Features of tunneling current-voltage characteristics in dielectric films with Ni, Fe and Co nanoparticles, investigated by conductive AFM and within the framework of the theory of 1D-dissipative tunneling

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1. Introduction

Experimental observation of theoretically predicted macroscopic quantum effects of dissipative tunneling in low-dimensional systems (see, for example, [1–3]) is one of the current interest problems of modern condensed matter physics [1, 4, 5], since it allows both to study fundamental observable macroscopically realizable quantum effects and to develop the innovative nanoelectronics and nanophotonics devices with controlled characteristics (optical THz-IR converters, tunneling photodiodes, etc.). In the last decade, the authors of this work have experimentally observed effects due to dissipative tunneling of electrons in a number of artificial nanoscale systems. The results achieved to date are summarized in Table 1.

In this paper, the authors provide experimental evidence for the presence of one-dimensional dissipative tunneling effects in the limit of weak dissipation in an external electric field for metal nanoparticles (Ni, Co, Fe), including those synthesized using a probe AFM. Experimentally observed features of the tunneling I–V curves are interpreted on the basis of the one-dimensional dissipative theory of tunneling in the limit of weak dissipation [1, 4, 6–8]. A qualitative comparison was carried out between the experimental (individual tunneling I–V curves) and theoretical results obtained in the...
Table 1. Experimentally observed effects of dissipative tunneling.

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<td>The maximum on tunneling I–V curves for Au nanoparticles in SiO₂ films [1]</td>
<td>A series of non-equidistant peaks in the tunneling I–V curve of InAs/GaAs(001) quantum dots [1,2]</td>
<td>2D-bifurcations on the tunnel I–V curves of the Au nanoparticles-arrays in SiO₂ films [1]</td>
<td>2D bifurcations on the field dependence of the photocurrent of a p-i-n diode with double asymmetric InAs/GaAs(001) quantum dots [3]</td>
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one-instanton semiclassical approximation in a model double-well oscillatory potential in the framework of the science of quantum tunneling with dissipation [1, 2, 4–7, 9–20] under conditions of an external electric field, and experimentally (by the method of conducting AFM). The experimental results are interpreted on the basis of the one-dimensional dissipative theory of tunneling in the limit of weak dissipation [1, 4, 6–8], and a qualitative comparison is made between the experimental and theoretical results (individual tunneling I–V curves and the field dependence of the probability of 1D dissipative tunneling). The experimental studies, presented in our work, based on the theoretical results most part of that was obtained in our previous papers mentioned above.

The essential advantage of the theory of quantum tunneling with dissipation is the possibility to obtain the main results for the tunneling probability in an analytical form (using the one-instanton semiclassical approximation). To date there are two main models which allows to obtain results in the exact analytical form within the framework of this theory: (1) “cubic parabola potential” simulating Josephson junctions [1, 4, 6]; (2) “double-well oscillatory potential”, which makes it possible to simulate tunnel transport through single nanoparticles in the system of a combined AFM/STM under conditions of an external electric field. The last approach was used by authors in this paper to theoretically describe the dissipative transport.

For the first time, the idea of using the double-well potential model in describing tunnel transport in a combined AFM/STM system under conditions of an external electric field was formulated in [21]. This approach was developed, in particular, in [8] (see, also, [1]) where authors used ideas and results of the theory of quantum tunneling with dissipation [1, 4, 6] to describe tunnel transport in this system. Note that Yu. N. Ovchinnikov have shown [10] that it is possible to qualitatively compare the experimental tunneling current (more precisely, the I–V curves) for planar structures of individual metal nanoparticles in a combined AFM/STM system with the probability of tunneling from the cantilever tip into the nearest nanoparticle.

In the considered double-well potential model, the positions of the minima of the double-well oscillatory potential, which depend on the strength of the external electric field, are mainly related to the “geometry” of the experiment. The left well simulates the AFM/STM cantilever needle (in our experiment, it is the platinum cantilever needle with an average radius of about 40 nm), while the right well models the metal nanoparticle closest to the cantilever needle (with a characteristic size of 2–5 nm in our experiment) separated from the cantilever needle by dielectric barrier. The real potential turns out to be much more complicated but our model potential makes it possible to obtain analytical results that are in good qualitative agreement with the experiment. In our model the control parameters (in addition to geometric factors) are the strength of the external electric field and the temperature. Also this model takes into account (as theoretical parameters) the frequency of the oscillators of the model potential, the frequencies of phonon modes and the coefficients of interaction with these modes (in the linear approximation).

In this paper, we use the following formula for the probability of the dissipative tunneling (up to a pre-exponential factor $B$):

$$\Gamma = B \exp(-S),$$

where $S$ is the one-instanton quasi-classical action in the one-instanton quasi-classical approximation in a model double-well oscillatory potential. We refer readers to the author’s theoretical paper [22] (see, also Appendix in [23]) where one can find our theoretical results for the probability of dissipative tunneling in the considered system using this formula.

