10-3-2019

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Abstract
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Keywords
dielectric breakdown, amorphous-to-crystallization transformation, in situ TEM, oxygen migration, TiO2

Disciplines
Materials Science and Engineering | Metallurgy

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In situ TEM Study of the Amorphous-to-Crystalline Transition during Dielectric Breakdown in TiO₂ Film

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Abstract: Dielectric breakdown of oxides is a main limiting factor for improvement of the performance of electronic devices. Present understanding suggests that defects produced by intense voltage accumulate in the oxide to form a percolation path connecting the two electrodes and trigger the dielectric breakdown. However, reports on directly visualizing the process at nanoscale are very limited. Here, we apply in situ transmission electron microscopy to characterize the structural and compositional changes of amorphous TiO₂ under extreme electric field (~100 kV/mm) in a Si/TiO₂/W system. Upon applying voltage pulses, the amorphous TiO₂ gradually transformed to crystalline sub-stoichiometric rutile TiO₂₋ₓ and the Magnéli phase Ti₃O₅. The transitions started from the anode/oxide interface under both field polarities. Preferred growth orientation of rutile TiO₂₋ₓ with respect to the Si substrate was observed when Si was the anode, while oxidation and melting of the W probe occurred when W was the anode. We associate the TiO₂ crystallization process with the electrochemical reduction of TiO₂,
polarity-dependent oxygen migration, and Joule heating. The experimental results are supported by our phase-field modeling. These findings provide direct details of the defect formation process during dielectric breakdown in amorphous oxides and will help the design of electronic devices with higher efficiency and reliability.

**Keywords:** dielectric breakdown, amorphous-to-crystallization transformation, *in situ* TEM, oxygen migration, TiO$_2$

1. **Introduction**

Continuous increase in the demand of energy consumption$^1$ and information processing$^2$ poses many daunting materials issues. One key issue revolves around dielectric breakdown in solid oxides, such as the failure of materials in energy storage devices at 2~3 orders of magnitude below their intrinsic dielectric breakdown strength$^3$ and the undesired increase in tunneling current flowing across gate oxides in Si microelectronics as a result of an aggressive device scaling.$^4$ In recent studies, resistive random-access memory based on reversible dielectric breakdown of oxides suffers from large variances in the switching parameters between different memory cells and from cycle to cycle.$^5$ In these devices, a thorough understanding of the structural and compositional changes in the dielectrics under extreme electric fields (i.e., near its dielectric strength) is a critical roadblock to increase the working efficiency and reliability of the devices.

Several models have been proposed to describe the dielectric breakdown process, such as the generation of electron traps in thin film oxides and the formation of a conductive path
connecting two electrodes when the trap density reaches a critical value.\textsuperscript{6} Other mechanisms have also been suggested to account for the origins of different electronic defects.\textsuperscript{7-8} Experimentally, structural and chemical changes during dielectric breakdown are usually characterized post-breakdown and no sufficient details of the dynamic processes are presented.\textsuperscript{7, 9-13} \textit{In situ} observation and characterization of the breakdown process can provide valuable information that otherwise cannot be obtained.

Due to the stochastic nature of the conductive path formation, direct observation of the dielectric breakdown process at high spatial resolution is difficult. Among the limited number of reports employing \textit{in situ} transmission electron microscopy (TEM), several different microstructural transitions were identified in crystalline TiO\textsubscript{2},\textsuperscript{14-17} amorphous SiO\textsubscript{2},\textsuperscript{18-19} and other oxides.\textsuperscript{20-24} \textit{In situ} TEM study of the dielectric breakdown process in insulating oxides is also curbed by various technical issues, such as surface tracking breakdown which poses requirement of embedded electrode and charging-induced image drift which limits the acquisition time and data quality. To the best of our knowledge, \textit{in situ} TEM study of amorphous oxides which consecutively transform to crystalline phases at the verge of dielectric breakdown has not been reported.

