Concentration of nano-sized objects in plasma-chemical material: estimation by tunnel resonance method

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Abstract. A new tunnel resonance method to estimate the concentration of nano-sized objects in the product obtained by plasma-chemical synthesis compared to pure fullerene is proposed. We have complied tunnel resonant structure (TRS) which includes two barrier layers (silicon oxide and silicon monoxide) with nanosized particles layer between them, placed on the surface of silicon plate and covered by copper layer. The obtained TRS is connected to power supply circuit, current recorder and voltage register. Based on measured current-voltage characteristic the local current maxima and resonant potentials have been determined. The concentration of nano-sized objects in the synthesis products was estimated from the current amplitude for the corresponding resonant potentials. The article provides theoretical substantiation of the proposed methodology and considers its practical implementation.

1. Introduction
Examining nanomaterials properties is directly related to the structure of nano-sized objects, so-called, size quantization effect, when the spectrum energy of elementary excitations is discrete and depends on structure shape and size. These energy characteristics can be considered as detection parameters [1]. The energy spectra can be determined using multilayer tunnel-resonant structures (TRS) with layer thicknesses of 1...10 nm, where the wave nature of charge carriers manifests itself. In particular, it becomes possible to observe resonant tunnelling of electrons through a system of potential wells and barriers.

Sizequantization effects to identify manufactured metal oxide nanostructures has been demonstrated in food and environment [2, 3]. Later, it has been shown that size quantization effect depends on the form and size of metal nano-sized objects [4].

The paper aims to develop the method for detecting and estimating the concentration of carbon nano-sized objects in the products produced by plasma-chemical synthesis.

2. Experimental part
To achieve the goal a TRS consisting of two layers of dielectric material forming two energy barriers was used. There was a quantum well from nano-sized objects between dielectric layers. Outside the structure we had injector copper layers and doped silicon n+-type. When an external voltage was applied to the TRS, the quantum well was under the action of an electric field, which changed the shape of the barrier and the position of the energy levels in the quantum well. In the case of coincidence of the electrons energy with the energy of stable energy level, resonant tunneling of electrons occurred through this level.
At the first stage we synthesized materials containing carbon nano-sized objects by plasma-chemical method on a plasmatron UPU-8M (RPO Elektromekhanika, Taganrog, Russian Federation): plasma-forming gas was argon, flow rate $\sim 50$ L-min$^{-1}$, the voltage on the electrodes $-50$ V, the current strength $-300$ A. The objects less than 10 nanometres in size were separated from the obtained product by ultracentrifugation ($5000r/min$, 5 min) on a Centrifuge Sorvall Lynx 6000 (Thermo Scientific, Finland) prior to nano-sized objects detection by a scanning electron microscope [5, 6].

At the second stage we formed a measuring cell presenting a multi-layered structure formed by thin-film technology ($+$) (figure 1).

![Figure 1](image.png)

**Figure 1.** Measuring cell used for the quantum characteristics measurement: 1 – silicon substrate; 2, 4 – layers of silicon oxide; 3 – nanosized objects; 5, 8 – pads; 6, 7 – ohmic contacts; 9 – insulating sealant.

