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TiN-Mediated Multi-Level Negative Photoconductance of the ZrO_2 Breakdown Path

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ABSTRACT We present new evidence that the non-volatile negative photoconductivity (NPC) response of the ZrO_2 breakdown path can be suppressed or tuned to different levels by repeated application of a positive voltage-bias on the TiN electrode prior to light exposure. A negative voltage-bias does not produce such a tuning effect but can restore the NPC response suppressed by the positive voltage-bias before a re-breakdown step. In samples with a non-metal (Si) electrode, the NPC tuning effect is absent indicating that a positively biased TiN electrode is needed to produce the tuning effect. We hypothesize that a positive voltage may induce the migration of Ti ions into the vacancy sites in the breakdown path. This then prevents the photo-assisted recombination of the interstitial-vacancy defect pairs, leading to a modulated NPC response. A negative voltage-bias expels the Ti ions back to the electrode and restores the NPC response.

INDEX TERMS High-k oxide, negative photoconductivity, optical sensor, plasmonic sensor, soft electrical-breakdown, silicon dioxide, wide-bandgap oxides.

I. INTRODUCTION

Wide bandgap oxides such as SiO_2, HfO_2, ZrO_2, etc. have played an integral role in the advancement of the CMOS technology. Besides serving as the gate oxide, they have also been intensively investigated for application in the resistive memory device [1]–[6]. Their relatively large bandgaps ($>$ 5 eV), have made them thermally stable and resistant to electrical breakdown [7] but non-photo-responsive. Hence, they are not used as the active components for optical applications.

Recent studies have shown that after electrical soft-breakdown (SBD) of SiO_2, HfO_2 and ZrO_2, the breakdown site can be partially or fully restored by exposure to white light [8]–[10]. Because the breakdown current is decreased upon illumination, the effect has been termed "negative photoconductivity" (NPC) [8, Fig. 2]. Through controlling the exposure dose, the breakdown current can be decreased to different levels [8, Fig. 3(b)]. Re-testing of the restored breakdown sites revealed a time-dependent-dielectric- breakdown distribution like the first SBD [10, Fig. 9(b)], indicating that complete restoration was achieved at numerous locations. It has been proposed that photo-induced migration of surrounding oxygen interstitials leads to their recombination with vacancy sites in the breakdown path, which in turn restores the breakdown oxide partially or completely. While the exact mechanism is still elusive, the finding suggests the possibility of using these oxides as active components in optical applications.

In this paper, we report a new effect related to the TiN electrode. Specifically, the NPC response of the ZrO_2 breakdown path, under a given illumination condition, can gradually be suppressed by applying positive-voltage sweeps to the TiN (relative to a non-metal counter-electrode) prior to light exposure. The suppressed NPC response can later be restored by negatively biasing the TiN and followed by a re-breakdown step. Such a behavior is, however, absent in the ZrO_2/Si stack (non-metal electrode). The results show that the breakdown path has a TiN-mediated multi-level

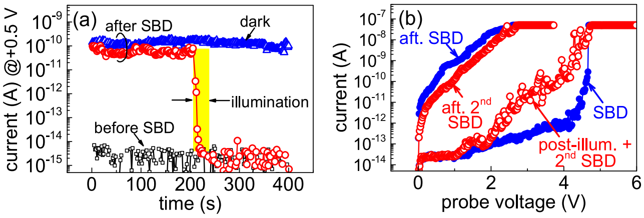


FIGURE 1. (a) Evolution of leakage current through a breakdown path in the ZrO_2/TiN stack. After soft-breakdown (SBD) was induced using a positive-probe-voltage sweep, measurement was first made in the dark for 400 s. In the second measurement, exposure to white light for 30 s was made, which saw the current decreasing abruptly upon illumination. (b) Current-voltage curves for the oxide region studied. The average breakdown field of the first SBD is ~12 MV/cm.

programmable NPC property. Similar behaviors are also obtained for SiO_2 and other electrodes (Cu, Ni, and Ti). A possible mechanism is proposed.

