ANODIC FORMATION OF HfO_2 NANOSTRUCTURE ARRAYS FOR RESISTIVE SWITCHING APPLICATION

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Abstract

Thin dielectric films are actively investigated as materials for novel resistive random-access memories based on resistive switching effect in metal/insulator/metal structures. Thin HfO_2 films are of particular interest due to the high thermal stability, low operating voltages of resulting devices, and complementary metal-oxide-semiconductor technology compatibility of this material. In this study, we investigate the resistive switching behavior of nanostructured HfO_2 film embedded in a porous anodic alumina matrix. The film was synthesized via self-organized electrochemical anodizing of a sputter-deposited Al/Hf bilayer on a Si substrate in an oxalic acid solution. The film was investigated by scanning electron microscopy. Simple metal/insulator/metal devices were prepared by sputter-deposition of Pt top electrodes through a shadow mask onto the nanostructured film. Assembled devices were characterized by I-V measurements. A bipolar eight-wise resistive switching was obtained, demonstrating a highly repeatable and stable low-voltage behavior in a set potential range. The achieved results indicate the high potential of the anodizing technique as an alternative to commonly used methods for producing insulating thin films for resistive random-access memory application.

Keywords: Resistive switching, anodizing, hafnium oxide, porous anodic alumina, memristor

1. INTRODUCTION

Resistive random-access memory (ReRAM) based on simple metal/insulator/metal (MIM) stacks is nowadays seen as a notable candidate for next-generation non-volatile memories, neuromorphic computing, alternative logic operations, or selector devices [1]. The demanded scalability of ReRAM systems to nano dimensions makes the fabrication, control, and prediction of their properties very challenging. Standard methods for producing the key elements of nanoscale ReRAM systems, such as atomic layer deposition, chemical vapor deposition, and pulsed laser deposition [2] require high-budged equipment, ultra-high vacuum conditions, and substantial consumption of energy. As an alternative approach, metal-oxide films for ReRAM can be formed by the cheap and accessible anodizing method [3]. The main benefit of the anodizing method is its simplicity since vacuum conditions or elevated temperatures are not required. Another notable advantage is that the substrate metal is already integrated into the device as the bottom electrode after the anodizing. Moreover, anodization of aluminum superimposed on a metal of interest can be utilized to create nanoscale arrays of various 3-D metal-oxide nanostructures inside the porous anodic alumina (PAA) film [4]. Such metal-oxide nanoarrays embedded in the PAA matrix may allow achieving resistive switching effects within the individual spatially separated nanostructures, thus introducing a new behavior advantageous to the continuous oxide films.

One of the most prominent oxides that can be utilized in metal/oxide/metal stacks for ReRAM fabrication is HfO_2. Owing to low operating voltages, high thermal stability, and full compatibility with complementary metal-oxide–semiconductor technology, HfO_2-based films can be utilized in a variety of low-cost resistive switching devices with simple circuitry [5]. Recently developed anodizing method for processing Al/Hf bilayer films [6] allows for creating thin HfO_2 layers densely covered by the nonstoichiometric nanoscale 3-D HfO_{2-x} structures.

Such nanoscale 3-D features might significantly affect resistive switching behavior of the films provided the population density of the nanostructures may potentially be as high as 10^{11} cm^{-2}. Moreover, each HfO_2 nanostructure size is comparable with the size of a conductive filament, which forms within the metal-oxide under polarization and is a primary phenomenon responsible for resistive switching behavior [7]. Investigation of resistive switching in the nanostructured HfO_2 films can potentially offer insights needed to commercialize anodically prepared oxides in ReRAM devices.

Here we report the fabrication of MIM stacks based on HfO_2 nanostructured layers prepared via the PAA-assisted anodization of Al/Hf bilayers on substrates. MIM micro-devices were assembled by magnetron sputtering of top Pt electrodes. The nanostructured HfO_2-in-Al_2O_3 films and the assembled microdevices were examined by high-resolution scanning electron microscopy (SEM). The electrical properties of the devices were investigated by I-V measurements.

