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Optically reversible electrical soft-breakdown in wide-bandgap oxides—A factorial study

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In an earlier work, we found that an electrical soft-breakdown region in wide-bandgap oxides, such as hafnium dioxide, silicon dioxide, etc., could be reversed when illuminated by white light. The effect is evidenced by a decrease in the breakdown leakage current, termed as a negative photoconductivity response. This finding raises the prospect for optical sensing applications based on these traditionally non-photo-responsive but ubiquitous oxide materials. In this study, we examine the statistical distribution for the rate of breakdown reversal as well as the influence of factors such as wavelength, light intensity, oxide stoichiometry (or oxygen content) and temperature on the reversal rate. The rate of breakdown reversal is shown to be best described by the lognormal distribution. Light in the range of $\sim 400\text{--}700\text{ nm}$ is found to have relatively little influence on the reversal rate. On the other hand, light intensity, oxygen content and temperature, each of them has a clear impact; a stronger light intensity, an oxide that is richer in oxygen content and a reduced temperature all speed up the reversal process substantially. These experimental results are consistent with the proposed phenomenological redox model involving photo-assisted recombination of the surrounding oxygen interstitials with vacancy defects in the breakdown path. *Published by AIP Publishing.*

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I. INTRODUCTION

The ability of semiconducting materials to directly convert light into electrical signals has served as the cornerstone for most photo-sensing devices having various applications in telecommunication, military services, medical appliances, smart control systems, solar energy harvesting, etc. Such conversion usually takes place via a widely observed phenomenon known as positive photoconductivity (PPC), whereby photon absorption by the semiconducting material leads to the generation of excess electrical charges, which are in turn detected by an external circuitry in the form of an additional photocurrent. Hitherto, application needs have been met by photosensors based on conventional semiconductors such as silicon and its III-V counterparts. Recent research efforts in this field are mostly centered on alternative materials such as graphene,^{1–3} two-dimensional transition metal dichalcogenides (2D TMDs),^{4–6} perovskites,^{7–9} and composite heterojunction materials.¹⁰ The extraordinary electronic and optical properties of these materials lend promise to novel devices with integrated electrical and optical functionalities, e.g., light-sensitive $\text{CeO}_{2-x}/\text{AlO}_y$ resistive random access memory or RRAM devices with combined optical demodulation and arithmetic capabilities.¹¹

On the other hand, the negative photoconductivity (NPC) phenomenon, characterized by a decrease of the electrical current upon illumination, is also observed in material structures that typically exhibit the PPC behavior, e.g., III-V nanowires,¹² graphene,¹³ 2D TMDs [e.g., MoS_2 (Ref. 14)], thin-film materials such as Nb,¹⁵ PbSnTe ,¹⁶ etc. Unlike the

intrinsic PPC effect, the NPC effect is often viewed as an extrinsic effect arising out of charge trapping at impurities^{17–21} or surface/bulk defects.^{12,13,16,22,23} For instance, the decrease in tunneling current or capacitance of the metal-insulator-semiconductor structure²⁴ was attributed to the trapping of photoelectrons generated in the semiconductor by bulk/interface oxide defects, which in turn increases the tunneling barrier and/or a space charge region in the semiconductor region.²⁴ The existence of both PPC and NPC behaviors in a given material has also been reported. As an example, the native-oxide-coated InAs nanowires displayed an NPC response under short-wavelength illumination, but a PPC response under long-wavelength illumination.²² A similar observation applies to graphene, which exhibited a PPC response near the zero carrier density, but an NPC response at high carrier density.²⁵ Many-body interaction in an extremely confined 2D space was proposed as the origin for the changeover.^{14,15,25,26}

Recently, an unusual NPC phenomenon pertaining to traditionally non-photo-responsive wide-bandgap oxides was revealed by Zhou *et al.*²⁷ The authors showed that when a wide-bandgap oxide such as HfO_2 was electrically stressed to a “soft-breakdown” state, the increased leakage current through the breakdown region was quenched when exposed to white light. The electrical breakdown of an oxide film has been linked to the creation of an oxygen-deficient defective region,²⁸ wherein tunneling assisted by the vacancy defect states leads to increased current conduction. On this basis, the NPC behavior is proposed to have resulted from a light-induced defect annihilation process, believed to involve the recombination between vacancy defects in the breakdown path and photo-excited interstitial oxygen ions surrounding the breakdown path.²⁷ Such a NPC response has been

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consistently observed on different oxide/electrode combinations, such as SiO_2/Si , SiO_2/Cu , HfO_2/Si , HfO_2/TiN , and ZrO_2/TiN ,^{27,29–31} all of which are compatible to the present mainstream integrated circuit manufacturing technology. This points to the option of leveraging on these ubiquitous oxides for implementing optical sensing functionality, a possibility which has not been considered along the traditional PPC route due to the large bandgaps of these oxides.

