems of nano-sized scale is the invasiveness of measurements. That means that the applied temperature gradient causes local changes near the contact and should be taken into account while calculating the final result. Furthermore, the electrical potential difference caused by the temperature gradient is very sensitive to the geometry of the contact. This fact leads to the appearance of dependence of the potential on the temperature gradient.

Moreover, the usual technique of measurement of thermoelectric power with the use of the applied temperature gradient may cause uncontrollable changes in physical and chemical properties of nanoobjects. This may lead to changes in sizes of nanoparticles, in phase state (liquid–solid transition) [9] or in appearance or smoothing of roughed surface, and may result in the phenomenon of electron localization [10].

Currently there are many experimental studies on the thermoelectric properties of various nanostructures (see e.g. [11–13]), which to some extent take into account the problems mentioned above. But the uncertainty of measured thermopower values remains big enough. In this way the task of thermoelectric properties of individual nanoobjects investigation is rather urgent. It should be noted that the possibilities of the scanning tunneling

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microscopy method for local recovering of thermopower value is currently under discussion (see e.g.[13]).

In this paper we present an original technique of recovery of thermoelectric power value of metal nanoclusters deposited on a surface of a conductive substrate. The technique is based on the analysis of tunnel current–voltage characteristics (*IV*-curves) obtained by scanning tunneling spectroscopy (STS). An advantage of this technique is the lack of necessity of temperature measurements and samples heating, as well as the possibility of local study of single nanoclusters formed on the surface of the conductive substrates.

The technique was applied to recover the thermoelectric power value of Au nanoclusters formed by a pulsed laser deposition technique (PLD) and thermal evaporation (TE) on the highly oriented pyrolytic graphite (HOPG) surface (0 0 0 1) at room temperature. It was found that the thermoelectric power decreases with decreasing of sizes of PLD nanoclusters so that thermoelectric power value of PLD nanoclusters with volume less than 1 nm^3 become negative. At the same time PLD clusters with volume of 10 nm^3 have the thermoelectric power value typical for bulk gold (1.94 μV/K at room temperature) and for clusters with volume of 0.1 nm^3 the thermoelectric power value is −60 μV/K that is 30 times greater in the absolute value compared with bulk gold. At the same time data obtained for TE nanoclusters showed no size dependence for volumes down to 0.5 nm^3. This behavior may be caused by different surface structure of PLD and TE Au nanoclusters, and therefore by different electronic properties.

2. Material and methods

The ensemble of PLD Au nanoclusters was prepared at the high vacuum conditions ($p \simeq 5 \cdot 10^{-10}$ Torr) on the HOPG surface at room temperature with the use of PLD technique implemented on the basis of XSAM-800 (Kratos) ultra high vacuum (UHV) spectrometer (the detailed description of the experimental technique can be found in [14]) For this purpose the radiation from a YAG:Nd^{3+} laser ($\lambda = 1.06$ μm) with energy $E = 80 \div 200$ mJ in the Q-switched regime ($\tau = 15$ ns) and a pulse repetition frequency of 25 Hz, which was focused on the Au target. The substrate (HOPG) was mounted at a distance of 5 cm from the laser in the direction of laser ablation plasma plume.

During the experiments, a series of Au/HOPG samples were obtained by PLD technique as a result of several single pulses of deposition with energy of 110 mJ and the amount of deposited Au $n \sim 1 \cdot 10^{14}$ cm^{-2}. The total amount of deposited material at a given geometry and energy of the laser radiation was determined by the number of laser pulses and measured *ex situ* by Rutherford backscattering (RBS) of He+ ions.

Samples obtained by the thermal deposition of equivalent amounts of gold on the surface of the HOPG (0 0 0 1) were also prepared for comparison. The rate of thermal deposition amounted to 10^{14} at./cm^2s.