Let us make some remarks about formula (1). This main theoretical formula for the probability of 1D-dissipative tunneling was obtained for the double-well oscillatory potential for the first time in the work [8] (see, also, [1]). Readers can find comments to Formula (1) in the pioneering works of A. I. Larkin, E. J. Leggett, Yu. N. Ovchinnikov and other authors [1, 4, 6].

The field dependence of the probability of 1D-dissipative tunneling was presented in the paper [16]. In this paper, the first qualitative comparison of the experimental tunneling I–V curves for individual zirconium nanoparticles (I–V curves have a single peak at one of the polarities) with a theoretical field dependence of the probability of 1D-dissipative tunneling...
in the model of a double-well oscillatory potential was carried out. It has been shown that the initially asymmetric doublewell oscillatory potential becomes symmetrical one at a certain value of the external electric field strength and at one of the polarities. In this case the pre-exponential factor $B$ of the probability of 1D-dissipative tunneling (1) gives a single (thermo-dependent) peak.

It should be mentioned here about the contribution of above-barrier transitions at a finite temperature (the real experiment was performed at room temperature). It is well-known that the de Broglie wavelength of the particle should be much smaller than the characteristic linear scale of the potential in the semiclassical approximation. As the temperature increases, the sub-barrier length in the double-well oscillatory potential decreases, and the standard semiclassical approximation is violated. It was shown by Larkin et al., in the papers mentioned above, that the value of the preexponential factor $B$ in the tunneling probability increases with increasing temperature and it can become comparable with the value of the exponential contribution $\exp(-S)$ in the formula (1) obtained analytically in the one-instanton semiclassical approximation. In this case, taking into account the pre-exponential factor makes it possible, with a certain accuracy, not to include in the consideration above-barrier transitions, which were studied in the works of A. I. Larkin in detail. In addition, it should be mentioned again that the appearance of a single peak in the field dependence of the probability of 1D-dissipative tunneling in the model of a double-well oscillatory potential is due to taking into account the pre-exponential factor at a finite temperature.

2. Experimental part

Films of $\text{ZrO}_2(\text{Y})$ and $\text{HfO}_2(\text{Y})$ (12 mol. % Y) 10 nm thick were deposited on conductive $\text{TiN}(25 \text{ nm})/\text{Ti}(25 \text{ nm})/\text{SiO}_2(500 \text{ nm})/\text{Si}(001)$ substrates with preliminarily deposited metallic sublayer (Ni, Co or Fe) 10 nm thick by high-frequency magnetron sputtering using a Torr International MSS-3GS vacuum setup for thin film deposition at a substrate temperature of 300 $\text{°} \text{C}$. AFM studies were carried out using AFM NT-MDT Solver Pro at 300 $\text{°} \text{K}$ in atmospheric conditions in the contact mode. NT MDT NSG-11 DCP probes with a DLC conductive coating were used.

Synthesis of Ni, Co, and Fe NPs in the thickness of $\text{ZrO}_2(\text{Y})$ and $\text{HfO}_2(\text{Y})$ films was carried out as follows: The AFM probe was brought into contact with the surface of the dielectric film, and sawtooth electric voltage pulses with an amplitude of ~8 V and a duration of 6 s have been applied. When a positive electric potential is applied to the substrate, due to the drift of metal ions from the metal sublayer, where they are formed as a result of the electrochemical oxidation reaction, a conductive thread (filament) consisting of metal atoms is formed to the AFM probe, which closes the conductive substrate and the AFM probe. When an electric potential of reverse polarity is applied, the filament is partially destroyed, and a metallic NP is formed in the thickness of the dielectric. Methods for the formation of dielectric films and metal NPs in them using an AFM probe are described in detail in [24, 25].

3. Experimental results and discussion

3.1. Features of dissipative tunneling in Ni, Fe and Co nanoclusters, comparison of experiment and theory

In the tunnel current-voltage characteristics of the contact of the AFM probe to the surface of dielectric films, peaks are observed at the locations of metal nanoparticles associated with dissipative tunneling of electrons between the AFM probe and the conductive substrate. During the synthesis of metallic NPs with a change in polarity, instead of NPs, synthesis of toroidal structures is possible (shown on the example of Ni NPs (see Subsection 4.2, Fig. 2). A qualitative agreement between the experimental and theoretical results was obtained (see Fig.1(a–c)), which suggests the possibility of experimental observation of the effects of macroscopic dissipative tunneling [1, 4].