In this paper, we examine the statistics for the rate of the NPC response as well as the impact of important factors such as the wavelength and intensity of light, the oxide stoichiometry and the temperature on the NPC behavior of soft-breakdown ZrO_2 and HfO_2 . The aim is to further elucidate the probable physics behind the NPC behavior. The rate at which the breakdown current is quenched is shown to follow a lognormal distribution. The current-quenching rate or NPC response speed is found to be relatively unaffected by light of wavelength ranging from ~ 400 to 700 nm covering the visible light spectrum. On the other hand, the intensity of light, oxygen content in the oxide and temperature affect the quenching rate profoundly. A stronger light intensity, richer oxygen content or reduced temperature accelerate the quenching rate significantly. The experimental results may be consistently explained by a photo-assisted migration of interstitial oxygen ions surrounding the breakdown path, and their recombination with the vacancy defects in the breakdown path.

II. EXPERIMENTAL DETAILS

Figure 1 shows a schematic diagram of the experimental set-up. The test sample, comprising a 4-nm thick ZrO_x or HfO_x film deposited on a $\text{TiN}/\text{Ti}/\text{Si}$ substrate, was placed inside a RHK 3500 HT ultra-high vacuum (UHV) conductive atomic force microscope (C-AFM). The ZrO_x or HfO_x film was formed by a conventional atomic layer deposition process at 250°C , involving H_2O as the oxidizing agent and tetrakis(dimethylamino)zirconium (for ZrO_x) or tetrakisdimethylamino-hafnium (for HfO_x) as the metal precursor. From x-ray photoelectron spectroscopy measurements, we found a metal to

oxygen ratio of $\sim 1:1.7$ for both oxides. After oxide deposition, the sample was immediately loaded into the C-AFM; no post-deposition annealing was carried out. A diamond coated Si cantilever probe was used, serving two purposes. First, the probe was used to induce a nanoscale breakdown path (~ 4 nm in diameter²⁷) in the oxide underneath using a voltage-ramp supplied by a Keithley SCS4200 parameter analyzer. Curve 1 of Fig. 2(a) illustrates this procedure applied on the ZrO_x dielectric. The state of breakdown was kept soft through imposing a current compliance limit I_{CL} on the analyzer, which capped the current flowing through the breakdown path to a preset limit by automatically aborting the applied voltage bias upon the occurrence of breakdown. Soft breakdown is typically characterized by an exponential current-voltage dependence observed during the subsequent voltage-sweep measurement following breakdown (curve 2), as opposed to the much higher Ohmic conduction current seen under hard breakdown.³² Second, the probe functioned as the top electrode during subsequent electrical testing. For all measurements taken, the voltage bias was applied to the probe with the TiN electrode grounded. A collimated white-light source was situated at a viewport of the UHV chamber, ~ 25 cm away from the test sample. The light intensity values given below refer to the value near the surface of the test sample, obtained in a separate measurement using a solarmeter placed at a similar distance from the light source as the test sample.

Possible heating up of the test sample by the white-light source was checked by measuring the sample temperature, using an infrared thermometer, in the presence of prolonged illumination. The same measurement was repeated in the absence of illumination. Under illumination, the average temperature over a 30-minute period was found to be the same as the case without illumination [see Fig. 1(b) in Ref. 31]. The measured deviation was only ± 0.1 K, which is the measurement resolution of the thermometer used. This indicates that thermal heating by the light source was negligible despite the prolonged illumination. As will be shown later, the response time for the current-quenching or NPC effect is on the order of several seconds at most. Thus, it is reasonable to rule out the influence of sample heating by the light source used in this study.