2. EXPERIMENTAL

2.1. Sample preparation

Si wafer covered with 380 nm of thermally grown SiO_2 was used as a starting substrate for the sputter-deposition. A 100 nm thick Hf layer followed by an 80 nm thick Al layer were deposited via magnetron sputtering from Hf and Al targets of respectively 99.95% and 99.999% purity. Anodization of sputter-deposited Al/Hf bilayer film was carried out in 0.6M $(COOH)_2$ aqueous solution by sweeping potential from 0 to 30 V at a rate of 0.5 V s^{-1} followed by 30 s of current decay. Subsequently, after the anodization process, reanodization was performed in the same electrolyte by sweeping potential from 30 to 80 V at a rate of 5 V s^{-1} followed by 60 s of current decay. A two-electrode polytetrafluoroethylene anodizing cell was used for anodization; a more detailed description of the anodizing setup is available elsewhere [8]. In selected samples, the PAA overlayer was completely dissolved in a selective etchant (0.45 M H_3PO_4, 0.2 M Cr_2O_3) heated to 65 ^oC. Prior to device fabrication, the PAA pore widening procedure was performed by dipping the samples in the selective etchant for 60 s.

2.2. Sample characterization

The morphology of the anodic films was examined by a FEI Verios 460L High-Resolution Scanning Electron Microscope utilizing InBeam secondary electron detector and magnetic immersion lens at 15 keV accelerated voltage.

2.3. Device fabrication and electrical characterization

Resistive switching devices were fabricated by depositing Pt top electrodes onto the oxide arrays via magnetron sputtering through a shadow mask. The I-V curves were recorded at ambient conditions by a Keithley Model 4200A-SCS Parameter Analyzer. Samples were mounted on a CASCADE M150 probe station equipped with magnetic micromanipulators and tested by applying a potential difference between the upper (Pt) and bottom (Hf) electrodes. In all measurements, the top Pt electrode was grounded while the voltage was applied to the bottom Hf electrode. To avoid an electric breakdown in the film, a compliance current of 10 mA was set during the positive polarization.

3. RESULTS AND DISCUSSION

3.1. The film morphology and device assembly

Anodizing of sputter-deposited Al/Hf bilayer films was expected to create a network of HfO_2 nanostructures protruding within the pores of the PAA matrix. Generally, the process involves converting the upper Al layer to PAA by anodizing in an acidic solution followed by anodizing the underlying Hf through the alumina nanopores.

The growing hafnium oxide mixes to some extent with the alumina barrier layer and further protrudes inside the pores. Additionally, reanodizing to higher voltages can be carried out to achieve a better fulling of the alumina pores with hafnium oxide. Full aspects of the PAA-assisted anodization of Al/Hf bilayer films were covered in our previous work [6].

Figure 1a shows a 3-D view of the film derived from the anodized/reanodized Al/Hf bilayer after dissolving the PAA layer. Thus, the approach resulted in an array of spatially separated 65 nm tall nanocones protruding from the oxide surface. The nanocones are separated from the Hf substrate by the oxide dimples of about 45 nm in depth.