II. EXPERIMENTAL DETAILS

The test samples consist of the ZrO_2/TiN stack, fabricated on a p-Si substrate. After HF cleaning, a Ti adhesion layer was first deposited, followed by the reactive-sputter deposition of a 50-nm thick TiN bottom electrode. The ZrO_2 layer is 4 nm thick and was grown by atomic-layer deposition. Samples with the same thickness of ZrO_2 deposited directly onto the p-Si were also fabricated. The samples were loaded into an ultra-high vacuum conductive atomic force microscope (C-AFM) system for measurement. A diamond-coated Si cantilever probe served as the top *non-metal* electrode. The ambient pressure was maintained at 3×10^{-10} Torr, which excludes the possibility of anodic oxidation.

The nanoscale spatial resolution of C-AFM has enabled current conduction through a very localized region to be studied [11]–[13]. The probe force was incrementally increased from a low value until topography and current maps were successfully obtained, to minimize mechanical damage to the thin ZrO_2. Negligible low-voltage pre-breakdown leakage (Fig. 1) and the relatively high breakdown field (~12 MV/cm) [14] confirmed minimal oxide damage. After probe-oxide contact, the feedback circuit and laser were disabled to prevent interference to NPC response measurement, in accordance to other studies on photoactive materials [15], [16]. A similar approach of feedback disablement was adopted in our earlier study [17]. SBD was induced by a voltage ramp supplied by a parameter analyzer to the probe, with the TiN or Si electrode grounded. The breakdown current compliance was capped at 50 nA or below, necessary for minimizing hard breakdown due to the extremely localized probe contact area (~20 nm^2) [8]. Exposure of the breakdown path to white light was achieved by a LED lamp position at a quartz window of the C-AFM chamber. Further details of the measurement set-up can be found in [8].

III. RESULTS AND DISCUSSION

The NPC behavior of a breakdown path in the ZrO_2/TiN stack is depicted in Fig. 1. The resistivity of the breakdown region is $\sim 10^3$ Ω.cm, which implies a semiconducting-like nature. The relatively low breakdown current (~0.1 nA) results primarily from the extremely small breakdown area. An abrupt decrease in the leakage current can be clearly observed upon exposure to white light, whereas the current remained nearly constant throughout when measurement was made in the dark (Fig. 1(a)). A post-illumination voltage-sweep yielded a partially "recovered" current-voltage curve (open circle; Fig. 1(b)), indicating that the breakdown path was disrupted by the white-light illumination. Direct evidence on the disruption of breakdown-path conduction was earlier provided by current maps of the breakdown region obtained before and after illumination ([8, Fig. 4]). For the breakdown and measurement conditions used, a current window (defined as the ratio of the pre- to pos-illumination current) of $>10^4$ is obtained.

Interestingly, the degree by which the current is quenched (or the current window) is gradually reduced if the breakdown path was subjected to multiple negative-voltage sweeps applied on the C-AFM probe (or positive-voltage sweeps applied on the bottom TiN electrode) prior to white-light illumination. This is illustrated in Fig. 2(a) for a breakdown location first induced using a negative-probe-voltage sweep. After SBD, the breakdown path was subjected to a negative-probe-voltage sweep again before it was exposed to white light. An NPC response was recorded but the current did not decrease completely to the measurement floor (see Fig. 1(a)). SBD was then reinitiated at the same location and the procedure was repeated several times. In each repetition, the breakdown path was subjected to an increasing number of negative-probe- voltage sweeps before it was exposed to white light. Remarkably, the current window gradually narrows down as the number of pre-exposure negative-voltage sweeps is increased. The window for the case of 40 negative-probe-voltage sweeps is only ~3×, a significant drop as compared to $\sim 10^4 \times$ in Fig. 1(a).

