Resonant tunnelling through individual Au nanoclusters embedded in ultrathin SiO₂ films studied by Tunnelling AFM

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Abstract. The observation of the resonant electron tunnelling through the individual Au nanoclusters (NCs) embedded in the ultrathin (4–5 nm thick) SiO₂ films on n-Si(001) substrates by Tunnelling Atomic Force Microscopy (TUNA) at 300K is reported. The nanocomposite SiO₂:NC-Au structures with Au NCs 3–7 nm in lateral size and 1–2 nm in thickness were formed by Pulsed Laser Deposition (PLD). The spots of increased probe current (or the current channels) on the sample surface 3–10 nm in diameter attributed to the electron tunnelling through the individual Au NCs have been observed. The I—V curves of the probe-to-sample contact measured in the current channels having larger (5–10 nm) size exhibited Coulomb staircase while those measured in the smaller channels exhibited the peaks attributed to the resonant tunnelling through the Au NCs less than 1 nm in thickness. In order to explain the experimental results we had employed a double barrier Pt/SiO₂/Au/SiO₂/Si structure model, which has provided a satisfactory description of the obtained experimental data.

1. Introduction
The metal nanoclusters (NCs) embedded into the thin dielectric films have attracted increased attention in recent years, in particular, as the promising materials for the nonvolatile memory applications [1] as well as for the applications in the novel nanoelectronic devices utilizing the single-electron and/or quantum size effects [2]. From this point of view, the investigations of the electron transport in the metal NC systems are important. Scanning Tunnelling Microscopy/Spectroscopy (STM/STS) has been widely used for the investigations of the electron transport through the metal NCs on the conductive substrates [3]. However, with respect to the metal NCs dispersed in the dielectric films the application of STM/STS is limited to the case when the NCs' concentration is high enough, i.e. when the films possess sufficient percolation conductivity [4, 5]. In this case, keeping STM feedback is provided by the continuous switching of the electrons tunnelling path through the film (hereinafter referred to as the current channel) from one chain of the NCs to another.

Since its development, Tunnelling Atomic Force Microscopy (TUNA) technique [6] has been mainly applied to study defects in thin dielectric films [4]. In [8] TUNA was applied to investigate the electron transport via Zr NCs produced by ion implantation in Zr(Y)O₂ films on p⁺-Si substrates. The peaks observed in the I—V curves of the probe-to-sample contact were attributed to the resonant tun-
nelling through the NCs of the highest resistance in the current channels (so called "bottleneck clusters" [4]).

In the present work, we used TUNA technique to investigate the electronic properties of individual Au NCs embedded in ultrathin (4-5 nm) SiO$_2$ films on the $n$-Si substrates.

2. Experimental
The ultrathin SiO$_2$:nc-Au films were formed on the $n$-Si(001) substrates by Pulsed Laser Deposition (PLD) in combination with plasma oxidation at 300K in a single vacuum cycle. Chemically cleaned $n$-Si substrates were pre-oxidized in the glow discharge oxygen plasma up to the underlying oxide thickness $d_a = 1$–2 nm and followed by the co-deposition of Si—Au mixture layer by PLD in UHV from the elemental Au and Si targets. The deposited Si—Au layer was further oxidized using the same glow discharge plasma procedure which leads to the segregation of Au from the oxidizing Si to form Au NCs. The size and shape of NCs was defined by the Si/Au concentration ratio and is limited by the lack of the long range thermal diffusion at 300K. Finally, the NCs were capped by the SiO$_2$ cap layer with the thickness $d_c = 1$–2 nm combining Si deposition in UHV and plasma oxidation. All the steps of the SiO$_2$:NC-Au structure formation (described in details in [9]) were monitored in situ by X-ray Photoelectron Spectroscopy (XPS) to control the chemical state and thickness of each layer. The technique described above allows forming the NC arrays arranged in a single sheet between the underlying and cladding layers, the thicknesses of which can be controlled precisely (unlike the NCs made by the ion implantation where some scatter in the NCs’ positions with respect to the film boundaries takes place always). Using the same growth procedure and additional amorphous graphite supporting layer (also produced by PLD), similar samples for Transmission Electron Microscopy (TEM) investigations were prepared on the cleaved NaCl(001) facets.

The TUNA investigations were carried out in Omicron® MultiProbe™ S UHV system at 300K. The sample surface was scanned using Pt coated Si probe in the contact mode. The $I$—$V$ curves of the probe-to-sample contact were acquired in every point of the scan.

3. Results and discussion
A plain view TEM image of SiO$_2$(1.5 nm)/nc-Au/SiO$_2$(1.5 nm) film grown on NaCl(001) is presented in figure 1 (a). The lateral size $D$ of the Au NCs was estimated from this image to be 3.0–6.5 nm. The NCs' height $h$ calculated from the overall Au amount in the film measured by Rutherford Backscattering Spectrometry (RBS) was 1–2 nm. These observations indicate that Au NCs formed in this process have a flattened shape.

