Probing and Manipulating the Interfacial Defects of InGaAs Dual-Layer Metal Oxides at the Atomic Scale

Xing Wu,* Chen Luo, Peng Hao, Tao Sun, Runsheng Wang, Chaolun Wang, Zhigao Hu, Yawei Li, Jian Zhang, Gennadi Bersuker, Litao Sun,* and Kinleong Pey*

The interface between III–V and metal-oxide-semiconductor materials plays a central role in the operation of high-speed electronic devices, such as transistors and light-emitting diodes. The high-speed property gives the light-emitting diodes a high response speed and low dark current, and they are widely used in communications, infrared remote sensing, optical detection, and other fields. The rational design of high-performance devices requires a detailed understanding of the electronic structure at this interface; however, this understanding remains a challenge, given the complex nature of surface interactions and the dynamic relationship between the morphology evolution and electronic structures. Herein, in situ transmission electron microscopy is used to probe and manipulate the structural and electrical properties of ZrO_2 films on Al_2O_3 and InGaAs substrate at the atomic scale. Interfacial defects resulting from the spillover of the oxygen-atom conduction-band wavefunctions are resolved. This study unveils the fundamental defect-driven interfacial electric structure of III–V semiconductor materials and paves the way to future high-speed and high-reliability devices.

Scaling the high-κ/Si system for future technology nodes requires a reduction in the thickness of the interfacial layer oxide.[1–3] However, such reduction results in a decrease in the carrier mobility of the metal-oxide-semiconductor field-effect transistor inversion layer, which has been attributed to the presence of charges in the high-κ gate stack and the possible contribution of remote phonon scattering from the high-κ layer. One potential solution is the heterogeneous integration of the silicon platform on high-mobility semiconductors, such as III–V materials.[4–8] In GaAs is one of the best candidates for the III–V substrate because of its high electron mobility and is thus of great interest for n-channel metal-oxide-semiconductor field-effect transistors (MOSFETs).[9–12] One of the principal challenges associated with the formation of insulating gate InGaAs MOSFETs is the characterization and passivation of electrically active defects at the interface between the InGaAs semiconductor and the high-dielectric-constant metal oxide.[13–15] Interface states affect the device operation in several ways. Interface states below the edge of the conduction band increase the sub-threshold swing, while those inside the conduction band trap electrons. Both effects reduce the on/off ratio for a given I_{ON}/I_{OFF}. Interface states can also shift the threshold voltage, degrade the channel mobility, and be a source of instability.[16–18] Therefore, the understanding and control of electrically active defect evolution at the high-κ/InGaAs interface is essential for the successful implementation of high-mobility-channel materials.[19,20]

However, the relationship between the interface state charges and the electronic structure, for example, the breakdown of the insulating oxide material, remains unknown. The inadequate understanding of the physical mechanism is due to the difficulties involved in determining and analyzing the type of microscopic breakdown that forms nanoscale conductive paths within oxide materials. In this work, we present a specifically designed in situ transmission electron microscopy (TEM) system equipped with electron energy loss spectroscopy (EELS) that can probe and manipulate the breakdown process of metal oxides in real time at the atomic scale under an external electrical field, during which the deformation behavior of dual-layer oxides and contrast propagation can be observed directly. Breakdown occurs at the ZrO_2/Al_2O_3 interface, and then, structural deformation extends vertically and horizontally.
The transformation from monoclinic ZrO2 to cubic ZrO can be seen from a series of high-resolution TEM (HRTEM) images. Obtaining these pieces of information could help improve the performance and reliability of future III–V devices composed of thinner metal oxide layers.[21,22]

To understand the physical mechanism of the breakdown process, an in situ TEM experiment was carried out. The difficulties and challenges of this method involve the efficient fabrication of the in situ TEM specimen. In general, the width of the TEM specimen produced by the traditional focused ion beam (FIB) technology is up to several micrometers. The drawback is that there is only one device in one TEM specimen, which greatly limits research efficiency. In view of the above issues, we design an FIB microscope stage possessing a large angle of inclination. By using this method, one TEM specimen can contain multiple independent, regular-shaped nanodevices with widths less than 20 nm. Hence, the experimental efficiency is improved. Moreover, an HRTEM image can include the whole device without losing sight of the other positions.

Figure 1 shows the sample preparation process and the corresponding scanning electron microscope (SEM) images. Low-kV milling is applied to remove the surface amorphous layer for further thinning of the specimen. Then, the film is cut and divided into several devices with smaller device widths. Typically, the width of the device is less than 20 nm, while the thickness is less than 50 nm. Thus, many III–V devices can be tested in one in situ TEM specimen under the same conditions. The advantage of this manner of testing is the avoidance of variabilities in experimental conditions, such as variabilities in film thickness and other experimental conditions. This general TEM-FIB preparation method can be applied to other electronic devices, too.