From a silicon wafer (YTV466, Yutai Optics, China) we cut a piece off ($50$ mm$^2$) with a diamond device Almaz-M (SORENG, Russian Federation) (1, figure 1). Then a SiO$_2$ layer with thickness of 50 nm (2 and 4 on figure 1) was deposited on the prepared surface substrate (2, figure 1) by thermal oxidation in an atmospheric pressure reactor at $900$ C$^0$ during 50 minutes. Thickness control was carried out on a laser ellipsometric microscope LEM-2 (Instrument-Making Plant, Ukraine). Then we put 5 mg of nano-sized objects on SiO$_2$ surface (3, figure 1). After we dispersed the sample in the 150 ml of hexane-toluene mixture (weight ratio hexane:toluene = 95:5) to release pure fullerene (C$_{60}$). Obtained C$_{60}$ liquid was dispersed in closed vacuum space and besieged on the surface of the first barrier layer (3, figure 1) at $70 \, ^\circ C$. The time of fullerene release was established experimentally: we needed to form the quantum-dimensional layer (3, figure 1) from the analysed sample with thickness causing size quantization effect $-10$ nm layer was formed during 20 seconds. The layer thickness was controlled on an interferometer MII-4 (AO LOMO, Russian Federation). Drying of measuring cell was carried out at 100 C$^0$ within 10 minutes. Later on the SiO$_2$ layer (4, figure 1) – material identical to dielectric material of layer (2, figure 1) was applied on the created layer of fullerene (C$_{60}$) on vacuum deposition unit UVN-71P (SORENG, Russian Federation). Then on the surface copper layer ($2 \, \mu m$, position 5 on figure 1) was applied by thermal sputtering in vacuum.

Further on, in fluoric acid, the etching of 30% of a sample to the first silicon layer was made to form the "window" for the second contact. Finally, the metal copper layer was applied on semiconductor surface cleared of oxide by thermal sputtering in vacuum.

Thus, in measuring cell (figure 1) we obtained the dielectric layer containing fullerene dispersion (position 3 on figure 1) forming the quantum well with the range of energy levels corresponding to nanomaterial structure.
At the same time we made a measuring cells with pure fullerene instead of plasma-chemical material. We used the fullerene of 99% purity supplied by High Technology industry Co (St. Petersburg, Russian Federation).

At the last stage we examined current-voltage characteristics (CVCs) by voltmetr B7-72 (MNPI, Belatus). Based on the measured resonance peaks we identified resonance potentials at which a sharp current increase and a maximum \( I \) and a background \( I_0 \) current value was observed. After data processing, we developed the curve excluding the random components and the noise in the coordinates voltage-current.

The simplest example of TRS is a two-barrier tunnel-resonant diode which is an example of a two-barrier heterostructure with the quantum well (figure 2a and 2b).

The structure consists of two layers of dielectric material creating two energy barriers (figure 2a, area 1 and 2). Between the layers of dielectric, the quantum well 3 is located of the layer of the nano-sized objects creating the set of steady energy levels with energy of \( E_1, E_2, ..., E_n \) is located. From outer sides of heterostructure injector layers 4 and 5 of copper and the alloyed n+ silicon is located.

Exposed to electric field TRS barrier shape changed. When applied voltage was not enough (figure 2a), and the energy of electrons in layer 4 was less than the steady-state energy levels of \( E_1, E_2, ..., E_n \), the current flowing in the structure was equal to the current over the barrier. When the electron energy coincided with the energy of a stable energy level, there was a resonance tunnelling of electrons through this level (figure 2b).

With an increase in the external voltage, the electron energy coincides with the energy of stable energy levels \( E_1, E_2, ..., E_n \) and several resonance values of the current were observed in accordance with the stable energy levels.

The heterostructure was affected by the voltage \( U \) which for simplicity we considered falling only on barriers attached to the diode (the positive pole of the source was attached to the right contact). Then we calculated \( J \) current density in the negative direction of the axis \( z \). As it was clear from the drawing, only the electrons falling from the emitter could pass through resonant level, therefore we neglected the current of electrons from the collector. Then the current density for tunnel resonant diode with one stable energy level was equal to [7]:

\[
J_r(U) = \frac{em^*kT^3}{2\pi^2\hbar^3} \int_0^\infty |D|^2 \ln \left( \frac{1 + e^{\frac{\mu-E}{kT}}}{1 + e^{\frac{\mu-E-eV_c}{kT}}} \right) dE,
\]

(1)
where $J_R(U)$ was the density of tunnel-resonant current; $e$ – electron charge; $m^*_n$ – the effective electron mass; $\mu$ – the Fermi level measured from the bottom of the conduction band of $n^+$ areas; $E$ – electron; $|D|^2$ – coefficient of TRS transparency; $W$ – height of potential barriers; $T$ – temperature; $V_i$ – voltage drop on the first barrier; $U$ – voltage value at the resonant current flow.