Photo-assisted recombination between oxygen dislodged from the breakdown location (and situated in surrounding interstitial positions) and vacancies in the breakdown path has been proposed to explain the NPC behavior [8]. The spatial distribution of interstitial oxygen is shown to depend on the Joule heating at the breakdown site [18]. A relevant question would be whether Joule heating caused by the multiple negative-voltage sweeps prior to light exposure have increased the lateral propagation of the interstitial oxygen, thereby limiting subsequent photo-assisted interstitial-vacancy recombination (hence recovery by light).

To check this, different numbers of positive-probe-voltage sweeps were also applied to a breakdown path before it was exposed to white light, following the procedure outlined above (Fig. 2(b)). In this case, the prior positive-probe-voltage sweeps did not have any effect on the current level after illumination. Regardless of the number of sweeps, the current is always decreased to the measurement floor upon exposure to white light. From this observation, one may rule out the possible Joule heating

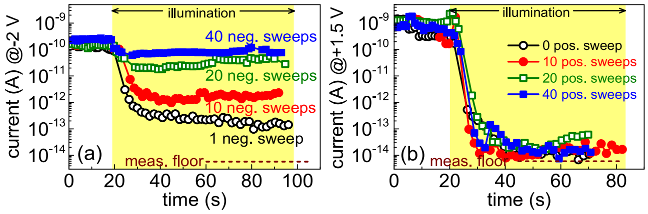


FIGURE 2. **(a) The level to which the current is decreased depends on the number of negative-voltage sweeps applied to the C-AFM probe before illumination. (b) Such dependence is not seen in the case where positive-voltage sweeps were applied before illumination. The negative- or positive-voltage sweep was made from 0 to −5.5 V or +5.5. V, subject to a current compliance of 50 nA.**

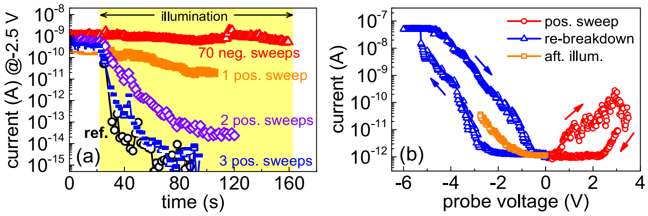


FIGURE 3. **(a) Restoration of near-complete loss of NPC behavior of a breakdown path by positive-probe-voltage sweeping. The "ref." curve is for the case without any applied negative-probe-voltage sweep before illumination. (b) Current-voltage measurements in the following order after the loss of NPC behavior in (a): 1) positive-voltage sweep; 2) negative-voltage sweep for re-initiation of SBD and 3) negative-voltage sweep after white-light exposure.**

effect mentioned above. The results in Fig. 2(a) are thus unique to the case of negative-probe-voltage biasing. The different post-illumination current levels indicate that the NPC response can be tuned or programed by a positive voltage-bias on the TiN electrode.

The loss of current window in the case of negative-probe- voltage biasing can be restored following several positive- probe-voltage sweeps, as illustrated in Fig. 3(a). A breakdown path was first created under negative-probe-voltage sweeping and exposed to white light, yielding the usual significant decrease in current (ref.). SBD was re-initiated and 70 consecutive negative-probe-voltage sweeps were applied. Subsequent light exposure did not result in any NPC response (triangle). A positive-probe-voltage sweep was then applied. During this voltage sweep, a decrease in current can be observed after ∼3 V (Fig. 3(b)), similar to the bipolar reset behavior of the valence-change resistive memory [19]. SBD was then re-initiated at the same location under negative-probe- voltage sweeping and exposure to white light was immediately made. Remarkably, the breakdown path now re-exhibits some NPC response again, although the current did not decrease completely to the measurement floor. The above procedure was repeated but in each repetition, the number of positive-voltage sweeps was increased. Intriguingly, the current window is gradually restored as the number of positive-probe-voltage sweeps is increased to 3.