Figure 2(b) shows the NPC behavior of the breakdown ZrO_2 , similar to that observed on breakdown HfO_2 .²⁷ A small voltage bias of 1 V was applied, and the leakage current through the breakdown region was monitored as a function of time. The measurement was initially carried out in the dark (i.e., the shutter of the light source was closed) and a large leakage current of ~ 1 nA was registered. When the breakdown region was exposed to white light around the time of 15 s after the measurement had started, the leakage current was immediately “quenched” to around 10 fA, producing a clear NPC response. The current remained at the lower level after illumination was removed, indicating that the light had restored the breakdown oxide. This is also evidenced by the much lower current obtained during a voltage-sweep measurement made after the illumination [curve 3 in Fig. 2(a)], as compared to that obtained after breakdown (curve 2). The restored oxide could be subjected to electrical breakdown again to obtain the NPC response; the electrical

FIG. 1. Schematic diagram of part of the experimental set-up. Uncapped HfO_x/TiN and ZrO_x/TiN samples were tested in an ultra-high vacuum (UHV) conductive atomic force microscope (C-AFM) system. The C-AFM probe functioned as the top electrode; the bottom TiN electrode was always grounded via the stage. A collimated white LED (light-emitting diode) light source, situated at one of the viewports of the UHV chamber, provided the illumination.

FIG. 2. (a) Current-voltage curves for the (1) soft-breakdown (SBD) step, (2) post-SBD measurement, and (3) post-white-light-illumination measurement. (b) Current versus time curve showing a decrease in the breakdown leakage current (@ 1 V) upon illumination by white light (shaded region). (c) Soft breakdown and optical reversal of the breakdown oxide are repeatable over many cycles. The low resistance state (LRS) @ 1 V after SBD and the high resistance state after illumination are separated by ~ 4 orders of magnitude. Thermal drift of the C-AFM probe, inherent in the current experimental set-up, limits the number of repetitions. The difference in the measurement floor for the current in (a) and (b) is a result of the different measurement ranges used. A 1-nA range was used in (a) to reduce the measurement time required, especially for curve 1; the lowest measurable current was ~ 1 pA. In (b), a 1-pA range was used and the lowest measurable current was ~ 10 fA. In the event that the current is increased beyond the chosen measurement range, the parameter analyzer automatically scales up the range, but retains the resolution of the original chosen range when the current becomes low again. This explains the measurement of current higher than the chosen ranges. When an abrupt decrease in current occurs [such as at the onset of illumination in (b)], the measurement time would be extended.

breakdown cum optical reversal are repeatable over many cycles, as shown in Fig. 2(c).²⁹ The resistance of the breakdown oxide before and after illumination differs consistently by a ratio of $\sim 10^4$. It should be mentioned that for the

current experimental set-up, the number of cycles is limited by thermal drift of the C-AFM probe. There may be a prospect for further increasing the cycle number in a device prototype that incorporates an optically transparent top electrode to a level comparable to that already achieved for pure electrical switching in RRAM devices.^{33,34}

To capture the decrease of the breakdown current during illumination in real time, a current-to-voltage pre-amplifier cum oscilloscope set-up was used [Fig. 3(a)]. After the soft breakdown step, current measurements were first carried out in the dark, with a small monitoring voltage (~ 0.5 – 1 V) applied to the probe to check for stability of the breakdown current. Once a relatively stable current was obtained, the shutter was opened for illumination. At the same time, the oscilloscope was triggered to capture the current transient. Figure 3(b) depicts a typical voltage-time plot recorded by the oscilloscope, for a breakdown path in ZrO_x created under an $I_{CL} = 50$ nA and subjected to an illumination of intensity of 12.5 mW/cm². When displayed on a log-linear plot [i.e., $\log(\text{current})$ versus time], a quasi-linear relationship such as the one shown in Fig. 3(b) can be seen in the initial stage of the illumination. We define the current-quenching rate or the

FIG. 3. (a) Block diagram of a real-time current transient measurement set-up. The current-to-voltage preamplifier converts the breakdown leakage current into a voltage signal which is captured by a high-speed oscilloscope card installed in the parameter analyzer. (b) A typical current transient curve captured using the set-up in (a). A quasi-linear current-time relationship is obtained on a log-linear plot (dashed line). The current quenching rate or speed of the negative photoconductivity response is given by the slope of the dashed line in seconds per decade decrease in current. The current transient deviates from linearity at a later stage, due in part to the measurement resolution of the oscilloscope.

NPC response speed as the slope of the line, given in seconds per decade (decrease in current). For the case depicted in Fig. 3(b), the extracted response speed is 0.38 s/decade. This sub-second response is encouraging, given that the set-up was not optimized. We envisage further improvement of the response speed in subsequent device level demonstration through, for instance, the use of a microlens, like in the case of a CMOS sensor.

