SPM Investigation of the Electron Properties YSZ Nanostructured Films

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ABSTRACT

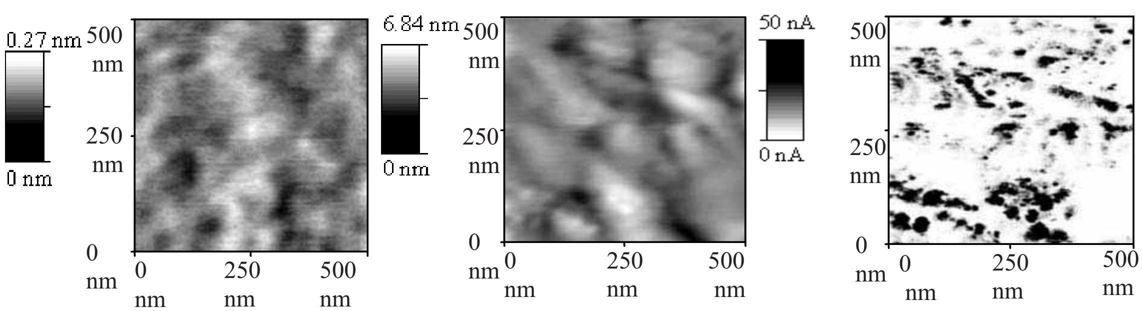
The electronic properties of the yttria stabilized zirconia (YSZ) films with Zr nanoclusters formed by implantation of Zr ions have been studied by combined Atomic Force Microscopy / Scanning Tunneling Microscopy (AFM\STM). The feedback was maintained by AFM in Contact Mode using a conductive cantilever. Simultaneously the I-V curves of the junction between the probe and the conductive substrate through the nanostructured YSZ film were measured. It is the evidence that we observed the localized channels of the tunneling current attributed to the successive tunneling through Zr clusters. The lateral sizes of the channels where 1-10 nm in thick (24 nm) YSZ films. The effects of resonant tunneling and Coulomb blockade of tunneling through the Zr clusters have been observed.

Keywords: nanoclusters, YZS films, STM, AFM, coulomb blockade, resonance tunneling.

1 INTRODUCTION

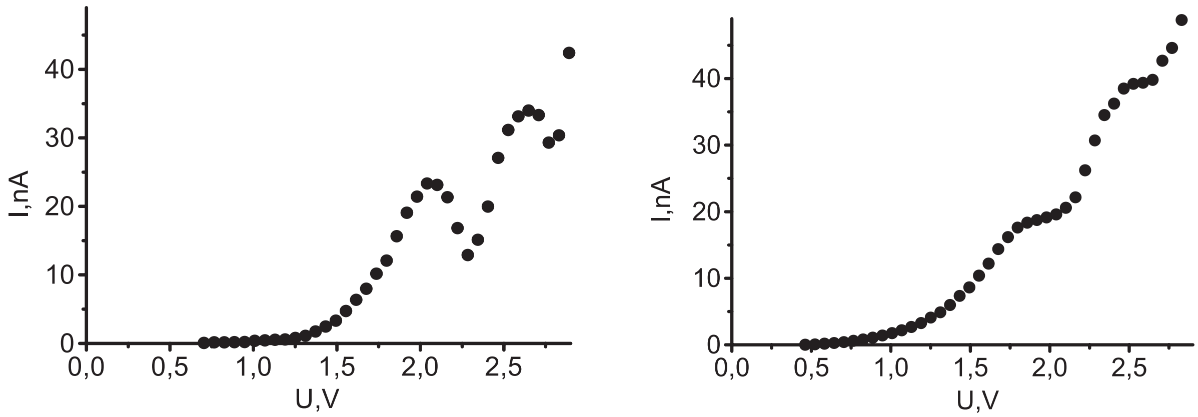
Formation of the metal and semiconductor nanoclusters in the dielectric oxide matrices is a promising scientific direction developed in the last years with the purpose of making new materials for opto- and microelectronics [1]. One of the ways of making such systems is implantation of ions of the metal or semiconductor in the oxide films [2-5].