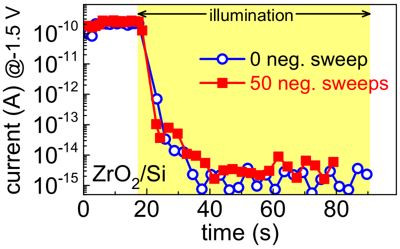


FIGURE 4. **The programmable NPC response revealed in the ZrO_2/TiN stack is not seen in the ZrO_2/Si stack. A similar number of negative-probe-voltage sweeps yields no apparent collapse of the current window.**

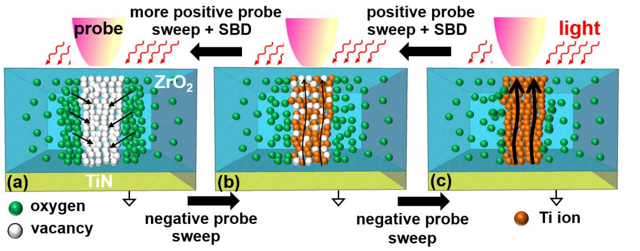


FIGURE 5. **(a) → (b) → (c) Illustration of the loss of NPC response by the inhibition of photo-assisted interstitial-vacancy recombination due to Ti ions occupying the vacancy sites under negative probe biasing. (c) → (b) → (a) Restoration of NPC response following the purging of Ti ions from the breakdown path back to the electrode under positive probe biasing.**

The tunable NPC response elucidated above is consistently observed on other randomly selected positions on the ZrO_2 after SBD. Although only the results for the ZrO_2/TiN stack are presented here, it should be mentioned that the same behaviors are also obtained on other oxide/metal stacks, e.g., HfO_2/TiN and SiO_2/Cu, SiO_2/Ti, SiO_2/Ni. However, the NPC tuning effect completely disappears in samples with the metal electrode replaced by Si, i.e., oxide/Si stacks. Fig. 4 shows an example for ZrO_2/Si stack where repeated negative-probe-voltage sweep made prior to light exposure is found to have no effect on the NPC response. A similarly large current window ($\sim 10^4\times$) is obtained for the case of 0 or 50 negative-probe- voltage sweeps.

The experimental results presented so far have clearly indicated the followings: 1) the NPC response of a breakdown path in ZrO_2 can be suppressed by a positive voltage but not a negative voltage applied on the TiN electrode before white-light illumination (Fig. 2); 2) the suppressed response can be restored by a negative voltage applied on the TiN electrode (Fig. 3); 3) such an effect is completely absent in the ZrO_2/Si stack having the same oxide but a non-metal electrode (Fig. 4). These findings all point to a definite role of the TiN electrode in the observed NPC response suppression.

A possible explanation is proposed in Fig. 5 for the ZrO_2/TiN stack. Spectroscopy studies on SiO_2 have shown that the breakdown path is depleted of oxygen [20]. Thus, it is believed that the breakdown of ZrO_2 proceeds via the dissociation of Zr-O bonds. The released oxygen (O) ions migrate towards the anode (driven by oxide electric field) as well as laterally away from the breakdown site (driven by Joule heating) [18]. When the breakdown is aborted quickly, some O ions may remain in interstitial positions near the breakdown path (Fig. 5(a)). In the absence of illumination, reverse migration of the interstitial O ions to the vacancies in the breakdown path is prevented by an energy barrier, ~0.59 eV for ZrO_2 [21]. Under illumination, photoexcitation of these interstitial O ions may enable them to overcome the energy barrier and migrate towards the breakdown path to recombine with the vacancies there (arrows), resulting in the disruption of the breakdown path [22], [23]. Photo-excitation and migration of O ions in MgO have been reported [23]. Having a migration barrier comparable to MgO, a similar mechanism may apply to the interstitial O ions surrounding the breakdown path in ZrO_2.