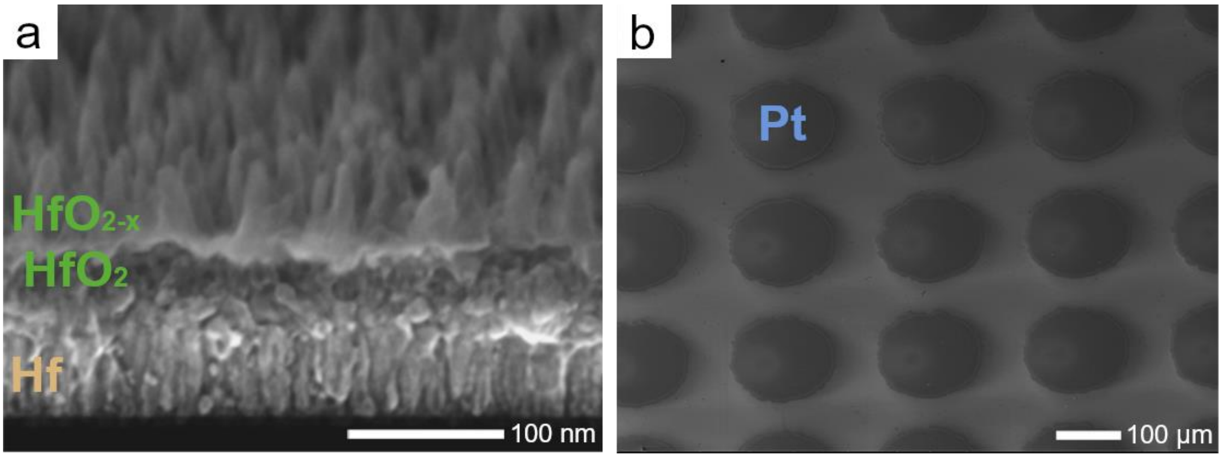

Figure 1 (a) SEM 3-D view of the anodized HfO_2 film after the PAA dissolution, (b) SEM top view of Pt contacts formed on the oxide surface via magnetron sputtering

To assemble MIM resistive switching devices, the PAA layer was not dissolved after anodizing but the pore widening procedure was carried out to make the pore mouths more expanded. Multiple microscale Pt/HfO_2-in-Al_2O_3/Hf stacks were assembled by sputter-deposition of round Pt contacts (**Figure 1b**), each of about 0.1 mm^2. During the sputter deposition, Pt was expected to permeate the PAA pore mouths, sandwiching the PAA-embedded HfO_2 nanostructures between the top Pt and the bottom Hf electrodes. The schematic design of the fabricated device based on the Pt/HfO_2-in-Al_2O_3/Hf stack alongside with the electrode setup for I-V characterization is presented in **Figure 2**.

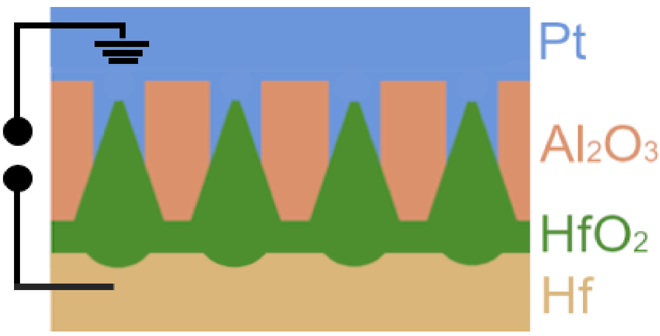

Figure 2 Schematic representation of the assembled MIM microdevice based on the Pt/HfO_2-in-Al_2O_3/Hf stack and the electrode setup for I-V characterization

3.2. Electrical characterization

Measured I-V characteristics of the assembled MIM microdevice are shown in **Figure 3**. The I-V cycling was performed in sequences following the pattern 0 → +1.7→ −1.9 → 0 V. A sweep rate of 250 mV s^{-1} and a compliance current of 10 mA was used for recording I-V data. The device appears to show a bipolar eight-wise switching. During the voltage sweep in the positive direction, the device demonstrates stable switching from the high resistance state (HRS) to the low resistance state (LRS), so-called SET process. The SET process is stable within low values of V_{SET} between 1.05 and 1.30 V. During subsequently sweeping the voltage in the negative direction, the device switches from acquired LRS back to the HRS via a RESET process. The RESET process is also highly stable with V_{RESET} values ranging between -1.70 and -1.75 V. The fabricated device demonstrates an excellent reproducibility of the resistive switching behavior throughout continuous I-V sweeps.

