Materials Physics and Mechanics 39 (2018) 68-74 Received: November 1, 2017

BREAKDOWN AND CONDUCTIVITY SWITCHING IN NANOSIZED HAFNIUM DIOXIDE

Denis A. Podryabinkin*, Alexander L. Danilyuk

Belarusian State University of Informatics and Radioelectronics, P. Browka 6, 220013, Minsk, Belarus

*e-mail: arm@tut.by

Abstract. Atomic migration and electronic switching of bi-stable centers in conducting filaments formed in nanooxide based resistive random access memory (RRAM) cells are modeled and analyzed as competitive mechanisms determining their operation frequency. They are mediated by the filament growth dynamics. Atomic migration is responsible for a slow change of the filament resistivity with typical switching times in the millisecond range. Fast switching with the shortest nanosecond delay can be achieved using bi-stable electronic centers in the filaments. Possible configurations of such centers are discussed.
Keywords: conductivity switching, memory cell, nanooxide

1. Introduction

At the present time nanostructures based on hafnium dioxide are promising for using as gate insulators in MOSFETs (metal-oxide-semiconductor) and non-volatile resistive memory with random sampling (RRAM). Hafnium oxide has a high dielectric constant, a relatively high energy of the forbidden band, and forms a thermodynamically stable interface with silicon. It is worthwhile for resistive memory, since its dielectric breakdown leads to switching to a low-resistance state and creating the high density of traps that makes possible the long-term storage of charge (up to 10^6-10^7 s). Therefore, the fabrication methods of nano-sized hafnium dioxide on a silicon substrate and nanostructures based on it are being developed. At this, the electrical, structural and spectroscopic characteristics, as well as the peculiarities of hafnium dioxide properties appearing as a result of electroforming, are being studied [1, 2]. In this area practical results have been already achieved, the main of which is the production of a stable nanosized layer of hafnium dioxide, switchable by a low potential. However, there are still many unsolved problems concerning to identification of the most important mechanisms, namely switching hafnium dioxide from a high-resistance to a low-resistance state, current transfer in the presence of trap high concentration and contribution of thermal processes.

2. Model

We propose a model of breakdown and fast switching the conductivity of nanosized hafnium dioxide containing bistable electronic states. Such states in hafnium dioxide are obtained by electroforming in an electric field with creation of conductive current filaments (Fig. 1a). At the electrical breakdown of nanosized hafnium dioxide, the filaments of diameter about 50 nm are formed (Fig. 1b), strong heating of the material up to its boiling point taking place. In fact, there is the electrical explosion of channel material limited by solid walls. Forming plasma produces pressure on the channel walls that leads to the channel expansion, as well as to certain mass release from the channel due to local heating the electrodes. In its turn it produces not only to a deficiency of oxygen atoms in the channel, but leads also to releasing

http://dx.doi.org/10.18720/MPM.3912018_11

the compound itself [3]. Due to strong heating and the subsequent increase of pressure on the walls and electrodes, the channel substance is pressed against the walls, like spreading along them, a part of it is pushed closer to the anode, and a part of the electrode material, mainly of cathode, is pressed into the channel (Fig. 1c).

After removing the electrical impulse and cooling down the channel substance, i.e. after the electroforming has finished, the evaporated material deposits on the channel walls. At first it is amorphous, then after cooling and under the pressure in the anode region it turns into a glassy nonequilibrium disordered system. Between the cathode and the glassy region, there forms a zone where the substance is absent, i.e. a vacuum cavity.