A negative-probe-voltage draws Ti ions from the TiN electrode into the vacancy sites in the breakdown path (Fig. 5(b)). Electric-field-driven metal-ion migration has been proposed to explain the resistance switching of conducting- bridge resistive memory (e.g., SiO_2/Cu [24], Ag_2S [25], etc.). Field induced metal-ion-migration in the oxide network is shown to be enhanced in the presence of vacancy defects [26]. In the ZrO_2/Si stack, migration of Si ions into the breakdown path does not readily occur due to the relatively large Si-O bond dissociation energy [27]. With the Ti ions occupying some of the vacancy sites, subsequent recombination between vacancies and interstitial O ions would be inhibited. Repeated negative biasing of the probe draws more Ti ions into the breakdown path, resulting in a larger number of the vacancy sites being occupied by Ti ions and hence a greater inhibition of vacancy-interstitial recombination. A complete loss of NPC response occurs when most of the vacancy sites are occupied by the Ti ions (Fig. 5(c)).

A positive-probe-voltage sweep drives the Ti ions back to the TiN electrode, resulting in a reset (Fig. 3(b)). In addition, O ions from the ZrO_2/TiN interface region are drawn into the breakdown path, disrupting it via the reduction of the vacancies there, resulting in the bipolar reset behavior of the valence-change resistive memory [28]. Removal of Ti ions from the breakdown path restores its NPC response following the path's reformation under a negative-probe-voltage sweep (Fig. 5(a)). The fewer number of positive-probe-voltage sweeps required for NPC restoration (Fig. 3(a)) as compared to the number of negative-probe-voltage sweeps needed to induce NPC loss (Fig. 2(a)) may be attributed to the smaller dissociation energy of Ti-Ti bonds (1.46 eV) as compared to those for Ti-O (6.86 eV) and Ti-N (4.81 eV) bonds [27].

IV. CONCLUSION

A new TiN-mediated multi-level negative photoconductance property of the breakdown path in ZrO_2 is revealed. The effect is only present when a positive voltage-bias is applied to the TiN electrode with respect to the non-metal C-AFM probe. A negative voltage-bias does not produce this effect but can restore the tuned response after a subsequent re-breakdown. The absence of this tuning effect in a sample with a non-metal (Si) electrode implies that it is due to the interaction between the breakdown path and the TiN electrode. Similar behaviors are obtained on other oxide/metal stacks, affirming the role of the metal electrode. It is proposed that under positive-voltage sweeping, Ti ions from the TiN electrode may migrate into the breakdown path and occupy vacancy sites there. As a consequence, the photo-assisted interstitial-vacancy recombination is inhibited, resulting in NPC response suppression. Besides the control of light-exposure dose [8, Fig. 3(b)], the results show that multi-level negative photoconductance can also be achieved through appropriate biasing of the TiN electrode, increasing the flexibility of the NPC phenonmenon in possible light-mediated or sensing applications. Study of an nanoscale crossbar device and nanodisk device is in progress to assess the device-application potential of our finding. The confinement of the breakdown path within a known area in such a test structure would also facilitate physical analysis of the breakdown oxide region to check the presence of Ti ions.

REFERENCES

[1] S. M. Yu, H. Y. Chen, B. Gao, J. F. Kang, and H. S. P. Wong, "HfO_x-based vertical resistive switching random access memory suitable for bit-cost-effective three-dimensional cross-point architecture," *ACS Nano*, vol. 7, no. 3, pp. 2320–2325, Mar. 2013, doi: 10.1021/nn305510u.

[2] J. Woo *et al.*, "Improved synaptic behavior under identical pulses using AlO_x/HfO_2 bilayer RRAM array for neuromorphic systems," *IEEE Electron Device Lett.*, vol. 37, no. 8, pp. 994–997, Aug. 2016, doi: 10.1109/led.2016.2582859.

[3] T.-L. Tsai, Y.-H. Lin, and T.-Y. Tseng, "Resistive switching characteristics of WO_3/ZrO_2 structure with forming-free, self-compliance, and submicroampere current operation," *IEEE Electron Device Lett.*, vol. 36, no. 7, pp. 675–677, Jul. 2015, doi: 10.1109/led.2015.2428719.

