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Argon-plasma-controlled optical reset in the SiO₂/Cu filamentary resistive memory stack

T. Kawashima,^{1,2,a)} K. S. Yew,¹ Y. Zhou,¹ D. S. Ang,^{1,a)} H. Z. Zhang,¹ and K. Kyuno³

¹School of Electrical and Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798

²Toshiba Corporation 33, Shin-Isogo-Cho, Isogo-ku, Yokohama 235-0017, Japan

³Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo 135-8548, Japan

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We show that resistive switching in the SiO₂/Cu stack can be modified by a brief exposure of the oxide to an Ar plasma. The set voltage of the SiO₂/Cu stack is reduced by 33%, while the breakdown voltage of the SiO₂/Si stack (control) is almost unchanged. Besides, the Ar plasma treatment suppresses the negative photoconductivity or optical resistance reset effect, where the electrically formed filamentary conductive path consisting of Cu-ion and oxygen-vacancy clusters is disrupted by the recombination of the oxygen vacancies with nearby light-excited oxygen ions. From the enhanced O-H peak in the Fourier-transform infrared spectrum of the plasma-treated oxide, it is proposed that the Ar plasma has created more oxygen vacancies in the surface region of the oxide. These vacancies in turn adsorb water molecules, which act as counter anions (OH⁻) promoting the migration of Cu cations into the oxide and forming a more complete Cu filament that is less responsive to light. The finding points to the prospect of a control over the optical resistance reset effect by a simple surface treatment step. *Published by AIP Publishing.*

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With the NAND-flash memory transistor facing severe scaling limitations, there has been intensive effort in searching for an alternative non-volatile memory technology to meet the demands of future terabit applications. Among the different candidates considered, the resistive switching memory has received broad interest owing to its simple, highly scalable metal-insulator-metal structure which suits three-dimensional crossbar implementation. To-date, two categories of resistive switching memory devices, namely, valence-change and electrometallization or conducting-bridge random access memory (CBRAM), have attracted much attention. For the latter, the Cu-based CBRAM has been a focus owing to its compatibility with the backend interconnect process and demonstrated fast switching, high endurance, and low-power operation, which make it not only suitable for flash memory but also storage class memory applications.¹⁻⁶

Although the exact mechanism of resistance switching may differ from one memory device to another, intrinsic defects in the insulating layer may significantly impact the switching characteristics. For oxide-based devices, the oxygen vacancy defect (V_O) is a classic example. Studies have found V_O's to profoundly change the bandgap, and the optical and magnetic properties of SrTiO₃.⁷⁻⁹ Recently, we have demonstrated negative photoconductivity (NPC) or light-induced resistance reset whereby the electrically-formed filamentary breakdown path in a wide-gap oxide, such as SiO₂, HfO₂, and ZrO₂, is disrupted by white light.¹⁰⁻¹³ It has been proposed that the reset is caused by the recombination of light-excited oxygen ions and oxygen vacancies (V_O's) created in the breakdown path during the forming/set sweep. Dependence of

the optical reset speed on light intensity and wavelength, oxide stoichiometry, and operating temperature are found to be consistent within the proposed framework.¹⁴ The NPC effect is also observed in the SiO₂/Cu CBRAM stack because V_O's which partly made up the conducting filament in-between Cu nano-filaments in the SiO₂/Cu stack may be refilled with light-excited oxygen ions, thus disrupting the filamentary conducting path.¹³ Since V_O's are important in resistive switching, it may be possible to control the NPC behavior by increasing/decreasing the density of V_O's in the oxide electrolyte. One way to increase V_O's in the electrolyte is by plasma treatment. A previous study has shown that the electroforming voltage of the TaN/SiO₂/n-Si device is reduced when a larger area of the sidewall is exposed to plasma etching, due to a higher defect density created at the sidewall during the etching.¹⁵ It is also shown that Ar plasma treatment forms V_O's on the oxide surface, leading to a uniform and reliable resistive switching in the Pt/HfO₂/Ti device¹⁶ and a stable interface-related resistance switching in the Au/BiFeO₃/Pt device.¹⁷

Here, we investigate resistive switching in an Ar-plasma-treated SiO₂/Cu stack using a conductive atomic force microscope (C-AFM), where the probe of the C-AFM is used as a counter electrode. Our study shows that the NPC behavior exhibited by the filamentary breakdown path is suppressed by Ar-plasma treatment of the SiO₂. The finding provides a means for modulating the optical reset effect in the SiO₂/Cu CBRAM device.