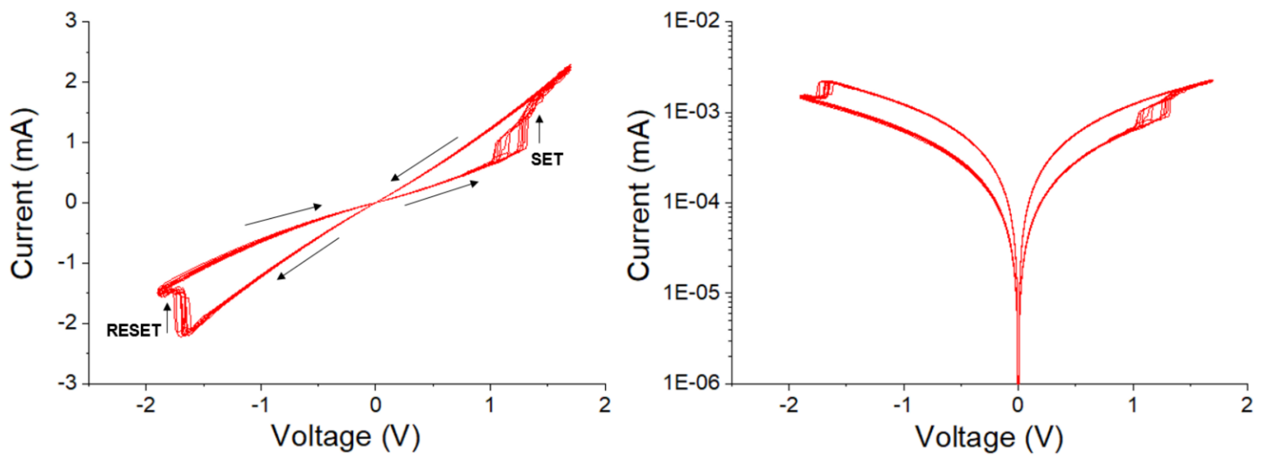

Figure 3 Measured I-V characteristics of MIM microdevices based on the Pt/HfO_2-in-Al_2O_3/Hf stacks

The mechanism responsible for the changes between the HRS and LRS states occurring in the HfO_2 nanostructured film sandwiched between the two metallic electrodes is not yet fully understood. However, the observed switching characteristics can be explained by forming and rupturing a conductive filament (CF) inside the individual HfO_2 nanostructures induced by the electric field, as the most generally accepted mechanism of resistive switching [9]. The initial distribution of oxygen vacancies in the dielectric HfO_2 layer might significantly affect its resisting switching behavior. The HfO_2 nanostructured films grown via the PAA-assisted anodizing of Al/Hf bilayers are known to possess unevenly distributed metastable HfO_{2-x} suboxides, resulting in a concentration gradient of oxygen vacancies across the film depth [6]. When a positive voltage is applied to the bottom Hf electrode, the abundant oxygen vacancies migrate towards the Pt cathode and serve as nuclei of CF. Possibly, the growing CF acts as an extension of the cathode towards the anode. With the assist of the applied electric field, the growing CF extends throughout the whole film thickness and creates a conductive path, setting a device to the LRS. Considering that the CF grows from the negatively charged Pt electrode to the positively charged Hf electrode, the thinnest region of the CF might be located at the Hf cathode. Thus, negatively biasing the Hf electrode would generate an extensive amount of Joule heat in the thinnest part of the CF, accelerating the mobility of vacancies in a localized region. Rapidly migrating vacancies then would be annihilated by oxygen ions on the film interface and grain boundaries, resulting in a rapture of the CF and resetting the device to the HRS [10]. Our MIM microdevice, based on the Pt/HfO_2-in-Al_2O_3/Hf stack, shows the excellent repeatability of forming and rapturing the CF throughout multiple I-V measurements.

In summary, the findings of the I-V tests demonstrated that a reliable low voltage resistive switching behavior could be obtained in the experimental memristive device utilizing the nanostructured HfO_2 films. In our work to date, the HfO_2 nanostructures have been scaled down to ~50 nm, which might already be comparable with the size of the conductive filament that forms within the oxide. In a future work, a much larger number of HfO_2 nanostructures, up to 10^{11} cm^{-2}, scaled-down to about 10 nm and embedded in a PAA matrix may be fabricated, potentially enhancing the device properties. Altering the electrical properties of the anodic nanostructured HfO_2 films by air or vacuum annealing is also to be considered for improving the memristive behavior.