Our group has recently developed an \textit{in situ} TEM technique to apply extremely high electric field to a desired region of the dielectric for breakdown study.\textsuperscript{25} To minimize the possible effects of flashover and surface tracking, we coat the dielectrics of interest on a conductive Si wedge substrate (\textbf{Figure 1a}) that is attached to one terminal of the voltage source. When a fine W probe that is connected to the other terminal of the voltage source is placed into contact with the dielectric at the apex of the wedge, the region of dielectric at the contact point experiences the highest electric field, thereby localizing the highest probability of breakdown.
within the observable volume and enabling detailed examination and analysis of the sample
during the breakdown process. The thickness of the coated film along the electron beam
direction is sometimes reduced to enhance image contrast using Focused Ion Beam (FIB) system.

In the present work, we investigate the failure mechanisms of amorphous TiO$_2$ (a-TiO$_2$) under
bipolar voltages. Amorphous TiO$_2$ is known to be a better dielectric than its crystalline
counterparts.$^{26}$

2. Results

In an initial tryout, we applied a constant voltage (9.6 V) to the Si/a-TiO$_2$/W system
where the Si was the anode and the W the cathode (Supplementary video). Immediately we
observed an abrupt contrast change in the a-TiO$_2$ film and a rapidly increased leakage current
from $\sim 1 \times 10^{-8}$ A to $\sim 5 \times 10^{-6}$ A (Figure S1), suggesting the dielectric breakdown of a-TiO$_2$
which underwent transition to more conductive phases. To resolve and image the gradual
microstructural change in a-TiO$_2$ during dielectric breakdown, we switched to square voltage
pulses with lower amplitudes and shorter durations. The region that experiences changes under
the applied voltage pulses is referred to as the “affected zone”.

As shown in Figure 1b, the as-prepared, pristine TiO$_2$ with thickness of $\sim 70$ nm is
amorphous, while the Si substrate has its [110] direction parallel to the electron beam confirmed
using nanobeam diffraction. When the Si substrate was at positive bias and the W probe
grounded (referred to hereafter as “normal bias”), we first applied a voltage with amplitude of
7.47 V and length of 100 $\mu$s (abbreviated “7.47 V, 100 $\mu$s”) to the a-TiO$_2$. After 1 pulse,
significant contrast change in both the a-TiO$_2$ and the adjacent Si substrate was observed (Figure
1c). Selected area electron diffraction (SAED) of the affected zone discloses at least two
coexisting phases: diamond cubic Si and rutile TiO$_{2-x}$ ($x \approx 0$) (Figure 1c). The interplanar spacings for the marked diffraction spots are: $d_{\text{Si(220)}} = 0.195$ nm; $d_{\text{Si(11-1)}} = 0.314$ nm; $d_{\text{TiO}_2-(2-10)} = 0.209$ nm; $d_{\text{TiO}_2-(110)} = 0.325$ nm. The angle between Si(220) and Si(11-1) is 35° and that between TiO$_{2-x}$(2-10) and TiO$_{2-x}$(110) is 68°. All of these values closely match those of diamond cubic Si (PDF#04-003-1456) and rutile TiO$_2$ (PDF#04-003-5855), respectively. A sharp spot that is close to (000), corresponding to a $d$-spacing of 0.521 nm, was assigned to (002) of the Magnéli phase, Ti$_3$O$_5$ (PDF#04-007-9058).$^{14}$

Figure 1. Crystallization of TiO$_2$ under extreme electric fields with normal bias. (a) Scheme illustrates the experimental setup for dielectric breakdown study. Under normal bias, the W probe is grounded and Si substrate at positive bias. The TiO$_2$ film was coated on a Si wedge substrate and thinned at the wedge apex using Focused Ion Beam (FIB). (b) TEM micrograph (left) shows the amorphous TiO$_2$ (a-TiO$_2$) and crystalline Si in the FIB milled window confirmed by nanobeam diffractions (right). The Si substrate has its (110) plane perpendicular to the electron beam direction. (c) After applied one square voltage pulse with amplitude of 7.47 V and length of 100 µs (abridged as “7.47 V, 100 µs”), large contrast change appears in
the a-TiO₂ and Si (TEM micrograph on the left), Selective area electron diffraction (SAED) on the right shows newly formed rutile TiO₂ₙ phases in the affected area (termed as “affected zone”). **(d)** Successive expansion of the affected zone at a different position upon applying a series of square pulses (7.00 V, 100 µs).