The chemical composition of the HOPG surface and Au nanoparticles was controlled at the level of 0.1% by means of X-ray photoelectron spectroscopy in the UHV analysis chamber ($p \approx 5 \times 10^{-11}$ Torr) of the Multiprobe MXPS RM VT AFM-25 surface analysis system (Omicron). The size, shape and tunneling *IV*-curves of the nanoclusters were determined by the scanning tunneling microscope (STM). For this purpose, directly after the attestation of the chemical composition the sample was *in situ* moved into the probe microscopy chamber of UHV surface analysis system. STM images and *IV*-curves were obtained with the use of the platinum tip at the values of feedback current of $I_0 = 1$ nA and bias voltage of $V_0 = 0.1$ V.

3. Results

Sets of thirty tunneling *IV*-curves measured for PLD and TE nanoclusters and values of averaged differential tunnel conductance $\langle D \rangle = \langle \frac{V_0}{I_0} \frac{dI}{dV}|_{V=0} \rangle$ for gold nanoclusters of various sizes v are shown in Fig. 1(a–d). It can be seen that the tunneling *IV*-curves measured between the tip and Au nanoclusters are linear within the range $V/V_0 = -0.1 \div 0.1$. In addition, the differential tunneling conductance is sensitive to the size of the clusters in case of PLD nanoclusters (see Fig. 1(a and b)). It should be noted that such behavior is not observed for TE nanoclusters (see Fig. 1(c and d)).

The analysis of the set of tunnel *IV*-curves measured for nanoclusters allowed us to restore the dependence of the average differential tunneling conductance of nanoclusters on their volume (see Fig. 2). The choose of the volume for characterizing the size of nanoclusters was determined by the strongly irregular structure of nanoclusters formed by PLD on the substrate surface [15] that lowers the accuracy of linear size determination. In this case the volume as the parameter that characterizes the size of nanoclusters allows the correct comparison of tunnel *IV*-curves of PLD and TE nanoclusters.

As can be seen from Fig. 2 the magnitude of the differential tunneling conductance for PLD nanoclusters (squares) with the decrease of their volume shows the significant decrease, and reaches the values $\langle D \rangle \simeq 0.5$ for clusters with volume of $v \simeq 0.1$ nm^3. For TE nanoclusters (circles), however, this dependence remains constant over the entire range of the measured volumes of nanolusters, and coincides within the error with the values of the differential tunneling conductance for PLD clusters of large volumes ($v \simeq 10$ nm^3) when $\langle D \rangle \simeq 1$.

It should be noted that the presented dependence of the differential tunneling conductance obtained for PLD nanoclusters (see Fig. 2) is similar to the results obtained earlier [10]. In [10] the observed decrease of the differential tunneling conductance was explained in the framework of the mechanism of electron localization in gold nanoclusters with rough surface, which are formed in a strongly nonequilibrium conditions at the PLD [15]. It leads to a significant change in the density of electronic states near the Fermi level. At the same time the connection of the value of the electronic density of states at the Fermi level with thermoelectric power value and it's effects on the thermoelectric properties of smooth and rough shaped nanoclusters were not discussed. Therefore, before starting the discussion of the results obtained in terms of the thermoelectric properties of single nanoclusters with smooth and rough surface let us discuss the essence of the proposed method of thermoelectric power value recovery of metal nanoclusters deposited on the substrate surface.

4. Theory

The differential tunneling conductance of metallic samples measured by STS technique depends on the density of the electronic states $(dI/dV)(V) = A\rho_s(E)$ [16] and therefore contains information on the qualitative behavior of $\rho_s(E)$ of the sample. For the ideal Fermi gas in low temperature approximation ($kT \ll E_F$) the differential tunneling conductance of a cluster can be expressed in the form [16,17]

$$\frac{dI}{dV}(V, \vec{r}) = \frac{eI_0 \rho_t(E_f)\rho_s(\vec{r}, E_f - eV)}{\int_{E_f - eV_0}^{E_f} \rho_t(E)\rho_s(\vec{r}, E - eV_0)\, dE}. \quad (1)$$

Here $\rho_t(E + eV)$ and $\rho_s(\vec{r}, E)$ are the density of the electronic states of the tip and a cluster at point $\vec{r}$, respectively; I_0 and V_0—feedback current and voltage at a constant interaction mode, respectively ($eV_0 = 0.1$ eV). Eq. (1) is valid for free electron gas at low temperatures $kT \ll E_f$ and low voltages $eV \ll E_f$. All experiments were carried