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<th>TiN-Mediated Multi-Level Negative Photoconductance of the ZrO2 Breakdown Path</th>
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<td>Author(s)</td>
<td>Zhou, Yu; Kawashima, Tomohito; Ang, Diing Shenp</td>
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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
The spatial distribution of interstitial oxygen is shown to ing interstitial positions) and vacancies in the breakdown from the breakdown location (and situated in surround-

region is \(\sim 10^3 \ \Omega \cdot \text{cm}\), which implies a semiconducting-like nature. The relatively low breakdown current (\(\sim 0.1 \ \text{nA}\)) 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 post-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-voltage sweeps 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-voltage sweeps 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)).

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.

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) $\rightarrow$ (b) $\rightarrow$ (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) $\rightarrow$ (b) $\rightarrow$ (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, \(~0.59 \text{ eV}\) for ZrO\(_2\) [21]. Under illumination, photo-excitation 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\(_2\)S [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 reformulation 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 phenomenon in possible light-mediated or sensing applications. Study of a 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


