Determination of activation energies of oxygen ion diffusion in memristor systems from the flicker noise spectrum

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***Abstract*—Noise in memristive systems based on the Yttria stabilized Zirconia (YSZ) thing films is investigated. Measurements are performed with the use of setup Omicron® UHV AFM/STM LF1 at temperature T = 300 K. The base pressure of remaining gases in the chamber of Atom Force Microscope (AFM) was at 10^{-10} Torr. Current through the cantilever of AFM is analyzed. The pdf and spectra of the noise in this current are treated for two states of conducting filament: "OFF" (high resistance), and "ON" (low resistance). Voltage applied to the cantilever is V_g = +3 V in both states. Noise in state "OFF" is caused by the inner noise of experimental setup only. In state "ON" the noise is considerably higher. Its spectrum has the flicker type with exponent $\gamma = 1.3$ in the whole frequency range analyzed. That allows us to determine the range of activation energies of oxygen vacancies diffusing within the filament, $E \in [0.52; 0.68]$ eV. This result coincides qualitatively with result obtained from measurements of electro–physical characteristics of the samples with macroscopic contacts at temperatures 300–500 K.**

***Keywords*—Memristive systems; flicker noise; diffusion; non-destroying analysis**

I. Introduction

Memristive systems are of increasing interest in various areas of science and technology ranging from digital to analog electronics, biologically inspired circuits and learning [1]. These systems have shown a great potential in realizing artificial synapses efficiently for neuromorphic computing [2]. There are a lot of investigations of such systems.

Reproducible bipolar resistive switching has been studied in SiO_x based thin–film structures for the development of nonvolatile memory and memristive systems for future electronics [3], see also [4].

Investigations of the role of noise in resistive switching are of special interest. These investigations cover two problems. The first one deals with the effect of external noise on the switching [5], [6]. The second problem is concerned with the non-destroying analysis of memristive systems, see, e.g. [7], [8].

The aim of this paper is to show that noise measurements may be applied for the determination of activation energies of oxygen vacancies diffusion in memristive systems. That is an additional method for the non-destroying analysis of solid state systems.

Noise in the Yttria Stabilized Zirconia (YSZ) thing films is investigated. The same samples and experimental setup were used as in [9], [10]. The structure and operation principles of such systems are described in [11]. Results of previous investigations on the determination of activation energies of oxygen vacancies diffusion in memristive systems are presented in [12], where electro–physical characteristics of the samples were investigated in the temperature range 300–500 K.

The model of flicker noise in the current through the sample, based on the model by Van der Ziel [13] (see also [14]), is used here. That allows us to estimate the range of activation energies of oxygen vacancies diffusion through the conducting filament in considered memristive system.

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II. EXPERIMENTAL SETUP

Measurements were performed with the use of setup Omicron® UHV AFM/STM LF1 at temperature $T = 300$ K. The base pressure of remaining gases in the chamber of Atom Force Microscope (AFM) is at 10^{-10} Torr. For more details see [9].

Input part of experimental setup is shown in Fig. 1.

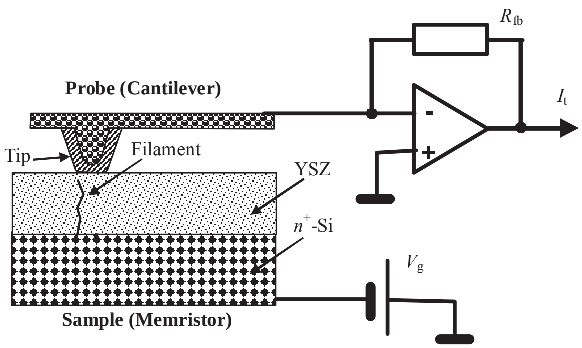

Fig. 1. Circuit for the measurement of current I_t through the tip of cantilever and the sample [9].

Here the probe (cantilever) is shown schematically. Its tip is in contact with the sample (memristor). The last one may contain the conducting filament. Voltage V_g is applied to the sample through the tip of cantilever. This voltage produces current $I_t = I_t(t)$ through the tip.

