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White-light-induced disruption of nanoscale conducting filament in hafnia

Citation: Applied Physics Letters 107, 072107 (2015); doi: 10.1063/1.4929324
View online: http://dx.doi.org/10.1063/1.4929324
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Visible-light-stimulated response of semiconductor devices may potentially expand the functionalities of electronics, which are presently limited to electrical stimulations. It was shown that the current flow through the multilayer Pd/Al2O3/SiO2/p-Si structure could be modulated by trapping, in the Al2O3, of electrons optically generated in the p-Si substrate. The finding provides a possible means for light-enabled information encoding in non-volatile memory applications. Light-stimulated resistive switching has been observed in structures such as the ZnO nanorod, BiFeO3 thin film, TbMnO3/Nb: SrTiO3, ZnO/SrTiO3, and TiO2/CoFe2O4 heterojunctions. Although the actual response may vary with material characteristics and fabrication conditions, and the underlying mechanisms are still subjects of further investigation, these studies demonstrate that light sources may serve as an additional parameter for enhancing semiconductor device functionalities.

With the exception of Ref. 2, where the photoconductivity effect arises from electron-hole pair generation in the Si substrate, nearly all studies on light stimulation reported to date have focused on photo-responsive oxide or perovskite materials having relatively small bandgaps (~3 eV or lesser). On the other hand, oxides such as SiO2 and HfO2, which are widely deployed in mainstream integrated-circuit manufacturing, have been excluded due to their much larger bandgaps (~6 eV or larger) which render them non-photo-responsive. In this study, we show that these wide-bandgap oxides can also be rendered photo-responsive by following an electrical-stress induced breakdown. In particular, it is shown that white light can either permanently or temporarily disrupt the nanoscale conducting filament in the HfO2 dielectric. In recent years, dielectrics such as HfO2 and Ta2O5 have been intensively studied as the active layer of resistive random access memory (RRAM) devices, by virtue of their compatibility with the mainstream integrated-circuit manufacturing technology. In the RRAM device, the change between high and low resistance state is usually induced by applying an electric field, which modifies the oxide resistivity by repeatedly disrupting and reforming a nanoscale-width conducting filament through the oxide film separating two metal electrodes. Here, we reveal an intriguing observation that the conduction through a nanoscale conducting filament in the HfO2 can be disruption by white light, an effect which we termed as the negative photoconductivity (NP) of the soft-breakdown HfO2. In addition, the filament resistance can be controllably changed to desired values by varying the duration of a light exposure. These findings point to the possibility of direct implementation of light-enabled functionalities using HfO2-based devices.

The measurements were performed at 300 K using a conductive atomic force microscope (C-AFM) in ultra-high vacuum (UHV) (~10^-10 Torr), as depicted schematically in Fig. 1(a). The test sample comprises of a 4-nm thick HfO2 layer, formed via the process of atomic-layer deposition on the TiN/Ti/p-Si substrate. Tetrakis(dimethylamino) hafnium was used as the metal precursor and H2O vapor as the oxidizer. The growth temperature and pressure were 250 °C and 10 Torr, as depicted schematically in Fig. 1(b).

**FIG. 1.** (a) Schematic of the experimental setup used in this study. The probe of the ultra-high vacuum (UHV) conductive atomic force microscope is connected to a source/monitor unit of a semiconductor parameter analyzer. A voltage ramp applied to the probe is interrupted when an abrupt current increase is registered, indicating the formation of a conducting filament (cf) on the probe-contact site. A white LED lamp, placed at a quartz window of the UHV chamber, at a distance of ~30 cm from the test sample and at an angle of 45°, is used for the light exposure experiments. (b) White-light illumination of the TiN/Ti/p-Si sample shows an increase in current.
0.1 Torr, respectively. No post-deposition annealing was carried out. A diamond-coated Si probe, connected to an external parameter analyzer, was used to form a conducting filament. A voltage-sweep was applied on the probe and the forming process interrupted when the increase in current reached a pre-set compliance limit. It should be clarified that the set-up comprising the unapped HfO$_2$ sample with the C-AFM probe functioning as the top electrode is to enable the white light to reach the filament underneath the probe via its periphery, as the top metal electrode in the typical metal-insulator-metal (MIM) structure of a HfO$_2$ RRAM device impedes light transmission to filament(s) embedded in the oxide. Surface contamination of the sample during testing was avoided by the UHV environment, which is not a prerequisite for the observation of the NP behavior. In principle, a MIM structure that has an optically transparent top metal electrode should exhibit the NP behavior.