The amplitude of the pulse was then gradually reduced in attempt to slow down the transition. When using a series of pulses (7.00 V, 100 µs) under normal bias, the step-by-step expansion of the affected zone was captured at a new location after applying different numbers of pulses (**Figure 1d**). It becomes clear that the affected zone initiated at the Si/TiO₂ interface and enlarged towards the TiO₂/W interface. At the last stage of the events, the probe front appears to be rounded indicating significant Joule heating and large leakage current.

High magnification TEM images and Fast Fourier Transform (FFT) were used to disclose further details of the structural and compositional changes during dielectric breakdown. TEM micrographs of the affected zone after 1 pulse (7.47 V, 100 µs) (**Figure 2a-b**) show the appearance of crystalline phases with some planar defects, whose morphology resembles Wadsley defects observed in nonstoichiometric TiO₂ₙ created by electrically stressing rutile TiO₂.¹⁵-¹⁶ Moiré patterns are also observed, suggesting the overlapping of different grain orientations along the electron beam direction. Lattice fringes are found to continue across the original Si/TiO₂ interface within the crystalline region, indicating the preferred orientation of the new crystalline phase with respect to the Si substrate. A closer look at the margin of the affected zone (**Figure 2b**) reveals the crystalline nature. Phase determination by measuring the interplanar distances and angles using FFT (**Figure 2c**) confirms that the newly formed crystalline phase matches rutile TiO₂ₙ. Such rutile phase also exists right across the Si/TiO₂ interface (diffraction spots with red masks in **Figure 2d**).
Figure 2. Structural analysis and orientation relationship in the affected zone under normal bias.

(a)(b) TEM micrographs show the affected zone in front of the W probe (a) and on the left side (b) after 1 pulse (7.47 V, 100 µs) to be crystalline with some planar defects. (c)(d) Fast Fourier Transform (FFT) images of the corresponding regions marked in (b) show the existence of rutile TiO$_{2-x}$ and confirms the crystallization of a-TiO$_2$ under normal bias. (e) TEM micrograph shows the structures at the Si/TiO$_2$ interface after 1 pulse (7.00 V, 100 µs). (f) FFT image and inverse FFT images of region “f” marked in (e) reveal the preferential orientation of TiO$_{2-x}$(110) planes along Si(111) at the Si/TiO$_2$ interface at the early stage of crystallization.
The orientation relationship is examined in an affected zone formed after 1 pulse (7.00 V, 100 µs) (Figure 2e) using FFT and inversed FFT images (Figure 2f). Region “f” in Figure 2e shows the preferred growth orientation of rutile TiO$_{2-x}$ where the TiO$_{2-x}$[110] direction aligns with the Si[111] direction. Previous work using vacuum arc deposition under high voltage pulses to grow substoichiometric TiO$_2$ thin film on Si substrate (on anode side) found an epitaxy relationship between the two materials: Si[111]//TiO$_2$[110] and Si[311]//TiO$_2$[110]. It is plausible that the observed preferential growth orientation in the present work is an indication of the existence of the same epitaxy relationship. As explained in detail in the Supporting Information (Figure S3 and Table S2), the misfit between Si(111) at the anode/oxide interface and TiO$_{2-x}$(110) is found to be only 0.6 % and smaller than that between their stoichiometric counterparts (i.e., 3.4%).

The presence of a Magnéli phase and possible Wadsley defects in a-TiO$_2$ and deformation in Si implies the electrochemical reduction of a-TiO$_2$ to TiO$_{2-x}$ and oxygen migration from a-TiO$_2$ to Si where Si is oxidized to SiO$_x$. To verify the redox reactions, we performed electron energy loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDS) in amorphous TiO$_2$, crystalline Si substrate, and the affected zone (Figure 3a-b). The “crystalline TiO$_{2-x}$” and “defective Si” refer to the region below and above the original a-TiO$_2$/Si interface within the affected zone, respectively. Peak fitting using a Gaussian model for Ti L$_{2,3}$ peaks showed that the two Ti peaks (L$_3$ and L$_2$) shift to lower energies in crystalline TiO$_{2-x}$ than those in amorphous TiO$_2$ (460.1 eV vs 460.5 eV for L$_2$, and 454.6 eV vs 454.8 eV for L$_3$, respectively). The convoluted Si L$_{3,2}$ peak shifts to a higher energy in defective Si compared with crystalline Si (101.2 eV vs 100.7 eV). These energy shifts are consistent with the reduction of a-TiO$_2$ and oxidation of Si. Oxygen deficiency in a-TiO$_2$ after crystallization was also evidenced.
by the decrease of the O:Ti atomic ratio from 2.00 to 1.89 (i.e., \( x \approx 0.11 \)) (inset of Figure 3c).

