Percolation conductivity in hafnium sub-oxides

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In this study, we demonstrated experimentally that formation of chains and islands of oxygen vacancies in hafnium sub-oxides (HfOₓ, x < 2) leads to percolation charge transport in such dielectrics. Basing on the model of Efros-Shklovskii percolation theory good quantitative agreement between the experimental and theoretical data of current-voltage characteristics were achieved. Based on the percolation theory suggested model shows that hafnium sub-oxides consist of mixtures of metallic Hf nanoscale clusters of 1–2 nm distributed onto non-stoichiometric HfOₓ. It was shown that reported approach might describe low resistance state current-voltage characteristics of resistive memory elements based on HfOₓ.

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Hafnium oxide (hafnia, HfO₂) and sub-oxides (HfOₓ, x < 2) play extremely important roles in modern microelectronics. Hafnia is used in modern MOSFETs as high-k gate dielectric with low leakage currents1–4. Hafnium sub-oxides are the most promising materials to be used as active medium in resistive random access memory (RRAM)5,6, which might be used for universal memory combining the most favorable properties of both high-speed dynamic random access memory, and non-volatile flash memory7–11. RRAM has many advantages: a simple metal-insulator-metal (MIM) structure, a small memory cell, potential for 3D integration, high read and write operation speeds, low power consumption, and the ability to store information over the long term. A RRAM operation is principally based on switching back and forth from the insulating medium’s high resistance state (HRS) to a low resistance state (LRS) when a current flows. Conductivity of HfOₓ used as RRAM active medium is limited by ionization of charge carrier traps when RRAM is switched to the HRS state6,12,13. Unfortunately, unlike the flash memory, the fundamental physics mechanism of RRAM is still inadequate, but that is vital to realize the ultra-low-power memory array.

In this letter, we report that the charge transport mechanism is described in terms of percolation theory when hafnium-sub-oxides-based RRAM is switched to the LRS state.

Transport measurements were performed using a Hewlett Packard 4155B Semiconductor Parameter Analyzer and an Agilent E4980A Precision LCR Meter. All measurement equipment were protected against short circuiting with the current through the sample limitation of 1 μA.

The most commonly used LRS description in RRAM structures consists of conductive filament (CF), approximately 1–10 nm in diameter (D)14–16. The CF forming is cause by charged ion movements due to temperature gradients and electric fields16. It was supposed, that CFs in Ni/HfO₂/Si RRAM structures consist of nickel, migrated from the metal electrode15, but these assumptions were based on results of RRAM measurements in Ni/NiO/Ni- type structures (i.e. with NiO dielectric medium with Ni electrodes). However, CF has metallic temperature dependence of resistance

\[ (R – R_0) \propto (T – T_0) \]  

(here R₀ is the CF resistance at temperature T₀), with average resistivity in three order smaller than resistivity of pure Hf metal14.

Assuming, that the current-voltage characteristics (I-V) are described by Ohm’s law, we compared calculated I-V for Hf metal wire 8 nm long with diameters of 10 nm (dashed light green line in Fig. 1), 1 nm (dashed with dots dark green line in Fig. 1), and sub-stoichiometric HfOₓ CF14 (D = 1 nm, dark cyan dotted line in Fig. 1) with experiment results, indicated by the colored characters in
HfO\(_x\) nanoscale clusters (blue drops) and non-stoichiometric in Fig. 2(a). According to this model, the CF in hafnium nitrides was developed for SiO\(_x\) the structure of non-stoichiometric sub-oxides and sub-islands in HfO\(_x\). Results from the literature, the current should decrease exponentially with temperature growing, while following regarding the intermediate structural model into phases of Hf, HfO\(_x\), and HfO\(_2\)\(_x\). Therefore, we suppose that LRS conductivity is conditioned by the presence of a non-stoichiometric HfO\(_x\) islands in HfO\(_2\) matrix as HfO\(_x\) with \(y \lesssim 1.89\) splits into phases of Hf, HfO\(_x\) and HfO\(_2\). The overview on the structure of non-stoichiometric sub-oxides and sub-nitrides was developed for SiO\(_x\), SiN\(_x\), and SiO\(_x\)N\(_x\). A 2D structural image of non-stoichiometric HfO\(_x\), regarding the intermediate structural model\(^{20}\), is presented in Fig. 2(a). According to this model, the CF in hafnium sub-oxide consists of a mixture of metallic hafnium nanoscale clusters (blue drops) and non-stoichiometric HfO\(_x\) (green islands) distributed onto HfO\(_2\) matrix (yellow area). The current grows exponentially with temperature growing, while following results form the literature, the current should decrease with the temperature increasing (1). Fig. 2(c) is an energy diagram of HfO\(_x\) in the intermediate structural model. According to this plot, spatial fluctuations in the chemical composition of HfO\(_x\) lead to local band gap width spatial fluctuations. The maximal fluctuation of the energy scale is equal to the HfO\(_2\) band gap width of \(E_g = 5.6\,\text{eV}\). The work function of metallic hafnium is 4.0 eV. The maximal fluctuation scale of the HfO\(_x\) conduction band is 2.0 eV, which equals the electron barrier height of Hf/HfO\(_x\) interface. The hole energy barrier of Hf/HfO\(_2\) is 3.6 eV (Fig. 2(b)), which leads to the maximal fluctuation scale of the HfO\(_x\) valence band of 3.6 eV. The nanoscale fluctuations at the bottom of conduction band \(E_v\) and at the top of valence band \(E_v\) are close to those proposed in the model developed in\(^{24,25}\), as shown in Fig. 2(d). The charge transport in such electron systems can be described according to percolation. This model assumes that excited electrons with energy higher than the flow level \(E^r\) are delocalized, and driving round a random potential, transfer the charge. The hole conductivity is realized through the excitation of electrons with energy \(E^h\) to the Fermi level. These excitations form