The sample is the film ZrO_2 (12% molar Y), thickness 4 nm (YSZ). This film is deposited on Au sublayer with the thickness 10 nm. Further on Ti sublayer is placed (50 nm) on n^+–Si(001) substrate. The Si diamond coated probes NT-MDT® DCP-11 are used. The radius of curvature of the tip is at 70 nm. The probe is brought to the surface of the sample in the contact state. Loading force is at 1 nN.

Current preamplifier of AFM has the range 1 pA–5 nA; frequency band 0–30 kHz; gain $K_{I\text{–}V} = 5$ nA/V. Voltage $V(t)$ at the output of the preamplifier is determined as follows:

$$V(t) = I_t(t) / K_{I\text{–}V}. \quad (1)$$

This voltage is applied to the input of 16-bit analog-to-digital converter (ADC) of AFM. The sampling rate is 15 995 Hz. Digitized samples $N(t)$ at the output of ADC are determined by input voltage:

$$N(t) = V(t) / S_D. \quad (2)$$

Here $S_D = 3\times10^{-4}$ V is scaling parameter of ADC.

Thus, the current through the sample may be found as:

$$I_t(t) = N(t)\times K_N. \quad (3)$$

Here K_N is transformation factor, $K_N = S_D\times K_{I\text{–}V} = 1.5$ [pA].

All digitized samples are processed by Multifunctional Analyzer ADSViewer developed in programming environment LabVIEW® (National Instruments®, USA) [15], see also [16], [17], [18]. The transformation of results obtained with ADSViewer to the current $I_t(t)$ is performed using Eq. (3). The following characteristics of records were analyzed: waveforms; pdf, and spectra. For calculation of spectra the 1024 points fast Fourier transform (FFT) is applied. The obtained spectrograms are averaged. The maximal analyzing frequency is 7 997.5 Hz; the frequency resolution is 15.62 Hz.

III. RESULTS OF MEASUREMENTS

Measurements are started from investigation of setup inner noise. The probe is in contact with the sample, $V_g = 0$. Conducting filament is absent (not formed). That is state “1” (in contact). After that the filament is created by applying of voltage $V_g = +6$ V to the sample. Then noise is measured in two states: “OFF” (high resistance), and “ON” (low resistance). Voltage applied to the sample is $V_g = +3$ V in both states. Measurements are finished by additional investigation of the inner noise. The probe is removed from the sample at a distance of about 4 μm. That is state “0” (no contact).

A. Inner noise of the Setup

The analysis shows that the recorded processes represent noise, which can be considered stationary.

The noise in state “1”, in addition to the converter noise, may contain the noise of the probe, and of the sample; recorded files contain 1 843 200 digitized samples. In state “0” the recorded files contain 614 400 digitized samples, which characterize only the preamplifier noise.

Digitized samples $N(t)$ in states “0” and “1” are distributed within 10 ADC bits. Effects of incomplete use of the ADC are taken into account [16], [19].

Waveforms show the presence of external interference, having almost harmonic character. The pdf is rather close to the Gauss law. The statistical error of obtained estimates is 0.3–0.4 percent in the area of maximum values and reaches 71 percent in the area of minimum values of pdf. The statistical error of spectrum measurement in state “0” is about 4 percent; in state “1” – about 2.4 percent. The spectrum in both states is highly heterogeneous.

It is found that the noise of AFM operating in states “0” and “1” does not depend on the presence of contact between the probe and the sample.

B. States “OFF” and “ON”

When processing “OFF” and “ON” files, data on the setup noise in state “0” are used. In state “OFF” the recorded processes represent the noise of setup only. A different situation is observed in state “ON”: the noise is non-stationary. Total spectrum $S_T(f)$ obtained for state “ON” clearly shows the presence of quasi-harmonic interferences, which are present in spectrum $S_0(f)$ of setup noise.

To define spectrum $S_{ON}(f)$ of the noise generated by the sample we subtract spectrum $S_0(f)$ from total spectrum $S_T(f)$:

$$S_{ON}(f) = S_T(f) - S_0(f). \quad (4)$$

The relative statistical error $\delta S_{ON}(f)$ of spectrum (4) is determined from the following relation:

$$S_{ON}(f) \times \delta S_{ON}(f) = S_T(f) \times \delta S_T + S_0(f) \times \delta S_0. \quad (5)$$

Relative statistical errors δS_T and δS_0 characterizing the accuracy of measurement of the corresponding spectra are determined by the number of processed spectrograms and do not depend on the analyzing frequency f. Typical error $\delta S_{ON}(f)$ is about 2 percent; in the frequency range, where quasi-harmonic interference is dominated, it reaches 10–60 percent.