The two spectra were collected both in the middle part of the TiO\(_2\) film between the Si and the W probe tip. The two collection spots were less than 10 nm apart. We also collected EDS spectra at another three spots in the crystallized TiO\(_{2-x}\) region which were >50 nm away from the previously measured spots. The calculated O:Ti ratios at the three additional spots are 1.91, 1.86, and 1.84, respectively. These values are less than 2.00 and close to 1.89, confirming the loss of oxygen.

Figure 3. Compositional analysis of the affected zone under normal bias. (a)(b) Electron energy loss spectroscopy (EELS) of different regions shows the left shift of the deconvoluted Ti L\(_3\) and L\(_2\) peaks and
the right shift of convoluted Si L\textsubscript{3,2} peak after application of normal bias (blue dash lines for reference). Signals for crystalline TiO\textsubscript{2-x} and defective Si were collected from the regions below and above the original Si/TiO\textsubscript{2} interface, respectively, inside the affected zone. (c) Energy-dispersive X-ray spectroscopy (EDS) of amorphous TiO\textsubscript{2} and crystalline TiO\textsubscript{2-x} as well as the quantified O:Ti atomic ratios of the two spectra (inset) show the decrease of oxygen content after experiencing normal bias. All error bars are standard deviation.

When the W probe was at positive bias and Si grounded (referred to hereafter as “reverse bias”), no intense contrast change was observed in the affected zone after 1 pulse (7.47 V, 10 µs) (Figure 4a-b). Yet, the W probe melted and bonded onto the a-TiO\textsubscript{2} film. When retracted, the W probe exhibited brittle fracture (Figure 4b). EDS of the spot C in Figure 4b shows considerably higher oxygen content in the otherwise pure W probe (Figure 4c). SAED of the fractured W piece confirms the existence of WO\textsubscript{3} phase (PDF#04-007-0979), though other WO\textsubscript{x} phases may also exist (Figure 4d). The oxidation of W implies oxygen migration from a-TiO\textsubscript{2} to W and concomitant reduction of a-TiO\textsubscript{2} to TiO\textsubscript{2-x} phases.
Figure 4. Structural and compositional analysis of the affected zone under reverse bias. (a) Under reverse bias, the Si substrate is grounded while W probe at positive bias. (b) After applied one pulse (7.47 V, 10 μs), the W probe tip melted and bonded onto the a-TiO₂ film. (c) EDS of the spot region marked in (b) shows the high oxygen content in the otherwise pure W probe. (d)(e) SAED of the two circular regions marked in (b) show the existence of both WO₃ and rutile TiO₂₋ₓ in the affected zone. Also, no diffraction pattern corresponding to planar defects appears in (e). (f) A montage of several higher magnification TEM micrographs shows the morphology and distribution of the crystalline phases (marked with yellow dash line).
Crystallization of a-TiO$_2$ to rutile TiO$_{2-x}$ under reverse bias is confirmed by SAED of regions marked “d” and “e” in Figure 4b. A montage of several higher magnification TEM micrographs of the affected zone in the a-TiO$_2$ film outlines the distribution of crystallized TiO$_{2-x}$ regions (marked with yellow dashed lines in Figure 4f). The montage also verifies the absence of Wadsley defects, consistent with the diffraction patterns in Figure 4e. The crystalline region on the right side of Figure 4f implies that the crystallization started near the TiO$_2$/W interface, opposite to the observed behavior under normal bias. Small nucleated crystallites are also present in the a-TiO$_2$ film.