The white light source (of wavelengths ranging from ~400 to 700 nm) used in this study was a standard light-emitting diode (LED) lamp, positioned at a quartz window of the UHV chamber at a distance of ~30 cm from the sample. The angle of incidence was ~45°. Measurement under light exposure was also performed on a bare TiN surface (i.e., a control sample without an active oxide layer). Fig. 1(b) shows a typical photoconductive response (i.e., current increase upon illumination) for this control sample.

Fig. 2(a) depicts the light-induced disruption of a nanoscale conducting filament in HfO$_2$, as evidenced from the comparison to the measurement on the same sample performed with no light exposure. Following the formation of a conducting filament using a positive voltage ramp (Fig. 2(b)), the filament current was monitored at a probe voltage of 1 V as a function of time. The relatively large resistance (~10 MΩ) of the filament may be attributed to its very small diameter of several nanometers (as revealed later in Fig. 4). The estimated filament resistivity is on the order of 10$^{-2}$ Ω·m, corresponding to that of a semiconductor-like material. As can be seen in Fig. 2(a), the current decays slowly over the 2000-s time interval, in the absence of light exposure, as expected from post-electrical-stress relaxation. Re-measurement following the first 2000-s interval shows a constant current (~10$^{-8}$ A), after the relaxation was completed.

Interestingly, a significant decrease of the current, from ~10$^{-7}$ A to the measurement floor (~10$^{-15}$ A) can be observed upon illumination with a white light, in contrast to the behavior shown in Fig. 1(b) for the control sample. After the light source is removed, the current recovers slightly to ~10$^{-14}$ A and remains at this level for the remaining duration of the measurement. A subsequent positive voltage sweep yields a current similar to the pre-forming level (Fig. 2(b), square), thus confirming that the conducting filament was disrupted during the illumination. Apparently, the white light has “reset” the conducting filament to a high resistance state. A subsequent transition back to a low resistance state, however, occurs at a lower positive voltage as compared to the initial forming process, indicating that the oxide region concerned was not fully restored to its pre-forming state. Following a typical bipolar (electrical) reset using a negative voltage sweep (triangle), a post-electrical-reset current-voltage (I-V) curve (circle) comparable to the post-light-reset I-V curve (square) is attained, indicating that the effect of light is similar to that of the electrical reset. By alternating between the light and electrical reset modes, similar post-reset I-V curves are obtained regardless of the type of the prior reset mode. The light-induced resistance reset revealed in Fig. 2(a) is also observed in ZrO$_2$ and SiO$_2$ samples.$^{11}$

It can be noted in Fig. 2(a) that the current decrease occurs after the sample was exposed to the light for ~100 s. To investigate this “delayed response,” the experiment was repeated on an untested location using two different light intensities. Initially, light of a lower intensity was applied to induce reset after forming. Then, the conducting filament was reformed by ramping up a positive voltage followed by the exposure to a light of a five times higher intensity. As can be seen in Fig. 3(a), the current decreases (following an initial no-exposure period of ~20 s) more gradually under the lower intensity light exposure, as compared to the higher intensity case where the current decreases spontaneously and more abruptly (showing a reset that occurred at a distinctively faster rate). In the case of the low-intensity light, it takes 52 s for the current to decrease to the measurement floor. As for the case of the high-intensity light, the time is