**FIG. 1.** (Color online) Experimental RRAM current-voltage characteristics hysteresis (characters) in Si/TaN/HfO\(_x\)/Ni MIM structures at different temperatures. Black, red and blue solid lines present LRS simulations in terms of percolation model. Green lines model current-voltage characteristics in a semiconductor layer. The current through non-stoichiometric HfO\(_x\) CF with diameter of 1 nm.
hole-type quasiparticles, which transfer the charge. In other words, to be involved in transport processes, electrons and holes must overcome energy thresholds ($W_{e,h}$ here, and $W^e \neq W^h$ in general). The current-voltage characteristics are exponentials:\(^24\):

$$I(T) = I_0(T) \exp \left( \frac{(CeFaV_0^e)^{0.9}}{kT} \right), \quad (2)$$

where $I$ is the current, $I_0$ is the preexponential factor, $e$ is the electron charge, $F$ is the electric field, $a$ is the space scale of fluctuations, $V_0$ is the amplitude of energy fluctuation, $k$ is the Boltzmann constant, $C$ is a numeric constant, and $\nu$ is a critical index. The values of the constants were derived from Monte-Carlo simulations and evaluated at $C \approx 0.25^{24}$ and $\nu = 0.9^{25}$. Percolation energy threshold $W$ can be evaluated based on the temperature dependency of the preexponential factor:

$$I_0(T) \sim \exp \left( -\frac{W}{kT} \right). \quad (3)$$

The solid colored lines in Fig. 1 indicate the results of LRS simulations regarding the percolation model, given in (2). Numeric fitting returns the value of combination as $CaV_0^{0.9} = 0.45 \text{ nm} \cdot \text{eV}^{0.9}$, which corresponds to $V_0 = 1.9 \text{ eV}$ when $a = 1 \text{ nm}$ and $C = 0.25$. The slope of a fitting line in a ln($I_0$)-vs-$T^{-1}$ plate according to (3) corresponds to a percolation threshold of $W \approx 1.0 \text{ eV}$. Because $W \lesssim V_0 \lesssim 2.0 \text{ eV}$ (for electrons), we can estimate the space size of nanoscale fluctuations as $a \approx 1–2 \text{ nm}$.

Previous experiments in charge transfer have demonstrated that hafnia conductivity is bipolar (or two-band)$^{4,26–28}$ electrons are injected from a negatively shifted contact in the dielectric, and holes are injected from a positively shifted electrode in the dielectric. In our model, LRS conductivity can also be studied using electrons and holes. For the reason of simplicity, the current study was limited to considering monopolar electron conductivity.

The results demonstrate that charge transport in non-stoichiometric hafnium sub-oxides is described according to the percolation model in electron systems exhibiting potential nanoscale fluctuations. This approach can be applied to explain RAM in GeO$_x$- and SiO$_x$-based structures$^{29,30}$

