In situ Investigation of Individual Filament Growth in Conducting Bridge Memristor by Contact Scanning Capacitance Microscopy

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Abstract. We report on the application of Contact Scanning Capacitance Microscopy (CSCM) to trace the growth of an individual Ni filament in a ZrO$_2$(Y) film on a Ni sublayer (together with a conductive Atomic Force Microscope probe composing a nanometer-sized virtual memristor). An increasing of the filament length in the course of electro-forming results in an increasing of the capacitance between the probe and the sample, which can be detected by CSCM technique. This way, the filament growth can be monitored in real time in situ.

1. Introduction
In recent years, resistive switching (RS) effect in thin dielectric films has attracted much attention due to its potential application in the next-generation non-volatile computer memory (Resistive Random Access Memory, RRAM) devices [1]. The electronic devices, the operation of which is based on the RS effect are called memristors [2]. The RS is a reversible switching of resistance of a thin insulator of a capacitor-like stack under a voltage applied to the plates. In most cases, the RS mechanism is understood in terms of forming and rupture of conductive filaments (CFs) formed inside the insulator under the electric field between the plates. In the memristors based on metal oxides (HfO$_x$, NiO$_x$, TaO$_x$, etc.), SiO$_x$, GeO$_x$, etc., the CFs are composed of oxygen vacancies (V$_{OS}$) [3]. In so-called conducting bridge (CB) memristors, the CFs consist of metal atoms (e.g. Au, Ag, Cu, etc.) injected into the insulator (SiO$_x$, etc.) [4].

To date, such methods as Cross-Sectional Transmission Electron Microscopy (X-TEM) and Scanning Tunneling Microscopy (STM) [5] as well as Conductive Atomic Force Microscopy (CAFM) [6] have been applied to study the growth/rupture of the CFs in situ. In the present work, we applied Contact Scanning Capacitance Microscopy (CSCM) [7] to trace the growth of an individual Ni CF in a ZrO$_2$(Y)/Ni film.

2. Experimental part
The ZrO$_2$(Y) film (~12% mol. Y$_2$O$_3$) with a thickness $d \approx 10$ nm was deposited by radio-frequency (RF) magnetron sputtering using Torr International$^\text{®}$ ***** vacuum setup onto an $n^+$-Si(001) substrate with a pre-deposited 10-nm thick Ni sublayer. The CSCM experiment was carried out in ambient air at room temperature with NT-MDT$^\text{®}$ Solver Pro$^\text{TM}$ AFM in the contact mode using NT-MDT$^\text{®}$ HA-HR DCP AFM probes with conducting diamond-like coated tips.
The probe was brought into a contact with the ZrO$_2$(Y) film surface, and a sawtooth voltage $V_g$ (amplitude 6 V, period 6 s) was applied between the CAFM probe and the Ni sublayer. The forming of the Ni CF inside the ZrO$_2$(Y) film started at a negative $V_g$ applied to the CAFM probe with respect to the sample due to an electrochemical (anodic) oxidation of the Ni sublayer surface at the Ni/ZrO$_2$(Y) interface, drift of the Ni ions in the electric field between the probe and the Ni sublayer, and reduction of the Ni ions at the growing filament tip (figure 1) [6].

3. Results and Discussion
Figure 2 shows typical cyclic current-voltage ($I$–$V$) curve of the contact of the CAFM probe to the ZrO$_2$(Y)/Ni/Si(001) film surface. The $I$–$V$ curve demonstrated a pronounced hysteresis typical for the CB memristors attributed to the forming and rupture of the Ni filaments inside the ZrO$_2$(Y) film under the voltage $V_g$ applied between the CAFM probe and the Ni conducting sublayer.

Figure 3 shows a surface topography image (figure 3a) and a current image (a map of the current flowing through the CAFM probe $I_t$ as a function of the in-plane probe coordinates $x$, $y$, figure 3b) acquired simultaneously with the surface topography with the bias voltage $V_g = 4$ V applied to the CAFM tip with respect to the Ni sublayer. Prior to this measurement, a single Ni filament was formed in the center of the frame by applying a triangular pulse of $V_g < 0$ (amplitude 6 V, duration 3 s) to the CAFM probe positioned in an arbitrary point on the sample surface.