3. Discussion

The above experimental observations agree with the polarity-dependent oxygen migration in oxides under electric fields.$^{29-31}$ Under normal bias, significant lattice shearing took place in the Si substrate while the W probe was unaffected. Combined with supporting evidence from the EELS spectra, it is plausible that Si was incorporating oxygen from a-TiO$_2$, consistent with our previous work on the Si/SiO$_2$ system.$^{25}$ Under reverse bias, the opposite scenario arose: Si remained intact while the W probe was oxidized and melted. Oxygen drifting in TiO$_2$ under electric field has been reported to create Wadsley defects at low temperatures (150 °C).$^{15-16}$ The absence of defects resembling Wadsley defects under reverse bias is probably due to the unconstrained W/TiO$_2$ interface which can be considered as a free boundary condition.

The mobile oxygen ions were released from the reduction reactions in a-TiO$_2$ which, similar to the anodic reactions of transition metal oxides during electroforming,$^{32-33}$ occurred at the anode/oxide interface. Once oxygen left, the local a-TiO$_2$ region was reduced to sub-stoichiometric TiO$_{2-x}$ with oxygen vacancies. It has been shown that oxygen deficiency in TiO$_2$
lowers the melting point and makes the crystallization process occur at lower temperatures.\textsuperscript{34} This supports the idea that reduction of a-TiO\textsubscript{2} to sub-stoichiometric rutile phases occurred prior to the crystallization.

Crystallization of a-TiO\textsubscript{2} under external electric field has been previously inferred from spectroscopy\textsuperscript{35} or resistivity measurement\textsuperscript{36} and attributed to Joule heating only. Formation of crystallites in amorphous TiO\textsubscript{2}\textsuperscript{9} and TaO\textsubscript{x}\textsuperscript{37} under applied voltages was previously confirmed with \textit{ex situ} TEM. In our \textit{in situ} study, the growth of crystalline TiO\textsubscript{2-x} is shown to be directional, an indication that the mechanism involves not only Joule heating but also the reduction reaction and the oxygen migration. The mechanism also differs from the dielectric breakdown-induced epitaxial growth with polarity-dependence observed in p-Si/SiO\textsubscript{2}/Si wherein the transition started at the cathode/oxide interface and the major cause was attributed to electromigration of Si.\textsuperscript{38}

The formation energy for crystalline TiO\textsubscript{2} from its amorphous counterpart measured with thermal analysis is 142 kJ/mol.\textsuperscript{39} In comparison, the energy supplied during \textit{in situ} experiments is about 50 times under normal bias and 5 times under reverse bias of this value, which is consistent with a significant amount of energy being dissipated in the Si substrate or the vacuum in TEM column during the application of the pulse (\textit{cf.} Supporting Information). Besides energy considerations, two other aspects also affect the crystallization process – nonuniform distribution of electric field and temperature in TiO\textsubscript{2} film at the oxide/W interface and the energy band alignment. Due to the high curvature of the W probe tip, the electric field strength is higher in regions near the W probe tip than other places. Temperature gradient around the W probe tip is also shown to be higher than anywhere else.\textsuperscript{40} Such nonuniformities will lead to faster oxygen diffusion and heating around the W probe than other part of the TiO\textsubscript{2} film; therefore, leading to a fast crystallization process in front of the W probe under reverse bias. Under normal bias, since
crystallization initiated from the Si/TiO$_2$ interface, there is no such advantages. When considering the bandgap of the amorphous TiO$_2$ and the fermi energies of a $n$-type Si and a W electrode, the energy gap for electron to tunnel through the a-TiO$_2$ film from W to Si under normal bias is lower than that for an electron to tunnel from Si to W under reverse bias even when the applied voltage is the same under different polarities, so the driving force for electron tunneling and current flow through the TiO$_2$ film is higher under reverse bias than that under normal bias (cf. Supporting Information). The original Si/TiO$_2$ interface has a saw-like profile (Figure 4f) and different Si facets are in contact with the amorphous TiO$_2$ film. This leads to the variation of the activation energy for the nucleation of rutile TiO$_{2-x}$ at different positions on the Si/TiO$_2$ interface, which is evidenced by the discontinuous crystalline regions along the Si/TiO$_2$ interface in the early stage of crystallization (Figure 2e). Upon nucleation and initial growth, the TiO$_{2-x}$ crystals at the Si/TiO$_2$ interface maintain a strongly preferred relation: TiO$_{2-x}$(110) // Si(111) (Figure 2a). Due to both oxygen migration and the lattice mismatch strain, the interface is accompanied with structural defects, such as stacking faults and dislocations. As the crystallization process proceeds further, new crystalline regions which appear at the crystalline/amorphous interface (i.e., crystalline TiO$_{2-x}$/amorphous TiO$_2$) may take on a different grain orientation. In addition, the crystalline/amorphous interface becomes rougher and the accumulated strain energy gets higher. This makes homogeneous nucleation of crystalline TiO$_{2-x}$ near the crystalline/amorphous interface more favorable and leads to a polycrystalline structure across the whole crystallized region.