[4] U. Chand, C.-Y. Huang, and T.-Y. Tseng, "Mechanism of high temperature retention property (up to 200 °C) in ZrO_2-based memory device with inserting a ZnO thin layer," *IEEE Electron Device Lett.*, vol. 35, no. 10, pp. 1019–1021, Oct. 2014, doi: 10.1109/led.2014.2345782.

[5] D. J. Wouters *et al.*, "Analysis of complementary RRAM switching," *IEEE Electron Device Lett.*, vol. 33, no. 8, pp. 1186–1188, Aug. 2012, doi: 10.1109/led.2012.2198789.

[6] S. Ambrogio, S. Balatti, D. C. Gilmer, and D. Ielmini, "Analytical modeling of oxide-based bipolar resistive memories and complementary resistive switches," *IEEE Trans. Electron Devices*, vol. 61, no. 7, pp. 2378–2386, Jul. 2014, doi: 10.1109/ted.2014.2325531.

[7] W.-J. Qi *et al.*, "Electrical and reliability characteristics of ZrO_2 deposited directly on Si for gate dielectric application," *Appl. Phys. Lett.*, vol. 77, no. 20, pp. 3269–3271, Nov. 2000, doi: 10.1063/1.1326482.

[8] Y. Zhou *et al.*, "White-light-induced disruption of nanoscale conducting filament in hafnia," *Appl. Phys. Lett.*, vol. 107, no. 7, Aug. 2015, Art. no. 072107, doi: 10.1063/1.4929324.

[9] T. Kawashima *et al.*, "Restoration of postbreakdown gate oxide by white-light illumination," *IEEE Electron Device Lett.*, vol. 36, no. 8, pp. 748–750, Aug. 2015, doi: 10.1109/led.2015.2445788.

[10] D. S. Ang *et al.*, "White-light-induced annihilation of percolation paths in SiO_2 and high-k dielectrics—Prospect for gate oxide reliability rejuvenation and optical-enabled functions in CMOS integrated circuits," *ECS Trans.*, vol. 69, no. 5, pp. 169–181, Oct. 2015, doi: 10.1149/06905.0169ecst.

[11] M. Rumler *et al.*, "Characterization of grain boundaries in multicrystalline silicon with high lateral resolution using conductive atomic force microscopy," *J. Appl. Phys.*, vol. 112, no. 3, Aug. 2012, Art. no. 034909, doi: 10.1063/1.4746742.

[12] W. Frammelsberger, G. Benstetter, J. Kiely, and R. Stamp, "C-AFM-based thickness determination of thin and ultra-thin SiO_2 films by use of different conductive-coated probe tips," *Appl. Surf. Sci.*, vol. 253, no. 7, pp. 3615–3626, Jan. 2007, doi: 10.1016/j.apsusc.2006.07.070.

[13] M. Lanza, "A review on resistive switching in high-k dielectrics: A nanoscale point of view using conductive atomic force microscope," *Materials*, vol. 7, no. 3, pp. 2155–2182, Mar. 2014, doi: 10.3390/ma7032155.

[14] B. H. Lee *et al.*, "Ultrathin hafnium oxide with low leakage and excellent reliability for alternative gate dielectric application," in *Int. Electron Devices Meeting Tech. Dig.*, Washington, DC, USA, 1999, pp. 133–136, doi: 10.1109/IEDM.1999.823863.

[15] G. H. Buh and J. J. Kopanski, "Atomic force microscope laser illumination effects on a sample and its application for transient spectroscopy," *Appl. Phys. Lett.*, vol. 83, no. 12, pp. 2486–2488, Sep. 2003, doi: 10.1063/1.1613800.