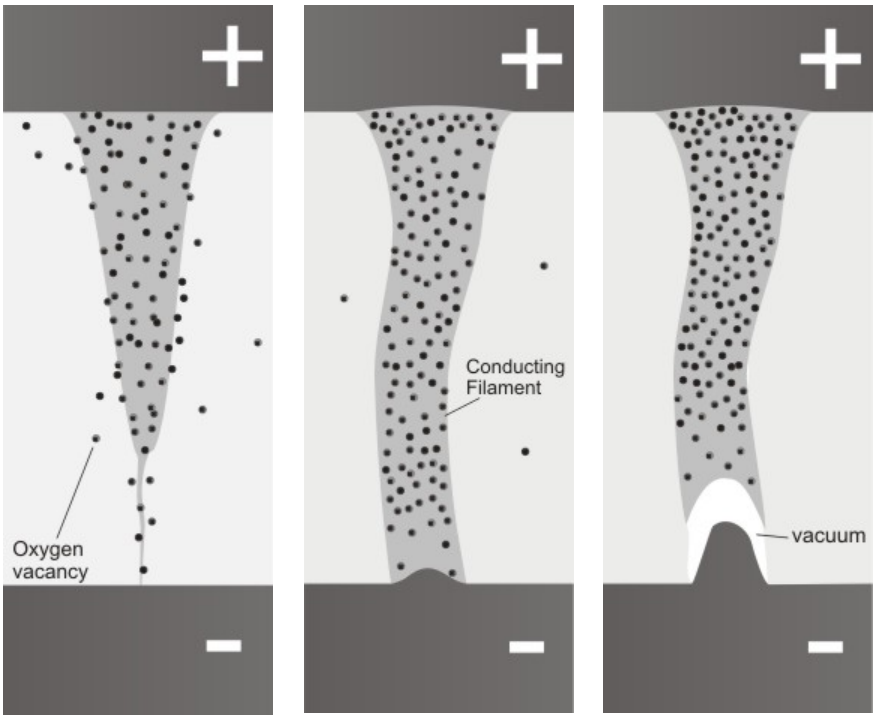

Fig. 1. Breakdown channel formation:
a) Initial stage; b) Heating the channel material; c) Final stage

Upon further applying the electric field, the current transfer mechanism changes. It is necessary to take into account the thermal emission of electrons from the cathode, they having energy higher than the cathode Fermi energy and can be accelerated in the vacuum gap. These electrons activate metastable trap states in the anode glassy region; facilitate its transition to a high-conductivity state without heating it up to melting and evaporation. Removing the field returns the system in a low-conductivity state. The anode glassy region can capture electrons, creating either a space charge after field removing or not forming it at all. In the first case, for the subsequent switching it is necessary to apply an external bias of opposite sign; this is a bipolar switching. In the second case, the opposite sign potential is not required, and we obtain a monopolar switching.

The current flow through the anode glassy region is realized by means of activation of the metastable trap states (Fig. 2). Several mechanisms are possible. One of them is the trap state excitation by the electron impact with energy of the order of several eV; here it is due to nonequilibrium hot electrons of the glassy region. The trap state excitation changes the ionization energy and produces cathodoluminescence with photon emission. For a bistable state, the interaction with hot electrons leads to transition to an excited state, decreasing their ionization energy up to delocalization. Besides in this case, the bistable trap state can pass

into an upper energy state not only by interacting with hot electrons, but under the influence of a noise and a periodic force. The noise appearance is facilitated by charge fluctuations induced by scattering hot electrons on defects. The periodic force is generated by vibration modes of the trap centers. Transition of the trap system to a highly conducting state occurs due to the stochastic synchronization effect connected with interaction of the traps [4]. It can be either Coulomb interaction or dipole one.