We further suggest possible reasons for the different changes between the Si/TiO$_2$ interface under normal bias and the TiO$_2$/W interface under reverse bias. First, the Si/TiO$_2$ interface is a material interior interface while the W/TiO$_2$ interface is two contacting free
surfaces. The former is naturally cleaner and more coherent. Crystallization of a-TiO$_2$ starts at this interface under normal bias and maintains a preferred orientation relation with the Si substrate, as it lowers the nucleation energy barrier. Second, the oxidation of W into WO$_3$ leads to the melting of the probe since the resistance of WO$_3$ is higher and the melting point much lower than that of W. The localized Joule heating at the contact point might have melted TiO$_2$ and then quenched to solid in the amorphous state as the voltage pulse is short (10 μs). Due to the absence of an epitaxial relationship at the TiO$_2$/W interface, nucleation within the a-TiO$_2$ film by Joule heating starts at a distance from the interface.

The newly formed crystalline TiO$_{2-x}$ phase and Magnéli phase are more conductive than both a-TiO$_2$ and rutile TiO$_2$. Once these conductive phases are formed, they effectively shorten the length of the a-TiO$_2$ resistor. Consequently, the leakage current escalates, which further enhances the Joule heating effect and accelerates the crystallization process, eventually leading to dielectric breakdown of the (formerly) a-TiO$_2$ film. Different from previous work on the in situ TEM study of the crystallization of amorphous oxide and phase-change memristors through heating, our study displays a polarity-dependent crystallization process. Such a process is the early stage of a general dielectric breakdown.

To further understand the experimental findings, we have developed a numerical model considering the migration of electrons and ions, electrochemical reaction, and crystallization processes under the normal bias condition. Typical results are shown by the snapshots in Figure 5, where the top edge corresponds to the Si/TiO$_2$ interface while the green line segment at the bottom edge of Figure 5b indicates the contacting W probe. For a relatively long time, prior to the nucleation of the crystalline phase, free electrons migrate gradually through diffusion and drift current under the applied electric field. Mobile oxygen ions are generated through the
reduction reaction, and also redistribute under the electric field. Upon reaching a certain concentration of the reduced oxide, when the more conductive crystalline phase is energetically favorable, the material nucleates a crystalline phase. Once a crystalline phase is nucleated, the high conductivity carries over much more free electrons which pushes the reduction reaction further in the neighborhood. Together with the more concentrated electric field next to the crystalline phase, the abundant reduced oxide promotes the fast growth of the crystalline phase, until it connects the two electrodes and causes the breakdown of the entire dielectric layer.\textsuperscript{44} The phase field modeling results in Figure 5 confirm the experimental observation that crystallization starts at the Si/TiO$_2$ interface under normal bias condition and reveal the essential role migrating oxygen ions play during crystallization of amorphous TiO$_2$ under extreme electric fields.
Figure 5. **Simulation of the charge migration and amorphous-to-crystallization transformation.** The concentration of mobile oxygen ions (a) immediately before, (c) shortly after, and (e) in the later stage of the formation of a crystalline phase. (b)(d)(f) The corresponding morphologies of the crystalline phase (shown by the phase field variable, red indicates the crystalline phase). The contours show the equipotential lines. The electrodes are marked by the green lines at the top and bottom edges in (b).