Stress-induced leakage current (SILC) measurement is recognized as a powerful diagnostic tool to characterize defects and the reliability of electronics. An effect frequently observed in thin electrical metal oxides is an enhanced metal oxide current, i.e., the SILC, which is defined as the increase in the oxide leakage current after high-field stress ($\approx 10^{12}$ MV cm$^{-1}$) compared to before electrical stress and was first reported in 1982.[13] The SILC effect is defect driven and results from the generation of neutral electron traps in the oxide, allowing more current to flow through the oxide layer, as these traps act as “stepping stones” for trap-assisted tunneling (TAT). Such defect measurement is of particular significance for determining and limiting the performance of nanoelectronics because its amplitude always increases with diminishing dimensions. Figure 2 shows the manipulation and evolution of interfacial defects during in situ electrical stressing. The in situ TEM experimental setup is shown in Figure 2a. A tungsten (W) probe with a sharp tip is inserted to contact the movable terminal of the TEM specimen. A voltage is applied to the fixed terminal, which was deposited to attach the TEM specimen to the Cu grid, while the movable terminal is grounded during electrical testing. A two-step defect-generation method is used in this study. First, a positive sweep voltage from 0 to 3 V is applied to the stack. The trends in current evolution show that SILC occurs at 2.6 V, where the gate current suddenly jumps from $1 \times 10^{-8}$ to $1 \times 10^{-7}$ A (one order of magnitude increase). Second, a stressing voltage of 1.9 V was chosen as the constant voltage stress in the experiment, which can generate defects with controllable growth. Such electrical measurements are classical and widely used in oxide device reliability studies.[24] At the initial stage, the interface between the TiN gate electrode and ZrO$_2$, ZrO$_2$, and Al$_2$O$_3$ is smooth, and no additional contrast was observed. At $\approx$0.5 s, breakdown occurs with an abrupt current increase. The structural differences in the device before and after breakdown are shown in Figure 2b,c. After breakdown, a black dot appears in the ZrO$_2$ layer, as shown in Figure 2c.
Figure 3a–d shows a series of low-magnification TEM images during real-time stressing, and the process is shown in Movie S1 in the Supporting Information. No additional contrast is observed in any layer in Figure 3a. At ≈60 s, SILC occurs with an abrupt current increase, and the area highlighted by a green dashed ellipse shows the vertical and horizontal expansion of the defects,[25] and a heavier contrast was observed during the whole process. The location of SILC and its expansion can be caused by defect generation. Figure 3e–g shows the high-magnification images. Figure 3e shows a cross-sectional HRTEM image of ZrO$_2$/Al$_2$O$_3$/InGaAs in which Al$_2$O$_3$ appears to be amorphous. At the initial stage, the sample is in good condition with no defects and a low gate current. Al$_2$O$_3$ exhibits granular-like features. The granular features indicate the presence of short-range order or even microcrystallites on the order of nanometers in size.[26] From the bright TEM images in the non-breakdown region, there is no evidence of defects in the InGaAs substrate. The ZrO$_2$/Al$_2$O$_3$ films are very dense and free of pin holes, as determined using HRTEM. This is consistent with the $I$–$V$ measurement of the sample, which shows a very low leakage current density ($10^{-8}$ A cm$^{-2}$) at low biasing voltages.

Then, a constant voltage of 1.9 V is applied to the sample. At 60 s, the gate current rises abruptly from $3 \times 10^{-8}$ to $3 \times 10^{-7}$ A, a one order of magnitude increase is observed from the electrical monitoring. Simultaneously, contrast changes abruptly occur in the ZrO$_2$ layer. Dislocations and more patterns were also observed. After breakdown, grain boundary twists, not present in the fresh sample, are observed in the ZrO$_2$ layer. Together with the grain boundary twists, a hillock-like shape appeared in the InGaAs substrate. These findings are in agreement with the previous study of dielectric breakdown-induced epitaxy (DBIE) in an SiO$_2$/Si gate stack.[27] DBIE is a nanomark that fingerprints an important physical signature for the defect-driven breakdown location such that the invisible percolation can be located unambiguously.[28] Compared with the non-breakdown region, the Al$_2$O$_3$ layer is fully amorphous, and the ZrO$_2$ layer is a mixed amorphous/crystalline film, exhibiting that transitions mainly occur in the dual Al$_2$O$_3$/ZrO$_2$ layer. As reported previously, the Zr atoms cannot diffuse into the TiN layer due to the high energy barrier.[29] The partial crystallization of the ZrO$_2$ film is of particular interest; as shown in Figure 3f–g, the fast Fourier transform (FFT) patterns show that the area after breakdown is cubic ZrO, while the initial ZrO$_2$ phase is monoclinic before breakdown. There is no known stable bulk ZrO phase, and so far, none have been reported in the literature by an unambiguous experiment.[30–33] Nicholls et al.[33] reported a hexagonal ZrO phase resulting from the oxidation of zirconium alloys; however, the formation of hydrides is questionable. The formation of hydrides does not occur in our experiment due to the high-vacuum environment during TEM.[30–32,34–36]
To further explain the results, we measured the corresponding interplanar distances and angles in the HRTEM images, and the result matches well with the FFT patterns, indicating the small measurement error (see Figure S1, Supporting Information). This result has been repeatedly observed in other devices, as shown in Figure S2 in the Supporting Information. The in situ results show many dislocations in the ZrO2 layer. This breakdown-induced failure phenomenon has been observed in many devices, confirming that the results are repeatable (see Figures S2 and S3 and Movies S2 and S3, Supporting Information). Additionally, to confirm that the contrast change is not induced by mechanical contact with the W tip, a series of experiments were carried out (see Figure S4 and Movie S4, Supporting Information). We suggest that the crystallographic similarity between the cubic TiN metal and cubic ZrO structures is the reason that this phase forms, similar to the hexagonal Zr metal and hexagonal ZrO structures reported by Nicholls et al.[33] It should be noted that the charging behavior and the electron beam shower have the negligible impact on in situ test results, as shown in Figure S5 in the Supporting Information. Defect generation is more severe at the interface than at other locations, and the theoretical calculation is given in Figures S6 and S7 in the Supporting Information.