CONCLUSION

Nanostructured HfO_2-in-Al_2O_3 films were prepared via the PAA-assisted anodizing of sputter-deposited Al/Hf bilayers and utilized as a solid electrolyte in memristive microdevices based on a simple metal/insulator/metal architecture. Top metallic electrodes were formed by sputter-deposition of Pt through a shadow mask. The fabricated Pt/HfO_2-in-Al_2O_3/Hf stacks were I-V cycled in a potential range of 1.7 to -1.9 V, revealing a reliable resistive switching behavior with a low onset voltage. The narrow dispersion of SET and RESET voltages was observed during the I-V cycling with V_{SET} between 1.05 and 1.30 V and V_{RESET} between -1.70 and -1.75 V. The devices demonstrate reproducible resistive switching over multiple I-V cycles.

This study contributes to understanding and utilizing anodically prepared nanostructured oxides as solid electrolytes in MIM based ReRAM devices. The nanostructured HfO_2-in-Al_2O_3 films fabricated via the PAA-assisted anodization can be used to manufacture low-cost and reliable memristive devices. It is of high interest to further explore their properties towards advancing the switching and memristive effects and creating relevant technology for incorporating the MIM-based nanostructured HfO_2 resistive switching stacks in a ReRAM prototype.

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REFERENCES

[1] MAZUMDER P., KANG S. M., WASER R. Memristors: devices, models, and applications. In: *Proceedings of the IEEE*. 2012, vol. 100, no 6, pp. 1911-1919.

[2] MOHAMMAD, B., ABI JAOUDE, M., KUMAR, V., AL HOMOUZ, D. M., NAHLA, H. A., AL-QUTAYRI, M., and CHRISTOFOROU, N. State of the art of metal oxide memristor devices. *Nanotechnology Reviews.* 2016, vol. 5, no. 6, pp. 311-329.

[3] ZAFFORA, A., MACALUSO, R., HABAZAKI, H., VALOV, I., and SANTAMARIA, M. Electrochemically prepared oxides for resistive switching devices. *Electrochimica Acta*. 2018, vol. 274, pp. 103-111.

[4] MOZALEV, A., SMITH, A. J., BORODIN, S., PLIHAUKA, A., HASSEL, A. W., SAKAIRI, M., and TAKAHASHI, H. Growth of multioxide planar film with the nanoscale inner structure via anodizing Al/Ta layers on Si. *Electrochimica Acta.* 2009, vol. 54, no. 3, pp. 935-945.

[5] CHEN, L., DAI, Y. W., SUN, Q. Q., GUO, J. J., ZHOU, P., and ZHANG, D. W. Al2O3/HfO2 functional stack films based resistive switching memories with controlled SET and RESET voltages. *Solid State Ionics.* 2015, vol. 273, pp. 66-69.

[6] MOZALEV, A., BENDOVA, M., GISPERT-GUIRADO, F., and LLOBET, E. Hafnium-oxide 3-D nanofilms via the anodizing of Al/Hf metal layers. *Chemistry of Materials*. 2018, vol. 30, no. 8, pp. 2694-2708.

[7] SUN, W., GAO, B., CHI, M., XIA, Q., YANG, J. J., QIAN, H., and WU, H. Understanding memristive switching via in situ characterization and device modeling. *Nature communications*. 2019, vol. 10, no. 1, pp. 1-13.

[8] MOZALEV, A., CALAVIA, R., VAZQUEZ, R. M., GRACIA, I., CANÉ, C., CORREIG, X., VLIANOVA X., GISPERT-GUIRADO, F., HUBALEK, J., and LLOBET, E. MEMS-microhotplate-based hydrogen gas sensor utilizing the nanostructured porous-anodic-alumina-supported WO3 active layer. *international journal of hydrogen energy*. 2013, vol. 38, no. 19, pp. 8011-8021.

[9] MEENA, J. S., SZE, S. M., CHAND, U., and TSENG, T. Y. Overview of emerging non-volatile memory technologies. *Nanoscale research letters*. 2014. vol. 9, no. 1, pp. 526.

[10] PAN, F., GAO, S., CHEN, C., SONG, C., and ZENG, F. Recent progress in resistive random access memories: materials, switching mechanisms, and performance. *Materials Science and Engineering: R: Reports*. 2014, vol. 83, pp. 1-59.