The result of subtraction (4) is shown in Fig. 2. The polyline "ON" is spectrum $S_{ON}(f)$ of the sample noise. Straight line – approximating spectrum $S_{Fit}(f)$. The subtraction of spectra led to a satisfactory result. The resulting spectrum has a pronounced flicker character. Manual approximation of this spectrum gives:

$$S_{Fit}(f) = A_0 / f^{\gamma} \ [\text{pA}^2/\text{Hz}]. \tag{6}$$

Here $A_0 = 2.3\times10^3$; exponent of this spectrum is $\gamma = 1.3$.

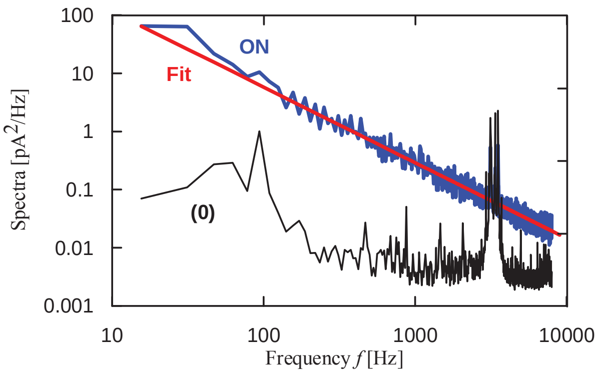

Fig. 2. Result $S_{ON}(f)$ of subtracting the spectrum $S_0(f)$ from the total spectrum $S_T(f)$ (polyline "ON"). Approximating spectrum $S_{Fit}(f)$ (straight line "Fit"). Bottom line "(0)" – spectrum $S_0(f)$ of setup noise, state "0".

IV. Analysis of Activation Energies

Diffusion of oxygen vacancies along the conducting filament is considered here as the origin of flicker noise in the sample. Model [13] by Van der Ziel is used as the basis, see also [14].

An elementary jump of the vacancy in the filament requires activation energy E. The mean frequency f_c of these jumps is determined as:

$$f_c = f_T \exp\left[-E / (kT)\right]. \tag{7}$$

Here $f_T = 10^{13}$ Hz is the mean frequency of the lattice thermal vibrations.

These jumps yield random telegraph noise (RTN) in the conductivity $G = G(t)$ of the filament. The spectrum of this noise $S_{RTN}(f \,|\, f_c)$ has the Lorentzian type:

$$S_{RTN}(f \,|\, f_c) = A_{RTN} \times f_c / (f_c^2 + f^2). \tag{8}$$

Here A_{RTN} is the parameter determined by the variance of RTN. Mean frequency (7) has a sense of the corner frequency for spectrum (8).

Vacancies inside the filament have different activation energies E characterized by probability density function (pdf) $W_E(E)$. Thus, for corner frequencies we have pdf $W_c(f_c)$. Both functions are connected by (7).

Total spectrum $S_G(f)$ in the conductivity noise is determined by diffusion jumps of all vacancies:

$$S_G(f) = N_T \int S_{RTN}(f \,|\, f_c)\, W_c(f_c)\, df_c. \tag{9}$$

Here N_T is number of vacancies diffusing in the filament. The integral is calculated over the full range of corner frequencies f_c.

Our aim is modeling of spectrum (9) with $\gamma \sim 1$. This is possible if pdf $W_c(f_c)$ of corner frequencies has the same kind, $W_c(f_c) \sim f_c^{-\gamma}$. In common case this distribution takes place in the restricted (but wide enough) limits $[f_L; f_H]$. For the simplicity the finite pdf is used here:

$$W_c(f_c) = B_c / f_c^{\gamma};\ f_c \in [f_L; f_H]. \tag{10}$$

If γ=1 the normalization factor is: $B_c = 1/[\ln(f_H/f_L)]$, see [13].