[16] Y. Ji *et al.*, "Characterization of the photocurrents generated by the laser of atomic force microscopes," *Rev. Sci. Instrum.*, vol. 87, no. 8, Aug. 2016, Art. no. 083703, doi: 10.1063/1.4960597.

[17] K. S. Yew, D. S. Ang, and G. Bersuker, "Bimodal Weibull distribution of metal/high-κ gate stack TDDB—Insights by scanning tunneling microscopy," *IEEE Electron Device Lett.*, vol. 33, no. 2, pp. 146–148, Feb. 2012, doi: 10.1109/LED.2011.2174606.

[18] B. Butcher *et al.*, "Modeling the effects of different forming conditions on RRAM conductive filament stability," in *Proc. 5th IEEE Int. Memory Workshop*, Monterey, CA, USA, 2013, pp. 52–55, doi: 10.1109/IMW.2013.6582096.

[19] S. Menzel, U. Böttger, M. Wimmer, and M. Salinga, "Physics of the switching kinetics in resistive memories," *Adv. Funct. Mater.*, vol. 25, no. 40, pp. 6306–6325, Oct. 2015, doi: 10.1002/adfm.201500825.

[20] X. Li, C. H. Tung, and K. L. Pey, "The nature of dielectric breakdown," *Appl. Phys. Lett.*, vol. 93, no. 7, Aug. 2008, Art. no. 072903, doi: 10.1063/1.2974792.

[21] S. Zafar, H. Jagannathan, L. F. Edge, and D. Gupta, "Measurement of oxygen diffusion in nanometer scale HfO_2 gate dielectric films," *Appl. Phys. Lett.*, vol. 98, no. 15, Apr. 2011, Art. no. 152903, doi: 10.1063/1.3579256.

[22] K. Huang and A. Rhys, "Theory of light absorption and non-radiative transitions in f-centres," *Proc. Roy. Soc. London A Math. Phys. Eng. Sci.*, vol. 204, no. 1078, pp. 406–423, 1950, doi: 10.1098/rspa.1950.0184.

[23] D. M. Duffy, S. L. Daraszewicz, and J. Mulroue, "Modelling the effects of electronic excitations in ionic-covalent materials," *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms*, vol. 277, pp. 21–27, Apr. 2012, doi: 10.1016/j.nimb.2011.12.059.

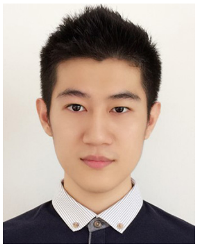
[24] W. Chen, H. J. Barnaby, and M. N. Kozicki, "Volatile and non-volatile switching in Cu-SiO_2 programmable metallization cells," *IEEE Electron Device Lett.*, vol. 37, no. 5, pp. 580–583, May 2016, doi: 10.1109/led.2016.2540361.

[25] Z. Xu, Y. Bando, W. L. Wang, X. D. Bai, and D. Golberg, "Real-time in situ HRTEM-resolved resistance switching of Ag_2S nanoscale ionic conductor," *ACS Nano*, vol. 4, no. 5, pp. 2515–2522, May 2010, doi: 10.1021/nn100483a.

[26] K. Kinoshita, T. Yamasaki, S. Yura, T. Ohno, and S. Kishida, "Elucidation of metal diffusion mechanism in conducting-bridge random access memory (CB-RAM) using first-principle calculation," in *Proc. Adv. Sci. Technol.*, 2014, pp. 91–95, doi: 10.4028/www.scientific.net/AST.95.91.

[27] A. D. McNaught and A. Wilkinson, *IUPAC. Compendium of Chemical Terminology*, 2nd ed. Oxford, U.K.: Blackwell Sci., 1997, doi: 10.1351/goldbook.

[28] H. Z. Zhang *et al.*, "Role of interfacial layer on complementary resistive switching in the TiN/HfO_x/TiN resistive memory device," *Appl. Phys. Lett.*, vol. 105, no. 22, Dec. 2014, Art. no. 222106, doi: 10.1063/1.4903341.



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