Scanning Tunneling Microscopy (STM) is used widely for investigation of the electronic properties of the clusters deposited on the conductive substrates [6] as well as embedded in the dielectric films [7-8]. Such effects as Coulomb blockade, resonant tunneling, and increasing effective gap with decreasing cluster sizes have been observed in these systems [9]. However, investigations of the clusters embedded in the dielectric films by STM encounter a number of problems. One of them is difficulty to maintain a stable tunneling current feedback through the thick dielectric films. In the present work we applied combined Scanning Tunneling/Atomic Force Microscopy (STM/AFM) to investigate the electronic properties of the Zr nanoclusters formed in yttria stabilized zirconia (YSZ) films by implantation of Zr ions. We used a standard beam deflection AFM with a conductive cantilever. The feedback was maintained by AFM technique in Contact mode. Simultaneously the I-V curves of the tunneling contact between the cantilever and p^+-Si substrate through the nanostructured YSZ film were recorded in every point of the scan. This approach has allowed us to decouple maintaining the feedback and measuring the tunneling current and to observe tunneling through the Zr



a б c

Fig. 1. The surface topography (*a, b*) and the current image (*c*) of YSZ film before (*a*) and after (*b,c*) implantation of Zr. The gap voltage U=+4V.



a *b*

Fig. 2. Typical I-V curves recorded on the separated channels of the tunneling current; in the spots with sizes < 2 nm (a), in the spots with size 2-4 nm (b).

nanoclusters including Coulomb blockade and resonant tunneling effects.

2 EXPERIMENT

The YSZ films were deposited on p^+-Si (001) substrates by magnetron sputtering of a target from 90 mol. % ZrO_2 + 10 mol. % Y_2O_3. The thickness of the films was 24 nm. The implantation was performed on the pulsed ion beam accelerator. The averaged ion energy was 190 keV, the ion dose was ~ 10^{17} cm^{-2}. The optical absorption spectra of the implanted YSZ demonstrated an absorption band in the wavelength interval of 400 ÷ 650 nm conditioned by Zr clusters with average radius ~ 1nm [5].

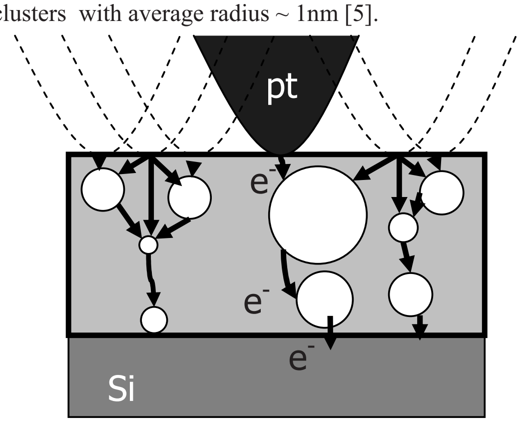


Fig. 3. Schematic of the mechanism of the electron tunneling through the dielectric film with the metal nanoclusters.

The morphology and electronic properties of the implanted films were studied by Omicron® Ultra High Vacuum (UHV) AFM/STM LF1 installed into Omicron® Multiprobe S™ UHV system. Soft p^+-Si I-type cantilevers coated with Pt were employed. The accuracy of the tunneling current measurements was ~10 pA.

3 RESULTS AND DISCUSSION

In Fig.1 the morphology of YSZ film before (*a*) and after (*b*) implantation of Zr ions is presented. Implantation results in increased surface roughness and formation of the areas of conductivity with lateral sizes ranging from 1 to 20 nm represented as the dark spots in the current image (Fig.1*c*). It should be noted that no correlation between morphology and the current image was observed. No current was observed before implantation even at the highest possible values of the gap voltage *U* (±10 V).

In Fig.2 typical I-V curves taken in the spots with high conductance (the tunneling current channels) are shown. In the I-V curves taken in the spots with small sizes (< 2 nm) the peaks typical for resonant tunneling through the nanometer sized clusters with the discrete energy spectrum [9] have been observed (Fig.2*a*). In the I-V curves taken in the spots with larger size (2-4 nm) the steps typical for the Coulomb blockade of the tunneling have been observed (Fig.2*b*). To estimate the cluster size the asymmetric contact model [9-10] was used for coulomb blockade of the tunneling through the junction with a largest resistance (this junction behaves like a bottleneck of the tunneling current [7]). Assuming the cluster to be a metal balls with the radius *r,* its capacitance *C* can be expressed as follows:

$$C = 4\pi\varepsilon_0 \varepsilon r \qquad (1)$$

Here ε_0 is the electric constant and $\varepsilon = 4$ is the dielectric constant of the material (YSZ) surrounding the metal clusters. On the other hand, C is related to the period of the steps in the I-V curve V (taking into account the temperature broadening of the steps ΔV) by expression

$$C = \frac{e^2 \Delta V}{2VkT}, \qquad (2)$$

where e is the elementary charge, k is the Boltzman's constant, and T = 300K is the measurement temperature. Finally,

$$r = \frac{e^2 \Delta V}{8\pi\varepsilon_0 \varepsilon VkT} \qquad (3)$$

For $V \approx 0.66$V and $\Delta V \approx 0.28V$ (from Fig.2*b*) the estimate of the cluster size gives $r \approx 2.9$ nm which is in a reasonable agreement with the STM/AFM and optical spectroscopy data.

In most cases the lengths of the steps on the I-V curves were not equal as it should be when tunneling through a single cluster took place. To explain this effect it was suggested that the size and number of clusters forming a tunneling current channel can change with changing gap voltage. A scheme of the tunneling in a film with random spatial distribution of the clusters is shown in Fig.3. Since the total conductivity of the cluster chain is determined by a "bottleneck" cluster having the highest tunneling resistance [7], switching of the current channels would make different clusters to determine the step parameters.

In Fig.4 the current images of an area of the increased conductivity with lateral sizes ~10 nm at different gap voltages U are presented. At low U the channels with the lowest tunneling resistance appeared first (Fig.4*a*). The lateral sizes of the current channels at low U were within 1 to 3 nm.

Increasing U resulted in switching on new current channels (Fig. 4*b*). At further increasing of U the channels began to overlap (Fig.4*c*).

Annealing the Zr implanted films at the temperatures T=300-540 C resulted in aggregation of the small clusters in the larger ones with the sizes ranging from 10 to 40 nm. No peaks or steps were observed in the I-V curves measured on these aggregated clusters. This effect confirms that formation of the current channels is caused by tunneling of the electrons through Zr clusters in the dielectric film but not through the local electronic states of the radiation defects created in the YSZ matrix by ion bombardment.

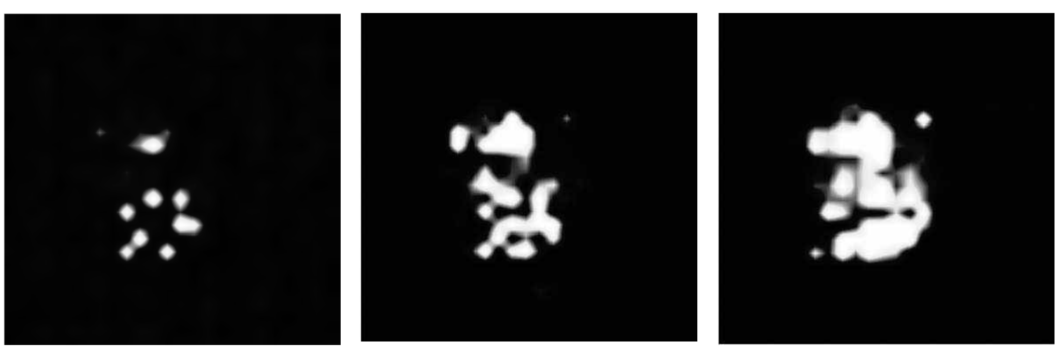
4 CONCLUSIONS

The results of this work have demonstrated that combined AFM/STM technique allows to study the electronic properties of the nanometer sized clusters in the dielectric films. Using this technique allowed us to study the electron tunneling through Zr nanoclusters formed by ion implantation in YSZ films and to observe the effects of Coulomb blockade and resonant tunneling through the metal clusters.

Authors are very grateful to Dr. V.A. Kamin who formed the YSZ films and to Dr Yu. A. Dudin who performed the ion irradiation of the films.

5 ACKNOWLEDGEMENTS

Authors gratefully acknowledge the financial support by joint Russian-American Program "Basic Research and Higher Education" (BRHE) sponsored by Russian Ministry of Education and by US Civilian Research and Development Foundation (CRDF), Award No. REC-NN-001.



a *b* *c*

Fig. 4. Current image of a YSZ after Zr implantation at different gap voltages. Gap voltage U (V): *a* - 0.88, *b* - 1.90, *c* - 3.72. Frame size 35 × 35 nm^2

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