A 30-nm Ti adhesion layer, followed by a 30-nm Cu electrode layer, was sputtered on a HF-cleaned p-Si substrate. Then, a 10-nm SiO₂ electrolyte layer was grown via a standard plasma-enhanced chemical vapor deposition process using SiH₄ and N₂O. This test sample is referred to as

^{a)} Authors to whom correspondence should be addressed: tomohito.kawashima@toshiba.co.jp and edsang@ntu.edu.sg

the Cu sample. A control sample consisting of a 5-nm SiO₂ grown by the same method directly on a p-Si substrate (i.e., SiO₂/Si stack) was also prepared; the thinner SiO₂ was used to avoid a high breakdown voltage. Then, both samples were exposed to an Ar plasma (50 W power, 45 mTorr pressure, and 50 sccm flow rate) for 20 s. Fourier-transform infrared (FT-IR) spectra of the SiO₂ before and after the Ar plasma treatment were collected via the attenuated total reflection method in vacuum. The electrical measurement was carried out in a RHK 3500 ultra-high vacuum ($\sim 5 \times 10^{-10}$ Torr) C-AFM with a diamond-coated Si probe acting as the counter electrode. The C-AFM probe was connected to a Keithley SCS-4200 parameter analyzer, and the substrate was grounded. The contact area between the C-AFM probe and SiO₂ is estimated to be 26 nm², based on an applied force of 28 nN and the properties of the diamond-coated Si probe.¹⁸ An ordinary white LED lamp providing a light intensity of 1 mW/cm² at the sample surface was positioned at a quartz window of the C-AFM system. Further details of the measurement set-up can be found elsewhere.^{10,13}

Figures 1(a) and 1(b) depict a typical set of current-voltage curves for the Cu sample without and with Ar plasma treatment, respectively. The current compliance limit was set at 1.1 nA. Under a first negative voltage ramp (A), both Cu samples exhibit an abrupt increase in the current, showing set switching from a high to low resistance state. In a subsequent positive voltage ramp (B), a current drop is observed, indicating a successful low to high resistance reset, which is confirmed by a following negative voltage ramp (C). A lower set voltage of -4 V is obtained for the plasma-treated sample, as compared to the -6 V for the untreated sample. On the other hand, the control sample shows a different behavior. The current-voltage curves for the case without and with Ar-plasma treatment are depicted in Figs. 1(c) and 1(d). The breakdown voltage is reduced slightly from -13 V for the untreated sample to -12 V for the plasma-treated sample. This small shift is reasonable, considering that the thickness

FIG. 1. Current-voltage (I - V) curves of (a) untreated SiO₂/Cu, (b) Ar-plasma-treated SiO₂/Cu, (c) untreated SiO₂/p-Si, and (d) Ar-plasma-treated SiO₂/p-Si samples. A negative-voltage ramp (curve A, black) for forming was applied, followed by a positive-voltage ramp (curve B, red), and then a negative-voltage ramp (curve C, blue). Arrows indicate the directions of voltage ramps.

of SiO₂ is decreased by 0.3 nm (as measured by ellipsometry) after Ar-plasma treatment, due to the physical sputtering effect. Therefore, the more significant decrease in the set voltage for the plasma-treated Cu sample, despite its twice larger SiO₂ thickness, may be due to an accelerated formation of Cu filament.

After the samples were set to the low-resistance state, a small monitoring voltage bias was applied to the probe and the effect of a light illumination on the leakage current was investigated. Figure 2(a) shows two typical response of the leakage current (@ -0.5 V) to light for the plasma-treated Cu sample. On some locations tested, the NPC effect was observed as soon as the light was turned on at 50 s (black curve). On some other locations, however, no NPC response was obtained (red curve). The percentage of NPC response, out of a total of 30 different locations tested on each sample, is compared in Fig. 2(b). For each sample, the monitoring voltage was adjusted to achieve around the same initial current of 10 pA as in the plasma-treated Cu sample. This voltage is -1.5 V, -1.3 V, and -1 V for the untreated SiO₂/p-Si, Ar-plasma-treated SiO₂/p-Si, and untreated SiO₂/Cu samples, respectively. It is interesting to note that Ar-plasma treatment of the SiO₂ has led to a reduction in the percentage of NPC response, with the plasma-treated Cu sample showing a larger decrease than the control sample.

To probe the reason for the reduced set voltage and suppressed NPC effect of the plasma-treated Cu sample, Fourier-transform infrared (FT-IR) spectroscopy measurement was performed on both the plasma-treated and untreated SiO₂. Figure 3 shows the results. The intensities of HO-H bond stretching (3300 cm⁻¹) and SiO-H bond stretching (3650 cm⁻¹) in the Ar-plasma-treated SiO₂ is higher than those in the untreated SiO₂. The increase in O-H bond intensity implies the destruction of the Si-O network near the surface and the increase in various defects like Si dangling bonds and oxygen vacancies. As the annihilation of E' center ($\equiv\text{Si}\cdot$) by water to form a silanol group (Si-OH) is reportedly an exothermic reaction,¹⁹ the V_O 's created by the Ar plasma treatment may adsorb water from the ambient.

Based on the results, we propose a possible explanation for the reduced set voltage of the plasma-treated Cu sample and the suppressed NPC effect in both the plasma-treated Cu and control samples. For the control sample, the Ar plasma treatment creates more V_O 's near the surface region of the SiO₂, depleting the oxygen from this region. As a result, a larger conducting filament composed of V_O 's is formed. It is

FIG. 2. (a) Typical current-time (I - t) plots of the Ar-plasma-treated SiO₂/Cu sample. The black line shows the significant current decrease upon light exposure at 50 s (exhibiting a negative photoconductivity (NPC) response). The red line is an example of a no-NPC response. (b) Probability of NPC occurrence calculated from 30 different probe locations in each sample.