Further, $eV_1$ value was determined to establish the energy distance between the two neighbouring levels in the quantum well:

$$\frac{2\pi^2 h^3}{e m^*_n k T |D|^2} \frac{dJ_R(U)}{dE} = \ln \left( 1 + e^{\frac{E_j-E}{kT}} \right) - \ln \left( 1 + e^{\frac{E_j-E-eV_1}{kT}} \right),$$

from which we obtained:

$$\exp \left( \frac{2\pi^2 h^3}{e m^*_n k T |D|^2} \frac{dJ_R(U)}{dE} \right) = \exp \left( \frac{\mu-E}{kT} \right) - \exp \left( \frac{E_F-E-eV_1}{kT} \right).$$

Then the expressions were compared under the exponent sign, multiply both expressions by $kT$ via equation (4):

$$eV_1 = \frac{2\pi^2 h^3}{e m^*_n k T |D|^2} \frac{dJ_R(U)}{dE}.$$  \hspace{1cm}

The equation for two-barrier TRS equation (1) was transformed where the quantum well was characterized by nano-sized objects. In this case the number of stable energy levels corresponded to type of nano-sized objects:

$$J_R(U) = \sum_{i=1}^{n} \frac{e m^*_n k T}{2\pi^2 h^3} S |D|^2 \int_0^W \ln \left( 1 + e^{\frac{E_j-E}{kT}} \right) dE$$

where $n$ was the number of stable energy levels; $|D|^2$ – considered a constant for each stable level; $S$ – area of structure; $E_j$ was the Fermi level before the first barrier. We considered that its position did not change under the influence of external electric field; after the second barrier a lowering of the Fermi level on energy $E_i$ occurred, $E_i$ – the energy value of stable energy level in relation to $E_F$ in the absence of external voltage (figures 2a and 2b).

Energy $E_i$ depended on the material of quantum well and barriers and on the geometrical characteristics of quantum well:

$$E_i = \frac{(U-U_k)e}{1 + \sqrt{\frac{\mu_1 \varepsilon_1 L_1^2}{\mu_2 \varepsilon_2 L_2^2}}}$$

where $U$ was the voltage value in resonant current flow calculated experimentally, $U_k$ – the voltage drops across the contacts (here $U_k=0.1...0.2$); $\mu_1$, $\mu_2$ – electron mobility in the conduction band of the barriers (referenced data); $\varepsilon_1$, $\varepsilon_2$ – relative permittivity of barrier material (referenced data); $L_1$, $L_2$ – barriers width.

3. Results and discussion

Using the technology described in the paragraph 2 (figure 1) 3 tunnel-resonant structures were developed. The first tunnel-resonant structure (figure 1) was developed without the 3rd layer. It served to determine the basic CVC according to which the resonance peak values were measured. In the second tunnel-resonant structure the 3rd layer was formed from the C_{60} fullerenes (C_{60}-TRS). In the third tunnel-resonant structure the 3rd layer was formed from plasma-chemical material with nano-
sized objects (PCM-TRS). Then the CVC of these TRS were determined, and we built CVCs presented in the figure 3 and 4.

There are no resonance peaks in the CVC of TRS without nano-objects (figure 3 and 4, curve 2). It indicates that the resonance peaks C60-TRS (figure 3, curve 1) and the resonance peaks PCM-TRS (figure 4, curve 2) are caused just by the presence of nano-objects in the 3rd layer (figure 1).

Based on the obtained CVCs we have determined the values of tension $U_1, U_2, ..., U_{13}$ (figure 3) at resonant current. Using equation (4) and (6) we have calculated the energy values on the barrier $E_i$ for each $U$ and the energy of stable levels in the quantum well $eV_1$ (table 1).