4. **Conclusions**

In summary, we studied the sequential events associated with dielectric breakdown in amorphous TiO$_2$ under bipolar voltage biases in a Si/a-TiO$_2$/W system. The data presented here suggest that (1) Joule heating, (2) reduction of amorphous TiO$_2$ to TiO$_{2-x}$, and (3) oxygen migration under electric field are involved in the amorphous-to-crystalline transitions in TiO$_2$. The redox reaction at the anode/oxide interface and the polarity-dependence of the oxygen migration are likely the factors that contribute to the different crystallization processes under different bias polarities. Our findings shed light on the structural and compositional changes in the premature dielectric breakdown process and serve as guidelines for engineers to optimize the structure and performance of future electrical devices.

5. **Experimental methods and theoretical calculations**

**Materials Preparation.** Amorphous TiO$_2$ films on Si wedge substrates were fabricated using a sol-gel method and dip coating. TiO$_2$ sols were prepared by mixing 1.137 g titanium isopropoxide (Aldrich, 99.9% purity) with 2.76 mL of acetic acid (Fisher, 99.9% purity) and 37.2 mL of methanol (Fisher, 99.8% purity) accompanied by magnetic stirring.
The Si wedge was chemically etched before dipping to remove the native oxide layer. The etching solution was prepared by dissolving 0.25 g KOH in 7.5 mL of isopropanol. The Si wedge was etched at 80 °C for 10 minutes and then rinsed with Milli-Q water and ethanol.

After rinsing, the Si wedge was dipped in the TiO$_2$ sol solution and lifted out slowly. The Si substrate was left on a Kimtech wipe with the wedge side facing upward for the coating to dry. Two times of dipping were applied. The coated Si wedge was then annealed at 500 °C for 10 hrs to ensure complete removal of the organics. The ramping rate for both heating and cooling was 1.5 °C/min. The thickness of the as-processed amorphous TiO$_2$ coating is about 100 nm.

The thickness of the as-processed TiO$_2$ coating along the direction perpendicular to the wedge was then thinned with a FEI Helios Focus Ion Beam (FIB) system. A layer of 300 nm thick carbon protection layer was first deposited on the TiO$_2$ coating at the top of the Si wedge at a current of 3.2 nA. A window 20 μm wide and 500 nm deep was milled out using a Ga ion beam at a current of 0.23 nA until a thickness of around 100 nm in the direction perpendicular to the wedge edge was reached (Figure 1a). Further thinning of the TiO$_2$ will risk the loss of most of the sample and was avoided.

The FIBed sample was kept in air for two days before it was loaded to the TEM specimen holder. The back side of the Si wedge substrate was scratched by a tungsten scribe to expose the crystalline Si and then glued using silver paste (Chemtronics®, cw2400) to a Cu mounting stub. The stub was screwed onto a PI95 TEM specimen holder manufactured by Hysitron. The PI95 holder is equipped with a mounting board wherein a replaceable W probe is mounted. The position of the probe can be finely adjusted in all directions in order to make point contact with the sample at desired locations. The PI95 specimen holder was connected to an arbitrary
waveform generator (Agilent®, 33220A) and a voltage amplifier (Trek®, 603) to provide the voltage bias between the Cu stub and the W probe during in situ TEM experiments.

**Material Characterization.** All in situ TEM characterizations were carried out on a FEI Tecnai G2-F20 scanning transmission electron microscope (STEM). The microscope was operated at 200 kV and was equipped with energy-dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS). Under TEM mode, the spot size was always 5 and the corresponding current dose was about $2.6 \times 10^3$ A/m$^2$. This would minimize the amount of charge accumulation on the sample. No objective aperture was used as it was speculated to cause discharge with the sample due to its close proximity. The smallest aperture for selected area electron diffraction with a diameter of 200 nm was employed. EDS and EELS spectra were collected under the STEM mode with a sub-angstrom probe size. The W probe was preferably retracted after the application of each pulse to avoid any damage to the sample caused by unexpected probe motion. The typical TEM micrograph acquisition time was from 0.5 s to 1 s. Nanobeam diffractions were obtained prior to in situ experiments on a FEI Titan Themis 300 Cubed probe aberration corrected STEM.