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1. Z. Xu, M. Houssa, R. Carter, M. Naili, S. D. Gendt, and M. Heyns, Journal of Applied Physics 91, 10127 (2002).
2. T. P. Ma, H. M. Bu, X. W. Wang, L. Y. Song, W. He, M. Wang, H.-H. Tseng, and P. J. Tobin, IEEE Trans. Device Mater. Rel. 5, 36 (2005).
3. J. Robertson, Reports on Progress in Physics 69, 327 (2006).
4. L. Vandelli, A. Padovani, L. Larcher, R. G. Southwick, W. B. Knowlton, and G. Bersuker, IEEE Trans. Electron Devices 58, 2878 (2011).
5. L. Goux, P. Czarnecki, Y. Y. Chen, L. Pantisano, X. P. Wang, R. Degraeve, B. Govoreanu, D. J. Jurczak, M. and Wouters, and L. Altimime, Applied Physics Letters 97, 243509 (2010).
6. Z. Wang, H. Y. Yu, X. A. Tran, Z. Fang, J. Wang, and H. Su, Physical Review B 85, 195322 (2012).
7. D. B. Strukov, G. S. Snider, D. R. Stewart, and R. S. Williams, Nature 453, 80 (2008).
8. J. J. Yang, M. D. Pickett, X. Li, D. A. A. Ohlberg, D. R. Stewart, and R. S. Williams, Nature Nanotechnology 3, 429 (2008).
9. M.-J. Lee, S. Han, S. H. Jeon, B. H. Park, B. S. Kang, S.-E. Ahn, K. H. Kim, C. B. Lee, C. J. Kim, I.-K. Yoo, D. H. Seo, X.-S. Li, J.-B. Park, J.-H. Lee, and Y. Park, Nano Letters 9, 1476 (2009).
10. J. Borchetti, G. S. Snider, P. J. Kuekes, J. J. Yang, D. R. Stewart, and R. S. Williams, Nature 464, 873 (2010).
11. M.-J. Lee, C. B. Lee, D. L. Seo, S. Lee, R. Chang, J. H. Hur, Y.-B. Kim, C.-J. Kim, D. H. Seo, S. Seo, U.-I. Chung, I.-K. Yoo, and K. Kim, Nature Materials 10, 625 (2011).
12. S. D. Ganchev, E. Ziemann, W. Prett, I. N. Yassievich, A. A. Istratov, and E. R. Weber, Phys. Rev. B 61, 10361 (2000).
13. D. R. Islamov, V. A. Gritsenko, C. H. Cheng, and A. Chin, Applied Physics Letters 105, 229901 (2014), arXiv:1409.6887.
14. G. Bersuker, D. C. Gilmer, D. Veksler, P. Kirsch, L. Vandelli, A. Padovani, L. Larcher, K. McKenna, A. Shluger, V. Iglesias, M. Porti, and M. Nafria, Journal of Applied Physics 110, 124518 (2011).
15. T.-H. Hou, K.-L. Lin, J. Shieh, J.-H. Lin, C.-T. Chou, and Y.-J. Lee, Applied Physics Letters 98, 105511 (2011).
16. S. Ambrogio, S. Balatti, D. C. Gilmer, and D. Ielmini, IEEE Electronic Device Lett. 61, 2378 (2014).
17. C.-H. Cheng, F.-S. Yeh, and A. Chin, Advanced Materials 23, 902 (2011).
18. V. N. Kruchinin, T. V. Perevalov, V. S. Aliev, V. A. Shvetz, D. R. Islamov, V. A. Gritsenko, and I. P. Prosvirin, (unpublished).
19. K. Hübner, Journal of Non-Crystalline Solids 35–36, Part 2, 1011 (1980).
20. V. N. Novikov and V. A. Gritsenko, Journal of Applied Physics 110, 014107 (2011).
21. V. A. Gritsenko, R. Kwok, H. Wong, and J. B. Xu, Journal of Non-Crystalline Solids 297, 96 (2002).
22. V. A. Gritsenko, J. B. Xu, R. W. M. Kwok, Y. H. Ng, and I. H. Wilson, Physical Review Letters 81, 1054 (1998).
23. V. Afanas’ev, Internal Photoemission Spectroscopy: Principles and Applications (Elsevier Science, Amsterdam, 2008) p. 312.
24. B. I. Shklovskii, Soviet Physics of Semiconductors, 13, 53 (1979).
25. B. I. Shklovskii and A. L. Efros, Physics-Uspekhi 18, 845 (1975).
26. D. R. Islamov, V. A. Gritsenko, C. H. Cheng, and A. Chin, Applied Physics Letters 99, 072109 (2011).
27. T. Ando, N. D. Sathaye, K. V. R. M. Murali, and E. A. Cartier, IEEE Electron Device Lett. 32, 865 (2011).
28. Y. N. Novikov, Journal of Applied Physics 113, 024109 (2013).
29. A. V. Shaposhnikov, T. V. Perevalov, V. A. Gritsenko, C. H. Cheng, and A. Chin, Applied Physics Letters 100, 243506 (2012).
30. A. Mehonic, S. Cueff, M. Wojdak, S. Hudziak, O. Jambois, C. Labb, B. Garrido, R. Rizk, and A. J. Kenyon, Journal of Applied Physics 111, 074507 (2012).