In the later stage of illumination, an obvious deviation from linearity in the form of slowing down of the NPC response can be seen. A similar observation is also obtained when the current is directly measured using a parameter analyzer having sub-pA resolution (not shown), ruling out the possibility that the slowing down is mainly caused by the limited voltage measurement resolution of the oscilloscope. We ascribe the slow down as a natural outcome arising from the recombination between a limited number of oxygen interstitials and vacancy defects.³⁵ The depletion of these entities in earlier recombination results in a slowing down of the recombination at a later stage.

III. RESULTS AND DISCUSSION

A. Photo-induced interstitial-vacancy recombination

To aid in the later discussion of the experimental results, here, we provide a brief review of the photo-induced interstitial-vacancy recombination model for the optical reversal of oxide breakdown, proposed earlier in Ref. 27. The model is adapted from the popular oxygen migration model proposed for the electrically induced resistance switching in an oxide-based bipolar RRAM device,³⁶ and is found to be most consistent with the experimental observations made to-date on the NPC phenomenon.

A breakdown path comprising oxygen vacancy defects^{36,37} is created in the oxide region under the probe contact when the applied electric field reaches a critical level that results in the dissociation of the metal-oxygen bonds.^{36,37} Gap states arising from the vacancy defects lower the electron tunneling barrier and the resultant increase in current may in turn accelerate the further generation of vacancy defects through a local Joule heating effect.³⁸ The liberated oxygen ions are either directed towards the anode, assisted by the applied electric field or directed laterally outwards, assisted by the localized Joule heating occurring at the breakdown site.^{36,37} When the applied voltage bias is interrupted after the analyzer detected that the current has reached the compliance limit, the oxygen migration slows down, resulting in some of the oxygen ions being “stored” in the interfacial region of the anode as well as in interstitial positions surrounding the breakdown path [Fig. 4(a)].

Oxygen ions stored within the anode interfacial region are believed to be responsible for the electrical reset switching, which is typically observed in the bipolar RRAM device. When the voltage polarity is reversed, these oxygen ions are driven back towards the breakdown path, and as a result, the vacancies there (and the related gap states that lead to the increased leakage current) are eliminated and the oxide resistance is partially restored.³⁶ The availability of oxygen ions in the anode interface region has been shown to

FIG. 4. Three-dimensional schematic illustration of the proposed photo-assisted interstitial-vacancy recombination model for the negative photoconductivity response of the oxide breakdown path. (a) After soft electrical breakdown, a conductive path comprising a cluster of oxygen vacancy defects is formed. Some of the oxygen ions from the dissociated metal-oxygen bonds propagated outwards and are situated at interstitial sites around the conductive path after the breakdown process is aborted. (b) During illumination, photons excite these interstitial oxygen ions and the latter migrate towards the conductive path (aided by the dipole field; see an example marked by a white arrow). Subsequent recombination with the vacancy defects results in the interruption of the conductive path and decrease in the breakdown leakage current.

play a key role; a reactive metal that could “bond” these oxygen ions at its interface and thereby ensuring their subsequent release back to the breakdown path is crucial in enabling the electrical reset under a reverse voltage polarity.³⁶

On the other hand, interstitial oxygen ions surrounding the breakdown path do not contribute to the electrical reset since they do not come under the direct influence of the applied voltage. However, under white-light illumination, these oxygen ions may be excited by the photons, allowing them to overcome the migration barrier and move towards the vacancies in the breakdown path, aided by the interstitial-vacancy dipole field [Fig. 4(b)].³⁹ Subsequent recombination with the vacancies there annihilates the breakdown path and gives rise to a NPC response in the breakdown current.²⁷ *Ab-initio* simulation studies⁴⁰ have found the migration barrier of interstitial oxygen ions in common oxides to be on the order of several hundreds of meV [e.g., ~ 0.11 – 0.27 eV for

SiO_2 ,⁴¹ $\sim 0.3\text{--}0.6\text{ eV}$ for HfO_2 (Ref. 42)]. It is therefore probable for these interstitial oxygen ions to overcome the migration barrier through absorbing photons having higher energies (of $\sim 1.8\text{--}3.1\text{ eV}$) from the white light. Photo-induced migration of anions in solid electrolytes have been proposed elsewhere.^{43,44} For instance, oxygen migration in magnesium oxide,⁴³ iodine migration in perovskite solar cells, etc.⁴⁴