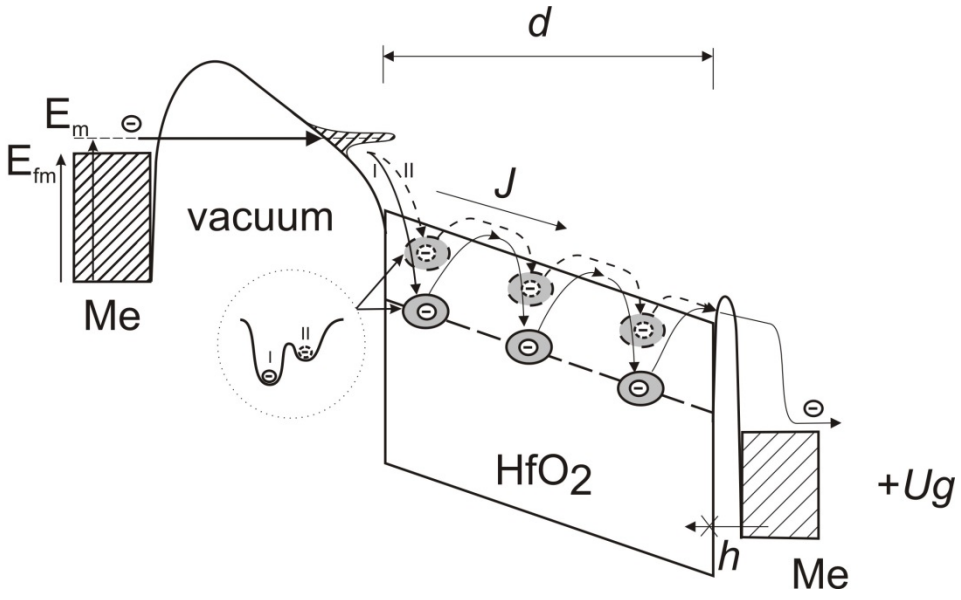

Fig. 2. Energy diagram of breakdown channel in hafnium dioxide with vacuum gap

For simulating the field emission the equations of Fowler-Nordheim model are usually used. This model is based on the Wentzel-Kramers-Brillouin approximation (WKB approximation). It is valid if the electron wavelength is less than the region of noticeable changing the electron potential energy. For rather complex potentials that vary at the de Broglie wavelength, the WKB approximation is not always applicable for the tunneling coefficient calculation because of restriction on the potential barrier shape. We use the phase functions method to model the tunnel emission from a cold cathode into a vacuum [5]. In this approach the wave function is not calculated, but only its changing due to the potential impact. The simplicity of the phase equation is connected with the fact that it is an ordinary first-order differential equation (Riccati equation). There is also the possibility of using various potential barriers, including those that depend on the electron momentum.

The reflection function $B(z)$ for potential barrier $U(z)$ can be written as [5]:

$$\frac{dB(z)}{dz} = -\frac{U(z)}{2ik}\left[\exp(ikz) + B(z)\exp(-ikz)\right]^2, \quad (1)$$

where z is the tunneling direction, $k=(8\pi^2 m^* E/h^2)^{1/2}$ is the wave vector of a tunneling electron.

The effective potential has the form

$$U(z) = \left(8\pi^2 m^* / h^2\right)\left(U_0 - qV(z) - q\varphi(z)\right), \quad (2)$$

where q is the electron charge, m^* is the electron effective mass for the corresponding spin component, E is the energy of a tunneling electron, h is the Planck constant, U_0 is the initial height of the potential barrier, $V(z)$ is the external field potential, $\varphi(z)$ is the potential of the image charges.

The reflection function modulus squared has the meaning of the reflection coefficient from the potential barrier: $R(z)=|B(z)|^2$. Assuming that $B(z) = a(z) + ib(z)$ and expanding

exp(±*ikz*), we obtain the following system of equations for determining the reflection function components:

$$\frac{da(z)}{dz} = \frac{U(z)}{2k}\left[-\sin(2kz) - 2b + (a^2 - b^2)\sin(2kz) - 2ab\cos(2kz)\right] \quad (3)$$

$$\frac{db(z)}{dz} = \frac{U(z)}{2k}\left[\cos(2kz) + 2a + (a^2 - b^2)\cos(2kz) - 2ab\sin(2kz)\right]. \quad (4)$$

The tunneling transparency coefficient of the barrier is:

$$T = \exp\left[\frac{1}{k}\int_0^d U(z)\left[b(z)\cos(2kz) - a(z)\sin(2kz)\right]dz\right], \quad (5)$$

where *d* is the potential barrier thickness.