Figures 1(a–c) (theoretical curve 2) of the text of this paper have curves containing a single peak for the case of a symmetric double-well potential at a certain value of the external electric field strength, obtained as the field dependence of the probability of dissipative tunneling $\Gamma = B \exp(-S)$, ( [1, 8], Appendix to [23]). This peak, obtained theoretically, qualitatively coincides with individual experimental tunneling I – V characteristics for single NPs in the combined AFM/STM system (see Fig. 1).

3.2. Formation of ring-shaped metal nanostructures using an AFM probe

It was found that when the polarity of the applied voltage was changed after the completion of the NPs formation (i.e., when a negative voltage pulse was applied to the metal sublayer after a positive one), the formation of toroidal structures was observed (Fig. 2). The formation of such structures is associated with local anodic oxidation of the central parts of metal NPs, followed by the drift of metal ions towards the conductive substrate (Fig.3)

These observations open up prospects for the development of an original technique for the controlled formation of ring-shaped metal nanostructures in thin dielectric films for use in nanoelectronics, nanophotonics, plasmonics, etc.
FIG. 1. Comparison of experimental I–V characteristics for NPs: (a) Ni, (b) Fe, (c) Co, with the theoretical field dependence of the probability of 1D dissipative tunneling.

FIG. 2. Current image (map of the current flowing through the CAFM probe) of a toroidal Ni nanostructure formed inside a ZrO$_2$(Y)/Ni/Si(001) film by local reduction/oxidation with a CAFM probe. Offset voltage 0.5 V.
4. Conclusion

In this work, the peculiarities of tunneling volt-ampere characteristics (CVC) in the case of one-dimensional dissipative tunneling in the limit of weak dissipation for various metal nanoclusters (Ni, Co, Fe) in a combined system of an atomic force and scanning tunneling microscope in an external electric field are studied experimentally and theoretically. It is shown that for individual tunneling I–V characteristics, a single peak is observed at one of the polarities. In the process of synthesizing metal nanoclusters with a change in polarity, instead of nanoclusters, toroidal structures can be synthesized (shown on the example of “growing” Ni-NPs). The studied effects of one-dimensional dissipative tunneling made it possible to develop an author’s method for the controlled growth of quantum dots in a combined AFM/STM system. Qualitative agreement between the experimental and theoretical results is obtained, which makes it possible to assume the possibility of experimental observation of macroscopic dissipative tunneling effects and thereby confirm the hypothesis expressed in the “pioneer” works of A. J. Leggett, A. I. Larkin, Yu. N. Ovchinnikov and other authors [1, 4, 6].

Note that the temperature dependence of a single peak was experimentally studied recently by co-authors of this paper from the Probe Microscopy Laboratory of the Lobachevsky State University of Nizhni Novgorod in an experiment with cobalt nanoparticles. This experiment has confirmed the theoretical prediction that “the amplitude of a single peak increases weakly non-linear with decreasing temperature”. These results will form the basis of a separate joint work.

Let us discuss here the interesting question about the relation between resonant and dissipative tunneling. Our experimental results with synthesized Fe, Co, and Ni nanoparticles (first, filamentous structures were formed, and then the “thread” was destroyed by a sawtooth voltage to get a nanoparticle) showed that additional peaks could be observed next to a single (usually larger amplitude) peak. These additional peaks are most likely resonant in nature. At small sizes of metal nanoparticles, a quantum size effect arises (in this case, metal differs slightly from semiconductor) and we see additional oscillations, in addition to a single thermo-dependent peak (due to the effect of dissipative tunneling). These oscillations are related with the participation of these levels in the nanocluster in resonant tunneling and with the fine tuning of energy levels in an external electric field.

Note also that in our first joint paper [16], it was shown that tunneling I–V curves (experiment with zirconium nanoparticles) with various features are also actually observed (for example, the “Coulomb ladder”, the case of several peaks of a resonant nature). Also the clear single peaks were observed at one (positive) polarity in a number of experimental tunneling I–V curves. In later experiments with gold nanoparticles, some I–V curves exhibited a single peak at one negative polarity (due to the influence of the nanometer protrusions on a non-ideal cantilever needle). Therefore, it should be noted that the observed effect of a single peak is realized only on separate I–V curves.

Our experiments showed that additional peaks formed due to resonant tunneling smear out with increasing temperature. Whereas a single temperature-dependent peak (higher amplitude) due to dissipative tunneling does not smear out with increasing temperature, but only decreases in amplitude. As a result, we can make an assumption about a possible new physical effect. Two tunneling mechanisms are realized on the observed tunneling I–V curves: resonant and dissipative with different behavior of the corresponding peaks with temperature change. As the temperature rises, the resonance peaks are smeared out, while the “dissipative” peak is retained.

The results of this work show that the development of nanotechnology has made it possible to experimentally observe the effects of dissipative electron tunneling in artificial size-quantized nanostructures.
References


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