High and low frequencies are determined, in accordance with (7), by limits of activation energies, $E \in [E_1; E_2]$:

$$E_1 = kT \ln(f_T/f_H);\ E_2 = kT \ln(f_T/f_L). \tag{11}$$

The pdf for activation energies is found from (10):

$$W_E(E) = B_E \times \exp[(\gamma-1)E/(kT)];\ E \in [E_1; E_2]. \tag{12}$$

Here B_E is the normalization factor.

Thus, we have:

$$S_G(f) = \frac{B_G}{f^{\gamma}};\ B_G = \pi N_T A_{RTN} B_c \frac{\sin[(\gamma-1)\pi/2]}{\sin[(2-\gamma)\pi]}. \tag{13}$$

Noise in the conductivity $G(t)$ of the filament is manifested as the noise in current $I_t(t)$ with spectrum $S_{It}(f)$. Relation between these spectra is as follows:

$$S_{It}(f) = V_g^2 \times S_G(f). \tag{14}$$

Thus, knowing spectrum $S_{It}(f)$ we can determine some statistical characteristics of vacancies diffusing within the conducting filament.

The model described above presents no information about low f_L and high f_H frequencies of the conductivity noise spectrum $S_G(f)$. That is why we use here limits of our experimental data: f_L=15.6 Hz; f_H=7.98 kHz.

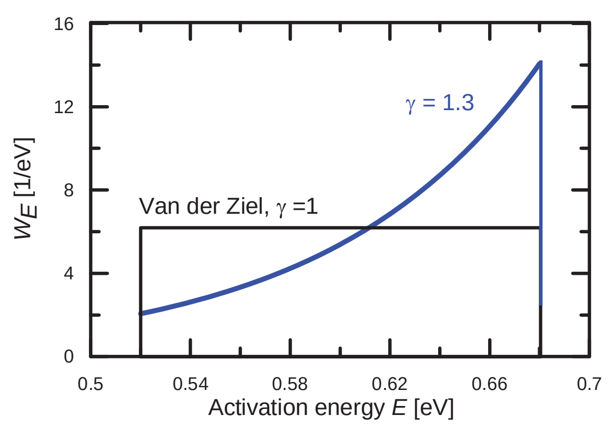

Fig. 3. Pdf $W_E(E)$ obtained from spectrum $S_{ON}(f)$. Uniform distribution by Van der Ziel [13] is shown as well.

Consider spectrum (6), which is the fit of spectrum $S_{It}(f)$ at V_g = +3 V, state "ON". Using in (11) $f_T = 10^{13}$ Hz, we can find limits of activation energies, $E \in [0.52; 0.68]$ eV. As far as $\gamma > 1$, spectrum (6) decreases faster than $1/f$. This means, following to (12), in difference with model [13], that pdf of activation energies is the increasing function, see Fig. 3.

V. Conclusions

Noise in memristive systems based on the Yttria stabilized Zirconia (YSZ) thing films is investigated. Measurements were performed with the use of setup Omicron® UHV AFM/STM LF1 at temperature T =300 K. The base pressure of remaining gases in the chamber of Atom Force Microscope (AFM) was at 10^{-10} Torr.

Current $I_t(t)$ through the tip of AFM probe is analyzed. The pdf, and spectra of the noise in this current are treated. Measurements are made for two states of the conducting filament: “OFF” (high resistance), and “ON” (low resistance). Voltage applied to the cantilever is V_g = +3 V in both states.

In state “OFF” the only noise of setup is pronounced. In state “ON” the noise is considerably higher. Its spectrum has the flicker type with exponent γ = 1.3 in the whole frequency range analyzed.

That allows us to determine the range of activation energies of oxygen vacancies diffusing within the conducting filament, $E \in [0.52; 0.68]$ eV. This result coincides qualitatively with result [12], $E \approx 0.53$–0.56 eV, obtained from measurements of electro–physical characteristics of the samples with macroscopic contacts at temperatures 300–500 K.

It is worth noting that the analysis presented here cannot reveal the spatial distribution of E along the filament. The values of E are averaged over the whole filament length. It is reasonable to assume that these values of E at the interfaces of the filament with the electrodes may differ from those inside the filaments. However, as the filament interfaces represent a minor part of the total filament length, the contribution of these ones into the averaged value of E can be neglected.

Thus, noise measurements may be applied for the determination of activation energies of oxygen vacancies diffusion in memristive systems. That is an additional method for the non-destroying analysis of solid state systems.

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