To study the trap switching, a bistable switching model is used in the presence of a periodic force associated with the electron-phonon interaction and the noise impact. The general form of the time-dependent generalized configuration coordinate of the trap *x*(*t*) is [4]:

$$\frac{dx}{dt} = \frac{dV(x)}{dx} + A\cos(\omega t + \varphi) + \sqrt{2D}Noise(t), \quad (6)$$

where φ is the phase shift, *A* is the periodic impact amplitude, *D* is the noise level. The bistable potential of the trap state is:

$$V(x) = V_0(x^4 + \xi x^3 - \eta x^2), \quad (7)$$

where $V_0 = \frac{1}{2}k_0 a_0^2$, k_0 is the characteristic atomic quasi-elastic constant, a_0 ~0.1 nm is the characteristic atomic length, ξ and η are structure parameters, *x* is the configuration coordinate.

The simulation of switching bistable trap states in hafnium dioxide is carried out using the bistable oscillator model under the assumption that switching is induced by a noise and is described by the equation:

$$dy/dt = ay + by^2 + cy^3 + A\cos(\Omega t + \varphi) + \sqrt{2D}\xi(t), \quad (8)$$

where *y* is the generalized coordinate of a trap state, characterizing the form of its potential energy, *a, b, c* are the parameters determining the potential well shape of a trap, *A*, Ω, φ is the amplitude, the frequency and the phase of center oscillations, *D* is the noise intensity, $\xi(t)$ is the white noise generating function.

Using the equation system (8), the main regularities of fast conductivity switching of the oxide dielectrics with bistable electronic states in strong electric fields are revealed. The transition of bistable trap state to a high-conductivity state (upper metastable level) is stimulated by the noise or electron impact and occurs simultaneously due to the stochastic synchronization process [5] under the noise influence. The connection between the traps can be either due to the Coulomb interaction, or due to the dipole interaction. To simulate the synchronization of two symmetrically coupled bistable oscillators (traps), the system of differential equations is used:

$$\begin{cases} dx/dt = ax + bx^2 + cx^3 + \gamma(y - x) + A\cos(\Omega t + \varphi) + \sqrt{2D}\xi_1(t) \\ dy/dt = (a + \Delta)y + by^2 + cy^3 + \gamma(x - y) + A\cos(\Omega t + \varphi) + \sqrt{2D}\xi_2(t) \end{cases} \quad (9)$$

Here $\xi_{1,2}(t)$ are the white noise generating functions, γ is the coupling coefficient, Δ is the detuning parameter (the frequency deviation from a resonant frequency) of the second system with respect to the first one.

3. **Results and discussions**

The equation system (3-5) allows calculating the dependence of tunneling transparency coefficient on the wave vector (electron energy *E*) for the barrier described by the effective

potential $U(z)$. In this case, the value of $T(E)$ for the system under consideration determines the current density of the field emission into the breakdown channel. Figure 3 shows such dependence for a metallic point emitter in the breakdown channel of hafnium dioxide for various values of the electric field intensity F. The following parameters were chosen for simulation: R = 5-7 nm, r = 15-20 nm. Here r is the radius of the point emitter, R is the distance from the tip of the point emitter to the anode. The height of the surface barrier (work function) U_0 = 100-120 k_BT, the temperature T = 300-500 K, k_B being Boltzmann constant.

If the energy exceeds a certain value below the total barrier height, a significant increase in the tunnel transparency coefficient of the cathode is observed. However, the significant electron emission current arises only in the region of emitter Fermi energy. In this case the field emission dominates at the Fermi level of cathode (Fig. 3).