A good support for the involvement of interstitial oxygen ions in the breakdown path's vicinity may be found in the NPC response of a breakdown path formed in an uncapped oxide layer using a positive voltage applied to the probe.⁴⁵ Due to the exposed oxide surface, storage of oxygen ions (liberated during breakdown and directed towards the positively biased probe) at the anode (probe) interface region does not occur. The low percentage (3%) of breakdown path showing electrical reset under a negative probe voltage corroborates this inference. However, almost 100% of the breakdown paths exhibited the NPC response when illuminated by white light. In the following, we will present new experimental results that further support the proposed photo-excited interstitial-vacancy recombination model for the NPC response.

At this point, it is worthwhile to point out the difference between Zhou *et al.*²⁷ and the earlier work by Emboras *et al.*⁴⁶ The latter made use of the plasmonic properties of Ag to confine light locally to an Ag filament, formed by the electric-field induced migration of Ag ions into an amorphous Si layer placed on top of the waveguide. As a result of the light confinement, the light intensity passed the filament was reduced significantly, thus allowing control of its transmission along the waveguide. *The formed Ag filament was stable under illumination.* In recent studies by Zhou *et al.*²⁹ and Kawashima *et al.*,⁴⁷ the authors also showed that a metal filament was generally not responsive to the illumination conditions examined in this study. Hence, the NPC response reported here should be distinguished from the behavior elucidated in Emboras *et al.*⁴⁶ The difference also rules out the possibility that the oxide breakdown path examined herein is a metal filament.

B. Lognormally distributed response speed

The soft-breakdown step (@ $I_{CL} = 50\text{ nA}$) followed by white-light illumination (@ 12.5 mW/cm^2 intensity) was carried out at numerous randomly chosen probe locations on the ZrO_x/TiN test sample, and the response speed extracted in the manner is explained above. As expected, the response speed varies from location to location. Among the common statistical distributions, the lognormal distribution is found to best describe the variation of the response speed [Fig. 5(a)]. Figure 5(b) shows the significant mismatch between the data and another common statistical function, the Weibull distribution. For the test conditions mentioned above, the mean response speed is 0.72 s/decade .

The lognormal distribution has been shown to apply to many fields of study, especially in cases involving a large variation in the observation concerned.^{48,49} In Fig. 5(a), the response speed ranges from 0.38 s/decade to 1.49 s/decade , approximately a four-fold variation. Such a large variation is not surprising, given that the two key steps, namely soft

FIG. 5. Statistical distribution for the speed of the negative photoconductivity response (s/decade) of the ZrO_x film when shown as (a) a lognormal plot and (b) a Weibull plot. A much better linear fit (line) is evident in the case of the lognormal plot.

breakdown and subsequent breakdown reversal, each entails a significant degree of randomness. The soft-breakdown step determines the state of the breakdown oxide region which in turn partly influences the subsequent reversal step. The state of the breakdown oxide is determined by numerous random factors, e.g., distribution of the chemical bond strengths/angles in the oxide underneath the probe contact,⁵⁰ stochastic nature of the (field-induced) bond dissociation process,⁵¹ and dispersion in the outward propagating oxygen ions,⁵² notwithstanding the current “overshoot” (related to the parasitic impedance of the set-up) that occurred and impacted transient heating at the instance of breakdown.⁵³ In the reversal step, fluctuation in the number of photons arriving at the nanoscale breakdown region, the random nature of photon absorption, and dispersion in the migration of the photo-excited oxygen ions⁵⁴ add further variations to the response speed. Moreover, the arbitrary distribution of vacancy defects in the breakdown path, which in conjunction with their random recombinations with oxygen interstitials, is expected to dictate the rate of decrease in the current to some extent. For instance, if the recombinations and disruption of the breakdown path occur at a constriction formed by only a couple of vacancy defects, then the resultant impact on the current is expected to be significant.

The large spread in the response speed may pose a challenge to subsequent efforts in exploiting the NPC behavior for the optical sensing application. While factors such as current overshoot during breakdown may be mitigated through design optimization, others such as the random state of the breakdown region and the reversal process are inherent in nature, and may require measures beyond device engineering

for them to be effectively addressed. Further study on this subject is needed.