**Computational Method.** To develop a model for the detailed microstructural evolution, we consider the interplay among four kinetic processes in the system: the migration of free electrons, the migration of free oxygen ions, the reaction $3TiO_2 + 2e^- \leftrightarrow 3TiO_2-x + O_2^-$, and the crystallization of the TiO$_{2-x}$ phase. To simplify the calculations, $x = 1/3$ is used in the following expressions corresponding to the formation of Ti$_3$O$_5$. Let $C_e$ and $C_O$ be the concentrations of the free electrons and oxygen ions, respectively, and $\phi$ be the electric potential, the conservation of the two species requires that
\[
\begin{align*}
\dot{C}_e &= \nabla \cdot (D_e \nabla C_e) + \frac{e}{kT} \nabla \cdot \left( C_e D_e \nabla \phi \right) - 2r \\
\dot{C}_O &= \nabla \cdot (D_O \nabla C_O) + \frac{2e}{kT} \nabla \cdot \left( C_O D_O \nabla \phi \right) + r
\end{align*}
\]

where \( D_e \) and \( D_O \) are the corresponding diffusion coefficients, \( e \) the electron charge, and \( kT \) the temperature in the unit of energy. The first terms on the right-hand side are the contributions from the diffusion current, the second accounts for that from the drift current, and \( r \) is the rate of the reduction reaction. Adopting the collision theory for the reaction, the rate \( r = \nu \)
\( (K_r C_e^2 - C_{Ti_3O_5} C_O) \), with \( \nu \) being a rate constant, \( K_r \) the equilibrium constant for the reaction, and \( C_{Ti_3O_5} \) the concentration of the resultant. As an immobile specie, the concentration of Ti\(_3\)O\(_5\) only changes with the reaction, \( \dot{C}_{Ti_3O_5} = r \).

Neglecting electromagnetic wave, the Gauss’s law of electrostatics dictates that
\[
\epsilon \nabla^2 \phi = e(C_e + 2C_O).
\]

where \( \epsilon \) is the permittivity, which is taken to be a function of the concentration of Ti\(_3\)O\(_5\) and its crystalline state (a very high permittivity is used to mimic the conductive crystalline phase). For simplicity, the charge migration and reaction in the silicon electrode is not modeled, and only the oxide region is considered.

To model the crystallization process, we adopt a phase-field model similar to that of dielectric breakdown,\(^44\) and introduce a continuous phase field \( s \) which varies from 0 in an amorphous phase to 1 in a crystalline phase. The phase field evolves in the direction of decreasing the total potential energy \( \Pi \) of the system: \( \dot{s} = -m \delta \Pi / \delta s \), where \( m \) is the mobility.

Including the electrostatic energy, the free energy difference between the crystalline and amorphous phases \( W_c f(s) \), and the interfacial energy \( k \frac{1}{2} |\nabla s|^2 \) in \( \Pi \), we arrive at the evolution equation for \( s \):

\[\Pi = \ldots\]
where $f(s)$ is a function smoothly interpolates between $f(0) = 0$ and $f(1) = 1$.

Lack of information on numerous thermodynamic and kinetic parameters, we convert the governing equations into dimensionless forms. For simplicity, we further assume that the reaction and the crystallization to be much faster than the migration of mobile species, and we also expect the free electrons to have higher diffusivity than the oxygen ions, and both are much higher in the conductive crystalline phase. The dimensionless partial differential equations are then implemented into a finite-element code in the commercial package COMSOL Multiphysics 5.4, and solved numerically with proper initial and boundary conditions for the crystallization process, as well as the co-evolution of the electric potential and the concentrations of various species.

ASSOCIATED CONTENT

Supporting Information

Caption for supplementary video, current-time plot for the supplementary video, calculation of the energy supply under different pulse conditions, energy band alignment, and epitaxy relationship.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, through Grant DE-SC0017839. All electron microscopy work was performed at the Sensitive Instrument Facility at U.S. DOE Ames Laboratory.

REFERENCE


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