FIG. 2. (a) Current versus time characteristics of a conducting filament: circle—measurement made immediately after forming in darkness throughout; square—re-measurement following the initial 2000-s period with a brief exposure to white-light as indicated. (b) Current-voltage curves: line—formation of the filament in (a); square—after the white-light exposure indicated in (a); triangle—electrical reset by an opposite-polarity voltage sweep; and circle—after electrical reset. Arrows indicate directions of voltage sweep. The current compliance limit (CCL) is 100 nA.
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The light induced resistance-reset phenomenon discussed above should be distinguished from the photo-related resistance switching effects reported in recent studies. It was reported by Yu and Wang that the resistance between two points along a thin Ti film could be continuously varied between two extreme values when a laser beam was scanned between these points. As shown in Ungureanu et al., the current through the Pd/Al2O3/SiO2/p-Si device biased in inversion was modulated by injecting optically generated minority carriers (electrons) in the p-Si substrate and trapping these electrons in the Al2O3 layer. Park et al. found that the resistance of a ZnO nanorod RRAM device was switched to a lower value at a smaller voltage under light exposure. After the light exposure, however, the resistance would transit towards a higher value at a rate determined by the decaying persistent photoconductivity (PPC) effect. A significant PPC effect in the ZnO/SrTiO3 heterojunction obscured the electrically induced resistance switching of this device following light exposure. In heterojunction structures, the PPC effect has been ascribed to the trapping of charges at interface defects, which modulate the junction barrier controlling current flow. A common feature in the abovementioned studies is that the test-sample resistance is modulated by a significant photoconductivity effect. In contrast, the HfO2, ZrO2, and SiO2 are non-photo-responsive materials due to their relatively large bandgaps. In contrast to photo-responsive oxides, white light has no impact on the I-V curve measured during the forming/set steps performed on HfO2. However, once the conducting filament is formed, a unique feature of the light-induced filament disruption (i.e., a “negative photoconductivity effect”) is observed in this study.

A possible explanation for the light-induced resistance reset phenomenon in HfO2 is illustrated in Fig. 5, based on the oxygen migration model. The proposed explanation is guided by two recent findings: (1) observation of an oxygen-depleted filament via atomic-scale electron-energy loss spectroscopy, and (2) observation, by simulation, of oxygen ions released from the filament site during formation, in the vicinity of the filament. Fig. 5(a) depicts the formation of an oxygen-deficient conducting filament through the HfO2 layer when a voltage sweep is applied via the C-AFM probe. Electron transport through the hafnia film induces HfO bond breakage and out-diffusion (assisted by the temperature and electrical field distributions) of the released negatively charged oxygen ions, resulting in the formation of an oxygen-deficient (metal-rich) conducting filament. As the forming process is interrupted when the current reaches a compliance limit, some of the released oxygen ions remain in the interstitial positions in the vicinity of the filament and may be subsequently driven back to the filament by the applied electrical field and temperature gradient during the electrically controlled reset. The diffusion of interstitial oxygen ions entails the over-compensation of an energy barrier of 0.3-0.6 eV. At a low voltage (below the electrical reset voltage), the diffusion rate would thus be negligibly small. It is suggested that a white light illumination generates a photon-induced excitation of the oxygen ions over the diffusion energy barrier, hence accelerating their diffusion towards the vacancy-rich filament, as illustrated in Fig. 5(b). The ion excitation proceeds more efficiently under a higher

FIG. 4. C-AFM current maps: (a) relatively uniform current distribution before forming; (b) a bright shade of ~4 nm in diameter denoting the conducting filament after forming (the peak current is >1 nA); (c) reduced filament size and brightness (i.e., current) after a 30-s white-light illumination; and (d) near-complete filament disruption upon a further 300-s illumination. Inset: Remnants of the filament are visible only at a much reduced current scale. 9.3 s. This 5.6-time reduction corresponds well to the difference between the two light intensities. Clearly, light intensity strongly influences the speed at which the conducting filament is disrupted. The current evolution in the absence of illumination is also shown for comparison.