C. Impact of light intensity on response speed

Figure 6 depicts the impact of light intensity on the distribution of the NPC response speed of soft-breakdown ZrO_x . For both light intensities used, the I_{CL} for the soft-breakdown step was fixed at 50 nA. Reducing the intensity from 12.5 mW/cm^2 to 2.5 mW/cm^2 slows down the response speed noticeably, shifting the entire distribution towards longer timings in an almost parallel manner. The mean response speed at 2.5 mW/cm^2 is 2.40 s/decade, ~ 3.3 times longer than that for 12.5 mW/cm^2 . The slowing down of the NPC response under a weaker illumination may be ascribed to a corresponding reduction in the number of photons interacting with the breakdown oxide region. The modulation of response speed by light intensity shows the potential of the NPC phenomenon to be engaged for optical sensing applications.

It should be cautioned that although the two distribution appears to be parallel, the respective spreads in the response speed are different, due to the logarithmically distributed timings. At lower light intensities, the standard deviation is 0.90 s/decade as compared to 0.30 s/decade at higher intensities. The larger spread at lower intensities is expected, and is probably caused by a greater fluctuation in the number of photons arriving at the nanoscale breakdown region as the photon density is reduced. This effect is deemed similar to the random dopant fluctuation issue in small-area metal-oxide-semiconductor field-effect transistors.⁵⁵

D. Wavelength dependence of response speed

The NPC response speed under blue light (450 nm $\equiv 2.76$ eV) and red light (650 nm $\equiv 1.91$ eV) illuminations is compared in Fig. 7. To obtain the colored light, a filter was placed in front of the collimated white light source. The intensity of the filtered light was kept approximately constant by increasing the intensity of the white light to offset the drop which occurred after filtering. Interestingly, relatively little impact on the NPC response speed is observed when changing from blue light (of a higher photon energy) to red light (of 0.85 eV lower in photon energy). The mean

FIG. 6. Lognormal distribution for the speed of the negative photoconductivity response of the ZrO_x film at two different white-light intensities.

FIG. 7. Lognormal distributions for the speed of the negative photoconductivity response of the ZrO_x film when subjected to red- and blue-light illumination. The distribution for white-light illumination is also shown for comparison. The light intensity for all three cases was fixed around 12.5 mW/cm^2 .

response time for the blue and red illuminations are 0.66 s/decade and 0.81 s/decade, respectively. For comparison, the response-speed distribution for white light illumination (at a similar intensity) is also shown. This weak dependence on wavelength should be contrasted against the stronger dependence of semiconducting materials which exhibit the PPC response (e.g., Si). The latter's PPC response is controlled by the rate of electronic transitions, described by an absorption coefficient that generally varies strongly with wavelength.⁵⁶

The weak dependence on wavelength suggests that electronic transitions are not limiting the breakdown reversal process. In the framework of the proposed redox model,³⁶ the recombination between surrounding oxygen interstitials with vacancy defects in the breakdown path accounts for the reversal process. The ability of the mobile oxygen species to migrate towards the vacancy defects should determine the recombination rate. From the oxygen tracer diffusivity measurements,⁵⁷ the energy barrier for oxygen migration in the ZrO_2 network is found to be ~ 0.51 – 0.61 eV, much smaller than the photon energy for red light. Thus, we reckon that all wavelengths in the visible light spectrum could excite and cause the surrounding interstitial oxygen ions to migrate towards the vacancy defects with similar effectiveness, which explains the weak wavelength dependence observed.

E. Impact of oxide stoichiometry on response speed

The dependence of the NPC response speed on oxide stoichiometry for a given light intensity is illustrated in Fig. 8 for two HfO_x films having Hf:O ratios of 1:1.6 (oxygen deficient) and 1:3.3 (oxygen rich), as determined by X-ray photoelectron spectroscopy analysis. The oxygen-content in the HfO_x films was varied by adjusting the duration of the H_2O pulse during the atomic layer deposition (ALD) process. Figures 9(a) and 9(b) shows the Hf 4f (left) and O 1s (right) core-level spectra of an oxygen-deficient and an oxygen-rich HfO_x film, respectively. For the oxygen rich film, the presence of a significant O 1s core-level spectra attributed to non-bonding or interstitial oxygen is evident. A very interesting impact on the response-speed distribution is obtained when the oxygen content in the HfO_x film is enhanced. Besides the improvement in the

FIG. 8. Lognormal distributions for the speed of the negative photoconductivity response of the oxygen-deficient and oxygen-rich HfO_x films in Fig. 9.

response speed, the distribution curve is also steeper than that of the oxygen-deficient HfO_x sample. This implies that the spread in the NPC response speed of the oxygen-rich sample is less than that of the oxygen-deficient sample.