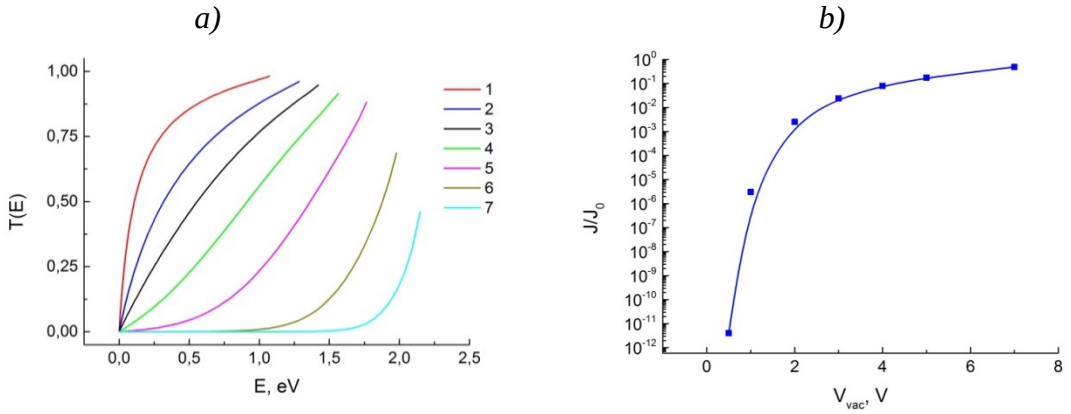

Fig. 3. Field emission coefficient of cathode in the hafnium dioxide breakdown channel as the function of a tunneling electron energy and the external field magnitude F (*a*).
Field emission current of cathode in the breakdown channel of hafnium dioxide, $J_0=(4\pi qm^*k_B^2T^2)/h^3$ (*b*)

The significant field emission current can arise at potentials in the vacuum gap above 2 eV. For the region of glassy hafnium dioxide the currents are hot since they are injected into a free zone with the energy 2-3 eV higher than the conduction band bottom (Fig. 2). These electrons irradiate the glassy hafnium dioxide of the breakdown channel changing the conduction mechanism due to transitions of metastable trap centers into a different charge state and due to the noise created by hot electrons, as well as by their direct impact on the metastable centers. In this case, the current transfer in the metastable region of the breakdown channel consists in trapping electrons at trap centers and their release due to changing their ionization energy, when they transfer from one bistable state to another (Fig. 2).

The simulation of electronic switching of bistable trap states was carried out on hafnium dioxide with the following parameters: the thermal ionization energy of traps being 0.48 eV, the oscillation frequency 10-12 GHz, the trap concentration 10^{19} cm^{-3}, and the noise intensity 0.08-0.15.

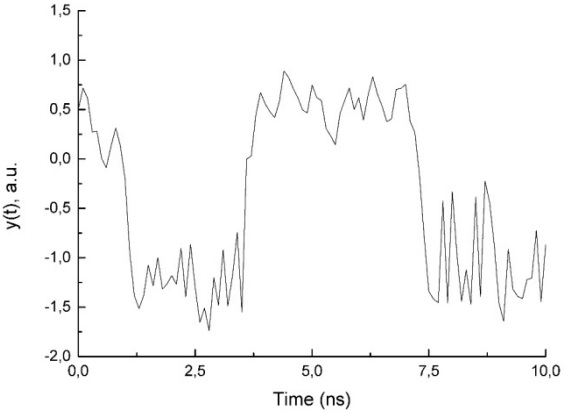

Fig. 4. Transition between metastable states of a bistable center caused by driving force and noise:
A=0.25, =0, =1, D =0.02, a=1, b=-1, c=-1