FIG. 3. FT-IR spectra of the untreated and Ar-plasma-treated SiO₂ film.

reported that V_O 's add new defect states within the SiO₂ band gap and lower the conduction band minimum, enhancing the leakage current in the SiO₂ by raising the transmission probability of electrons.²⁰ Therefore, a higher current is obtained during the reverse sweep following the breakdown (A) or during the 2nd negative sweep (C) in Fig. 1(d) for the plasma-treated sample, compared to Fig. 1(c) for the untreated sample. Since oxygen ions are depleted near the conducting path, the likelihood of disruption by light is decreased.¹¹ The explanation for the Cu sample is depicted schematically in Fig. 4. As the FT-IR results (Fig. 3) have shown, the V_O 's created in the surface region of the SiO₂ by the Ar plasma treatment may adsorb water molecules. It has been reported that the existence of water in the oxide could help the formation of the metal filament, because the OH⁻ ions from the adsorbed water molecules may oxidize the metal electrode and draw positively charged metal ions into the SiO₂ film.²¹ It was also proposed that a high V_O density might facilitate the migration of Cu ions in the oxide network.²² In our case, since the plasma-treatment was done on the top oxide surface and not at the bottom SiO₂/Cu interface from which Cu migration originated, the OH⁻ counter-anion effect is believed to have played a more dominant role. Nonetheless, local heating, due to increased current conduction in a region of high V_O density, could indirectly drive the migration of Cu ions.²³ Simulation study has also found that

the Cu adsorption energy at a V_O defect site is significantly reduced,²⁴ suggesting that V_O 's in the surface region of the plasma-treated sample could serve as nucleation sites for Cu filament formation. Therefore, surface modification by the Ar plasma treatment may accelerate the formation of Cu filament in the SiO₂, resulting in a larger decrease in the set voltage as compared to the control sample.

Next, a possible reason for the suppression of the NPC effect in the Cu sample is considered. Former studies have shown that light can disrupt the conducting filament due to the recombination of V_O 's and oxygen ions.^{10–13} However, when more Cu ions migrate into SiO₂, part of the conducting filament made up of V_O 's may be replaced by a Cu filament [Fig. 4(e)]. It was reported that more Cu was observed in the filamentary conducting path after repetitive voltage sweeps.²⁵ In our earlier study,¹³ we subjected the filamentary conducting path in the SiO₂/Cu stack to repeated voltage sweeps and indeed observed that the likelihood for the path to exhibit the NPC effect was reduced. In this work, surface modification by the plasma may increase the ease of Cu migration into the SiO₂, resulting in the formation of a more complete Cu filament. It is harder for light to disrupt a Cu filament due to the strong Cu-Cu bond. The barrier energy for the back-migration of interstitial oxygen ions to the V_O 's in the breakdown path is ~ 0.27 eV for SiO₂.²⁶ On the other hand, the dissociation energy of Cu-Cu bonds (2.08 eV²⁷) and the ionization energy for Cu (7.73 eV²⁸) are significantly higher, indicating that a filamentary conducting path composed of Cu could remain intact during the light illumination [Fig. 4(f)].

The effect of Ar plasma treatment on resistive switching in the SiO₂/Cu stack and the SiO₂/Si control stack was investigated. Compared to the slight decrease (7%) in the breakdown voltage of the control sample, a more significant decrease in the set voltage of the Cu sample (33%) is observed, despite the latter's twice larger SiO₂ thickness. In addition, the conducting filament in the plasma-treated Cu sample is less likely to be disrupted by light illumination. It is considered that oxygen vacancies produced in the surface region of the SiO₂ by the Ar plasma treatment may adsorb water molecules, which play a counter-anion role that

FIG. 4. Schematic diagrams depicting resistive switching in the SiO₂/Cu sample. (a) and (d) Initial state of the sample without or with Ar plasma treatment. The latter sees more oxygen vacancies being created in the surface region of the SiO₂ and the resultant adsorption of water molecules by the vacancies. (b) and (e) Low resistance state of the sample without or with Ar plasma treatment after negative-voltage forming. The latter sees an enhanced Cu-ion migration. (c) and (f) Photo-response of the sample without or with Ar plasma treatment. Unlike the former in which the conducting path (red arrow) is disrupted by the oxygen-vacancy recombination (black arrows) induced by light illumination (green dashed arrows), the latter shows the conducting path is less likely to be disrupted due to the more complete Cu filament formed.

enhances Cu diffusion from the electrode into the SiO₂. As a consequence, a nearly complete Cu conducting filament is formed, leading to the non-responsiveness to light. The results point to the possibility of modulating the recently revealed optical resistance reset effect in soft-breakdown wide-bandgap oxides via metal-oxide interface modification.

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