As the data in Fig. 3(a) show, the change in resistance in a specific time interval is determined by the amount of light energy that the filament received, indicating a possibility of achieving multiple resistance levels for a given filament. This is indeed observed in Fig. 3(b), where different levels of the conducting filament disruption can be controlled by changing the duration of light exposure. Upon illumination, the current is decreased from the low-resistance state (LRS) to a first high-resistance state (HRS1) in a 20-s interval. The current decrease is obviously arrested when the light illumination is removed, as is evident from the current plateau. When the illumination is resumed, the current is decreased to the next higher resistance state (HRS2). Clearly, by controlling the light exposure, one can generate multiple resistance values for the conducting filament. This result suggests the possibility of a light-enabled RRAM-resistance tuning approach, as an alternative to the electrical counterpart, for neuromorphic computing applications. The electrical tuning method might be challenging because it requires the control of a set current compliance limit (for DC switching) or set/reset pulse timing (for AC switching). To further illustrate that the disruption of current conduction observed in Figs. 2 and 3 is a consequence of light induced “dissolution” of the filament, current maps of a selected region of the HfO2 before and after forming, and after various stages of light exposure are compared in Fig. 4. Compared to uniform current map before forming (Fig. 4(a)), the presence of a distinct bright shade, of ~4 nm in diameter, after forming (Fig. 4(b)) is due to the generation of a conducting filament. Interestingly, after a 30-s exposure to white light, the level of brightness and size of the filament are drastically reduced (Fig. 4(c)), which correspond to a decrease in current. Upon further illumination, the filament became almost indistinguishable from the surrounding oxide region (Fig. 4(d)). The results confirm that white light can erode a conducting filament formed in the soft-breakdown HfO2.
The effect of the conducting filament dimension as determined by the current compliance limit (CCL) used during the DC forming process on light-induced reset is also studied and the results are shown in Fig. 6. When the conducting filament is formed at a low CCL (of 10 nA), the light-induced reset state is relatively stable (i.e., after the light is turned off, the current remains constant at a low level throughout the entire duration of the observation time). On the other hand, when the conducting filament is reformed at a higher CCL of 100 nA, the light induced reset is less complete and unstable (i.e., the current after illumination is much higher than the case of low CCL and can be seen to gradually increase back to the pre-reset level). Similar results are obtained on the ZrO$_2$/TiN/Ti/p-Si sample. These observations are consistent with the model discussed in Fig. 5. When a lower CCL is used during DC forming, fewer oxygen ions are released due to a smaller required filament cross-section. Since the process involved is shorter (terminated once the low CCL is reached), a larger portion of the released oxygen ions populate interstitial sites in the immediate vicinity of the filament (Fig. 5(a)). These interstitial oxygen ions may then recombine with the filament vacancies during light-driven reset (Fig. 5(b)). On the other hand, a DC forming process using a larger CCL releases more oxygen ions (due to a larger filament cross-section) and also enables a larger share of the released ions to propagate further away from the filament as a result of the greater Joule heating and longer process involved (Fig. 5(c)). Then, during a subsequent light exposure, a smaller share of the light-activated interstitial oxygen ions distributed throughout the dielectric volume may potentially reach the filament, resulting in only partial filament disruption. As the recombination of filament vacancies may also involve light-stimulated migration of weakly bonded lattice oxygen ions in the filament vicinity towards the filament vacancies, the resultant vacancies formed would in turn trigger the back-diffusion and reformation of filament vacancies (Fig. 5(d)) after the light was turned off. This could explain the gradual recovery of the current towards the pre-illumination level. It should be noted that in Fig. 2, the filament was also formed at a CCL of 100 nA but a stable light-induced reset was achieved (i.e., no increase of current after removal of illumination). The better reset stability may be attributed to the much longer light-exposure period (200 s) as compared to that of Fig. 6(b) (10 s).

In summary, we have shown that the resistance of a nanoscale conducting filament (formed using voltage sweep under a certain current compliance limit) in the HfO$_2$ dielectric can be increased by exposing the dielectric film to white light. Resistance values can be modulated by varying the light intensity and exposure duration. The light-induced resistance increase in the reset process is ascribed to a conducting filament disruption caused by a recombination of the oxygen vacancies there with oxygen ions, whose transport from the surrounding interstitial locations is activated by the white light. These findings point to a possibility of extending the application range of HfO$_2$-based devices to the optical domain, e.g., imaging sensors and photodetectors with built-in non-volatile memory capability.

Partial funding support by Singapore Ministry of Education research Grant Nos. RG 78/12 and MOE2013-T2-2-099 was gratefully acknowledged.

11See supplementary material at http://dx.doi.org/10.1063/1.4929324 for the light-induced resistance reset observations on the ZrO$_2$/TiN/Ti/p-Si and SiO$_2$/Cu/Ti/p-Si samples.