In figure 3 we have 13 resonant peaks ($U_1 - U_{13}$, table1), in figure 4 we have only 5 peaks corresponding to the values of the voltage $U_6, U_8, U_{11}, U_{12}, U_{13}$ (table 3). This means that in nanosized objects from in plasma-chemical material, there are nanosized objects other than the C60.

**Table 1.** Resonance voltages and the corresponding energy changes on the barrier

| Peak on figure 3 | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $U_i, V$         | 0.39| 1.14| 1.95| 2.56| 3.11| 3.71| 4.72| 5.29| 5.81| 6.44| 7.89| 8.60| 9.09|
| $eV_1$           | 0.04| 0.42| 0.82| 1.13| 1.40| 1.70| 2.21| 2.49| 2.75| 3.07| 3.79| 4.15| 4.39|

Using the values of $eV_1$ table 1 we calculated (eq. 5) current density values $J_i$ (table 2) for each resonance peak on the supposition that the area occupied by nano-sized objects is equal to the area of TRS.

**Table 2.** Current density values $J_i$ for each peak of the analysed nano-sized objects in plasma-chemical material

| Peak on figure 4 | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $eV_i$           | 0.04| 0.42| 0.82| 1.13| 1.40| 1.70| 2.21| 2.49| 2.75| 3.07| 3.79| 4.15| 4.39|
| $J_i, A/m^2$     | 4.4 | 9.8 | 4.0 | 6.0 | 17.8| 8.2 | 8.4 | 11.8| 8.4 | 10.6| 16.4| 13.2| 10.6|
As a result, based on the values of table 2, we constructed figure 5 with the resonant peaks of all nano-sized objects in plasma-chemical material, and having size quantization effects.

Dimensional quantization effect allowed us to calculate the energy values ($eV$, figure 5) under which resonance tunneling occurs for all nano-sized objects located in the 3rd layer (figure 1) of PCM-TRS. Now we can identify the different types of nano-sized objects by their energy values. As it is shown in the formula 5, the current density value ($J$, figure 5) depends on the area occupied by nano-sized objects. It allows us to estimate the number of nano-sized objects located in the 3rd layer of PCM-TRS. So, the dependency graph $eV$-$J$ (figure 5, table 2) gives a visual representation of quantitative and qualitative characteristics of nano-sized objects located in the 3rd layer of PCM-TRS.

To identify the types of nano-objects it is necessary to calculate the dependencies $eV$-$J$ for the already identified, pure nano-sized objects. Let's calculate such dependencies for C$_{60}$ fullerenes. For this purpose, we analyzed the CVC C$_{60}$-TRS (figure 4).

We determined the voltage values $U'_6, U'_8, U'_{11}, U'_{12}, U'_{13}$, with a resonant current flow (figure 4). According to the eq.(6) calculated the energy values on the barrier $E_i$ for each $U'$, and sustainable energy levels in a quantum well $eV'_1$ (table 3).

![Figure 5. The dependence of current density for the investigated nano-sized objects in plasma-chemical material on energy change on the barrier (PCM-TRS).](image)

**Table 3.** Resonance voltages and corresponding energies on the barrier for test-object.

| Peak on figure 5 | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $U', V$          | -   | -   | -   | -   | 3.71 | 5.29 | -   | -   | 7.89 | 8.60 | 9.09 |
| $eV'_1$          | -   | -   | -   | -   | 1.70 | 2.49 | -   | -   | 3.79 | 4.15 | 4.39 |

The table 3 shows that the voltage values $U$ and $U'$ (with the numbers 6, 8, 11, 12 and 13) coincide. It indicates that the 3rd layer of PCM-TRS contains the same nano-sized objects as the 3rd layer of C$_{60}$-TRS, i.e. C$_{60}$ fullerenes.