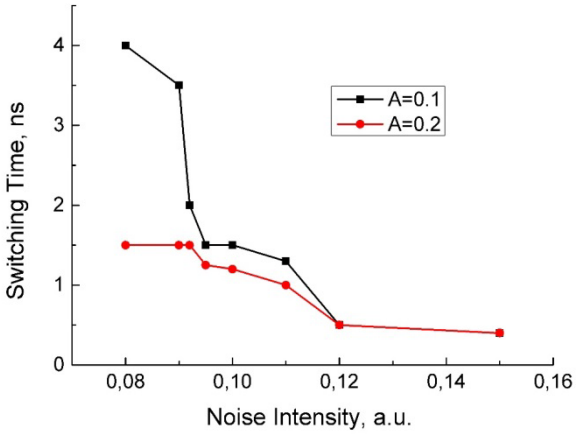

Fig. 5. Switching time vs noise intensity at different noise amplitude A

The calculations of the electronic properties of bistable centers have shown that in the presence of periodic impact and noise the transitions from one metastable state to another state are possible. These transitions substantially depend on potential well depth ratio and are determined by the noise level. Figure 6 shows the stochastic synchronization of two interacting traps under the influence of noise; at some time switching bistable trap states occurs synchronously.

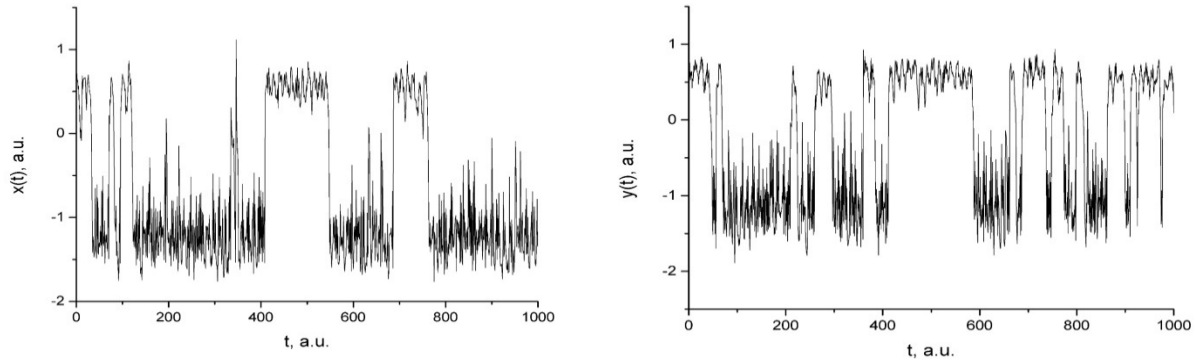

Fig. 6. Switching bistable trap states of two interacting traps under noise influence

4. Conclusions

In hafnium dioxide the mechanism of current transfer in the metastable region of the breakdown channel consists in the capture of electrons by trap centers and their release due to changing their ionization energy, when they transfer from one bistable state to another. The bistable potential of the trap center under the action of a weak periodic modulation undergoes the transition from one state to another only under the noise impact. The noise exposure leads to switching the trap state from one metastable state to another during a few nanoseconds. Upon the noise intensity growth, scattering the output signal increases and the switching occurs. With the growth of periodic impact amplitude, frequency switching from one state to another increases. The periodic frequency growth increases frequency switching, and with the phase growth, the time of finding the trap center in a metastable state; the characteristic switching time being of order ns. Synchronous switching under noise influence for interacting traps is shown.

Acknowledgments. *The work is supported by the Foundation for Basic Research of the Republic of Belarus (grant No. F15-028).*

References

[1] F. Pan, S. Gao, C. Chen, C. Song, F. Zeng, Recent progress in resistive random access memories: Materials, switching mechanisms, and performance // *Materials Science and Engineering R* **83** (2014) 1.

[2] P. Sheridan, K.-H. Kim, S. Gaba, T. Chang, L. Chen, W. Lu, Device and SPICE modeling of RRAM devices // *Nanoscale* **3** (2011) 3833.

[3] G.A. Vorob'ev, S.G. Ekhanin, N.S. Nesmelov, Electrical breakdown in solid dielectrics // *Physics of the Solid State* **47** (2005) 1083.

[4] L. Gammaitoni, P. Hänggi, P. Jung, F. Marchesoni, Stochastic resonance // *Rev. Mod. Phys.* **70(1)** (1998) 223.

[5] V.V. Babikov, *Method of Phase Functions in Quantum Mechanics* (Nauka, Moscow, 1976).