The above observations show that the oxygen content in the HfO_x film plays an important role in determining the NPC response speed, and are consistent with the proposed redox model for breakdown reversal.²⁷ The random distribution of interstitial oxygen ions around the breakdown path, which in turn impacts the vacancy recombination process, represents a source of variation to the NPC response speed. In a perfectly stoichiometric HfO_x sample, these interstitial oxygen ions originate from the breakdown process; oxygen ions from the dissociated Hf-O bonds propagate outwards from the breakdown site, due to Joule heating, and takes up random interstitial positions around the breakdown site after the breakdown process is aborted. The stochastic nature of the breakdown process itself contributes a large part to the randomness in the interstitial-oxygen distribution and to the spread of the response speed, as already discussed above. In

an oxygen-deficient HfO_x sample, some of the oxygen ions may take up vacancy positions, “locking” them there because oxygen ions in these positions form strong covalent bonds with the Hf atoms and may not readily migrate under illumination unlike the interstitial counterparts. This limits the NPC response speed. On the other hand, in the oxygen-rich HfO_x sample, a significant number of oxygen ions introduced during the oxide growth step are already present in interstitial positions everywhere within the oxide network. Their presence could in turn mitigate the randomness of the distribution arising from the breakdown process. Hence, besides the expected improvement in the NPC response speed due to the more abundant supply of interstitial oxygen ions, the spread in the response speed is also reduced.

F. Temperature dependence of response speed

The impact of temperature on the NPC response speed is also examined as a further check on the consistency of the proposed redox model for breakdown reversal.²⁷ In this framework, dispersion in oxygen migration is expected to become worse at higher temperatures, due to a more significant phonon scattering effect. The increased dispersion in oxygen-ion transport, in turn, limits their recombination with the vacancy defects in the breakdown path, slowing down the NPC response. This inference is indeed borne out by the response-speed distribution curves shown in Fig. 10, for testing carried out at two different temperatures. The higher temperature was achieved by direct heating of the test sample via a built-in heater in the sample holder; the temperature was determined using a built-in thermal couple in the sample holder as well. For the case of the higher temperature, an overall slowing down of the response speed is evident, as manifested in the shift of the distribution curve towards longer timings. At 295 K, the mean response speed is 2.2 s/decade, and this is increased to 3.7 s/decade at 390 K. In conjunction with this increase is an increase in the spread of the response speed at 390 K. These observations are in-line with the above prediction of the model. Since the oxygen ion migration process becomes more dispersive at the elevated temperature, the increased randomness in the ion motion results in a larger spread in the response speed.

FIG. 9. Hf 4f (left column) and O 1s (right column) core-level spectra (symbol) from x-ray photoelectron spectroscopy measurements made on two 4-nm thick HfO_x films having different stoichiometries or oxygen content. The component spectra are given by the solid lines. The top row is for the slightly oxygen deficient HfO_x ($x = 1.7$) film, while the bottom row pertains to the oxygen-rich HfO_x ($x = 3.3$) film.

FIG. 10. Lognormal distributions for the speed of the negative photoconductivity response of the ZrO_x film after soft breakdown, at two different temperatures.

IV. SUMMARY

In this paper, we present experimental data from a more extensive study on the NPC response of wide-bandgap oxides following electrical soft-breakdown revealed earlier. The response speed, defined as the time taken for the leakage current to decrease by one decade, is shown to follow the lognormal distribution, and the possible random effects contributing to the statistical variations are discussed. It is recognized that some of these effects are ultimately inherent in the nanoscale breakdown path and may require other mitigating measures if the NPC response is to be exploited for optical sensing applications. The impact of relevant factors such as intensity and wavelength of light, oxide stoichiometry (or content of oxygen in the oxide) and temperature on the NPC response speed are also examined. It is shown that a higher light intensity, an oxide richer in oxygen content and a reduced operating temperature can speed up the NPC response distinctively. On the other hand, the NPC response is relatively unaffected by the wavelength in the visible-light range ($\sim 400\text{--}700\text{ nm}$). All the above experimental results can be consistently accounted for by the proposed photo-excited interstitial-vacancy recombination model.

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