Using the values of $eV'_1$ table 3 we calculated the current density values $J_2$ (eq. 5, table 4) for resonance peaks with a maximum amplitude, on the supposition that the area occupied by C$_{60}$ equal to the area of tunnel-resonant structure.
Figure 6. The dependence of current density for the investigated test-object \((C_{60})\) on energy change on the barrier \((C_{60}-\text{TRS})\).

Table 4. Current density values \(J_2\) for maximum peaks test-object

| Peak on figure 6 | 6  | 8  | 11 | 12 | 13 |
|------------------|----|----|----|----|----|
| \(eV_1\)         | 1.70 | 2.49 | 3.79 | 4.15 | 4.39 |
| \(J_2, A/m^2\)   | 15.4 | 23.0 | 28.4 | 26.0 | 20.2 |

The dependency graph \(eV-J\) for \(C_{60}-\text{TRS}\) shows that the pure \(C_{60}\) fullerene has 5 resonance peaks (figure 6). The current density reaches its maximum value in the chosen area of \(C_{60}-\text{TRS}\) (table 4); it allows us to determine the quantitative content of \(C_{60}\) fullerene in the 3rd layer of PCM-TRS, because the \(C_{60}-\text{TRS}\) and PCM-TRS are equal in space.

According to eq. 5 the magnitude of the current density depends on the area occupied by nano-sized objects in the tunnel-resonant structure. Comparing the maximum current density values for the plasma-chemical product and pure fullerene use as nano-sized object \(C_{60}\) we made a quantitative evaluation of nanoobject content in the test product (table 5).

Table 5. Comparison of current density values for the investigated sample and test object

| Peak on figure 6 | 6  | 8  | 11 | 12 | 13 |
|------------------|----|----|----|----|----|
| \(J_1, A/m^2\)   | 8.2 | 11.8 | 16.4 | 13.2 | 10.6 |
| \(J_2, A/m^2\)   | 15.4 | 23.0 | 28.4 | 26.0 | 20.2 |
| \(J_1/J_2\)      | 0.53 | 0.51 | 0.58 | 0.51 | 0.52 |

We assumed that the nano-sized objects occupy the entire area of the TRS, hence the ratio of the current densities depending on the area of the TRS is proportional to the ratio of the concentration of nano-sized objects. Consequently, the \(C_{60}\) concentration in the synthesis products is approximately half the \(C_{60}\) concentration in the test volume \((J_1/J_2\approx0.5,\) table 5).

Taking the concentration of \(C_{60}\) in the test-object for 100% we concluded that the analyzed nano-sized objects in plasma-chemical material contains about 50% of nano-sized objects \(C_{60}\). Considering the fact that after separation of nano-sized objects by the method of ultracentrifugation with a size of less than 50 nanometers, we obtained 12.7% of the mass fraction, we came to the conclusion that the product of plasma-chemical synthesis contains about 6% of nanostructured objects corresponding to the nano-sized object \(C_{60}\).
Conclusion
A new tunnel resonance method to identify and estimate the concentration of nano-sized objects in a product obtained by plasma-chemical synthesis compared to pure fullerene is proposed. We have compiled tunnel resonant structure (TRS) which includes two barrier layers (silicon oxide and silicon monoxide) with nanosized particles layer between them, placed on the surface of silicon plate and covered by copper layer. The developed TRS is connected to power supply unit, current registrar and voltage. Varying the voltage on tunnel-resonant structure from 0 V to 10 V we measure the current and voltage values according to which the current-voltage characteristic is developed. Then according to current-voltage characteristic we have defined the local maxima of current and fix the corresponding resonant potential values according to which we identify the concentration of nano-sized objects in the layer.

The mathematical description of quantum and physical processes in the created TRS allowed the authors to model the mechanism of nano-sized objects in fluence on current-voltage characteristics, to identify and estimate the concentration of nano-sized objects in the products of plasma-chemical synthesis.

Using the database of resonant potentials and the current amplitude for the corresponding resonant potentials we make a quantitative assessment of nanosized object content in synthesis products.

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