Figure 3. Topography (a) and current image (b) of the ZrO$_2$(Y)/Ni/Si(001) film surface after forming an individual Ni filament. $V_g = 4$ V.
A local increasing of $I_t$ in the center of the frame in figure 3b was attributed to the Ni CF formed between the ZrO$_2$(Y) film surface and the Ni sublayer: once the CAFM probe encounters the upper end of the Ni CF, an increased current flows between the CAFM probe tip and the Ni sublayer directly through the highly conductive Ni CF. Note that a small hillock (of ~ 1 nm in height) was observed in figure 3a at the place of the local increasing of $I_t$ attributed to the accumulation of the Ni atoms under the CAFM probe tip in the course of the Ni filament forming (as shown schematically in figure 1). Figure 4a shows the kinetics of the capacitance between the CAFM probe and the sample $C_{CF}(t)$ (t is the time) measured in the course of the forming process using an add-on for CSCM to NT-MDT® Solver Pro$^\text{TM}$ AFM.

The increasing of $C_{CF}$ was attributed to the increasing of the CF length $l_{CF}$ in the course of forming (as shown in figure 1). A dependence of $C_{CF}$ on $l_{CF}$ can be expressed in the flat capacitor approximation as

$$C_{CF} = \frac{\varepsilon \varepsilon_0 S}{d - l_{CF}},$$

where $S$ is the effective filament cross-section area, $\varepsilon$ is the dielectric permittivity of the insulator material, and $\varepsilon_0$ is the electric constant. As $l_{CF} \to d$, $C_{CF} \to \infty$. In the experiment, the overload of the CSCM add-on lock-in amplifier took place at $t \approx 1.25$ s (figure 4a).

Figure 4b shows a dependence $l_{CF}(t)$ calculated from the one $C_{CF}(t)$ according to (1).

Once the dependence $l_{CF}(t)$ was obtained, one can calculate many other characteristics of the filament growth process. For example, a time dependence of the filament growth rate $v_g(t) = dl_{CF}(t)/dt$ is shown in figure 5a. The dependence $v_g(t)$ shown in figure 5c was calculated from the one $l_{CF}(t)$ in figure 4b by numerical differentiation with non-linear smoothing (7-point adjacent averaging). One can see $v_g$ to be almost constant at $t < 0.8$ s. Then $v_g$ increased rapidly and saturated at $t > 1$ s.

Figure 5c shows a dependence of $v_g$ on the electric field strength in the gap between the CF tip and the Ni sublayer $F$. The latter was calculated as

$$F(t) = \frac{V_g}{d - l_{CF}(t)}.$$

One can see in figure 5b that $v_g$ was almost constant at $F < 3 \cdot 10^6$ V/cm, increased abruptly at $F \approx 3 \cdot 10^6$ V/cm, and saturated again at $F > 5 \cdot 10^6$ V/cm. Such a behavior of the dependence $v_g(F)$ can be interpreted as follows. At low $F$ (that corresponds to low $l_{CF}$ and low $V_g$) $v_g$ is limited by the rate of arrival of the Ni ions (dispersed inside the ZrO$_2$(Y) film) to the growing Ni filament tip. However, at higher $F$ (corresponding to higher $V_g$), the electrochemical reaction of anodic oxidation of the Ni sublayer at the Ni/ZrO$_2$(Y) interface starts [8]. In this case, $v_g$ is limited by the anodic oxidation rate because all Ni ions generated at the Ni/ZrO$_2$(Y) readily arrive at the Ni filament tip.
To date, a lot of mathematical models for the CF growth have been published in the literature starting from the simplest current-driven memristor model [3]. However, very few studies on in situ monitoring CF (usually by X-TEM) have been published because such studies are extremely difficult and expensive. The results of the present study show the prospects of the CSCM technique in the in situ studies of the CF growth. This technique provides the information on the dynamics of the CF sizes, which can be compared to the modeling results directly. It should be stressed that such experiments can be carried out in ambient air. Also, more realistic models of the CF shape (e.g. a conical CF) can be used in future studies.

4. Conclusion
In the present study, we have demonstrated experimentally a capability of CSCM technique to trace the growth of the CF in the virtual memristors composed of the CAFM probe contact to the functional dielectric film on the conductive substrate and, moreover, to measure the time dependence of the CF dimensions, at least, semi-quantitatively. In this scope, the CSCM technique worked out in the present study seems to be very promising for application in future studies of the CF dynamics during the forming and RS processes in various material systems.

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