A TUNA image of the SiO$_2$(1.5 nm)/NC-Au/SiO$_2$(1.5 nm)/$n$-Si film is presented in figure 1 (c). The inverted contrast in this image (the larger the probe current $I$, the darker is the spot) corresponds to the negative polarity of the bias voltage $V_b$ between the probe and the sample which, in turn, corresponds to the injection of the electrons from the Pt coated tip into the $n$-Si substrate through the nanocomposite film. It is worth noting that the TUNA image correlates with the topographic one presented in figure 1 (b) weakly (the Pirson's correlation coefficient $R_F \approx 0.015$ for this particular pair of images).

![Figure 1](image-url)

**Figure 1.** A plain view TEM image of SiO$_2$(1.5 nm)/NC-Au/SiO$_2$(1.5 nm) nanocomposite film on NaCl(001) (a); the AFM (b) and the TUNA (c) images of the similar film on $n$-Si(001); $V_b = -2.5$ V.
Figure 2. The $I-V$ curves measured with a Pt-coated Si AFM tip on the SiO$_2$/NC-Au/SiO$_2$/n-Si structure in different current channels of larger (a) and smaller (b) sizes.

The spots of 3–10 nm in size in the TUNA image (the current channels) were attributed to the electron tunnelling through the individual Au NCs [10]. The $I-V$ curves of the probe-to-sample contact measured in the channels of the larger size (5–10 nm) presented in figure 2 (a) exhibited weakly expressed Coulomb staircase. Earlier, the Coulomb blockade has been observed at 300 K in similar structures using TUNA [14] and was discussed in more details therein. In the present work, we used the model of an ellipsoidal NC (taking into account the flattened shape of the NCs as revealed above) between two flat electrodes to estimate the size of NCs from the Coulomb staircase period. Assuming $h = 1$ nm, we obtained $D = 3–5$ nm that is consistent with the TEM data.

The $I-V$ curves measured in the channels of the smaller (3–5 nm) size are shown in figure 2 (b). The peaks at the negative $V_g$ were attributed to the resonant tunnelling through the Au NCs. The interpretation of the tunnelling spectra was based on a double barrier Pt/SiO$_2$/Au/SiO$_2$/Si structure model (figure 3) similar to the one described in [11]. The model was based on the exact solution of one-dimensional Schrödinger's equation in the effective mass approximation. The applicability of the one-dimensional model is justified by the flattened shape of the NC, so that they can be treated as the thin disks and the size quantization in the film plane can be neglected. The band diagrams of the model structures were calculated by solving the one-dimensional Poisson's equation taking into account the band bending at the $n$-Si/SiO$_2$ interface (figure 3). The NCs were assumed to be completely charge depleted due to the quantum size effect that allowed us to neglect the screening of the external electric field by the electrons confined in the NC.

Figure 3. The calculated band diagram of a Pt/SiO$_2$/NC-Au/SiO$_2$/n-Si structure for $V_g = 5.7$ V; a calculated envelope wavefunction $\chi(z)$ for a resonant state.

Figure 4. The calculated (1) and measured (2) $I-V$ curves of the contact of an AFM probe to the SiO$_2$(1.5 nm)/SiO$_2$/NC-Au/SiO$_2$(1.8 nm)/n-Si structure.
Earlier, STM/STS and Auger Electron Spectroscopy (AES) investigations revealed that similar Au NCs formed on the highly oriented pyrolitic graphite can undergo metal-to-insulator transition at $h<1$ nm, and an energy gap was observed in their tunnel spectra [12]. In this case, the electron-electron scattering inside the NCs would not affect the coherent tunnelling through them. However, it is not the case for the NCs of larger size ($\geq 2$ nm), which are filled with electrons.

The typical fitting of a measured $I-V$ curve of the probe-to-sample contact with a model one is presented in figure 4, $d_u$, $d_c$, and $h$ were the fitting parameters. The best fit was achieved at $d_u = 1.4$ nm, $d_c = 1.1$ nm, and $h = 1.3$ nm (the band diagram in figure 3 has been calculated just for these values) which is in satisfactory agreement with XPS [12] and TEM data despite the fact that the described model is rather crude. Particularly, the resonant peaks in the calculated $I-V$ curve (figure 4) are narrower than those in the measured one which should be attributed to the inhomogeneous broadening due to the non-uniformity of the actual NC thickness. Also, one can notice the splitting of the resonant peaks in the measured $I-V$ curve that can be ascribed to the stepwise fluctuations in the NC thickness. Nevertheless, from the comparison of the results of the modelling with the experimental data one can conclude that the used model provides satisfactory description of the electron tunnelling through the small NCs and that the peaks observed in the measured $I-V$ curves originate from the resonant tunneling effect.

4. Conclusion
In the present study, the TUNA technique was applied to observe the resonant electron tunnelling through the individual Au NCs $\leq 1$ nm in thickness embedded in the ultrathin SiO$_2$ films on the Si substrates. The charge depletion of the Au NCs was found to be an essential condition for the manifestation of the resonant tunnelling. The observed effect can be exploited in a nanoelectronic devices based on the single metal NC embedded into the ultrathin dielectric films.

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