To analyze the chemical nature of interface state defects, EELS analysis was performed at the breakdown location (DBIE). Figure 4a shows the sample configuration and beam-sample interaction. The scanning transmission electron microscopy (STEM)-EELS spectra were collected using a point-to-point vertical scan across the dual-layer at the breakdown site and the nonbreakdown site. The background-corrected Zr M edge spectra from the breakdown (red line) and nonbreakdown (blue line) metal oxides are given in Figure 4b. The EELS profiles of the Zr M edge before and after breakdown are similar, which prove that Zr atoms cannot diffuse into the TiN layer. The inset shows the enlarged plot from 170 to 195 eV for the breakdown and nonbreakdown oxides and reveals that the amount of Zr atoms almost does not change before and after breakdown. The background-corrected O K edge spectra measured from the breakdown (red line) and nonbreakdown (blue line) metal oxides is given in Figure 4c. The first absorption peak at 541 eV corresponds to the nonbreakdown metal oxide. The peak position shifts from 541 to 539.6 eV upon breakdown. Such shift is believed to be a result of conduction-band density of states (p-DOS) redistribution within the percolation path.[37] The breakdown metal oxide shows significantly lower O K core-loss signals than the nonbreakdown metal oxide. The decrease in the intensity arises from the missing O atoms at the breakdown site. The deficiency of O atoms within the breakdown dual ZrO2/Al2O3 layers can be calculated using the core-loss signal intensities.[38] Compared with the nonbreakdown signal intensities, the deficiency of O atoms is ≈50%, which is the same as the result obtained by the FFT patterns. Figure 4d shows the EELS mapping results of the breakdown region. O, Zr,
Al, and N atoms are represented in red, blue, yellow, and green, respectively. The mapping results also show the missing O atoms at the breakdown site, which is consistent with the EELS spectra. These results show that oxygen vacancies generate defects in the sub-band below the edge of the conduction band.

Figure 5 shows structure, EELS mapping, defects, and temperature distribution for a cross-section of the TiN/ZrO$_2$ (5 nm)/Al$_2$O$_3$ (2 nm)/InGaAs metal-oxide-semiconductor (MOS) structure after breakdown. Simulation combined with experiment is performed to examine the real situation of a dual-layer metal
oxide after breakdown. Figure 5a shows the HRTEM image of the breakdown area and the green dashed rectangle shows the percolation path. In the percolation path area, the interplanar spacing is uniform in the upper half of the ZrO2, showing the cubic ZrO. In the lower half, the interplanar spacing is irregular. The distortion is especially severe at the ZrO2/Al2O3 interface. Figure 5b shows the EELS mapping result of oxygen elements at breakdown area, and the white rectangle shows the deficiency of O atoms is ≈50%. Figure 5c shows the simulated O vacancies distribution profile of breakdown area. From the EELS mapping and simulated result, the percolation path induced by O vacancies and the severe distortion at the ZrO2/Al2O3 interface can be seen. Figure 5d shows the simulated heat profile image of the breakdown area. The heat distribution induced by percolation current shows the percolation path clearly. And the heat distribution is severe at the interface. At the beginning, the vacancies generate randomly and heat is mild (close to room temperature). The distance between defects is large that cannot lead to breakdown. Then, there is a sudden increase in defects or heat at the ZrO2/Al2O3 interface, and the breakdown process occurs, extending vertically and horizontally. Both the simulated and experimental results show the breakdown process to occur at the interface between ZrO2 and Al2O3 and then expand, indicating the important role the interface plays in the breakdown process.

In summary, a specifically designed in situ TEM experiment was developed, and the site-specific structural element composition as well as the chemical environment of dual-layer metal oxides along the breakdown percolation path were analyzed using HRTEM and EELS mapping and STEM-EELS. We unveiled the breakdown mechanism of the metal oxide under an external electrical field. The results show that O atoms missing from the breakdown site are the critical cause of atomic-scale structural changes along the breakdown path. Grain boundaries are observed at the breakdown region, which may be caused by the missing O atoms. Similar to other high-κ oxide materials,[39] the local energy gap at the breakdown path is believed to narrow, indicating these localized states in the band gap are mainly contributed by unbonded Zr d-orbitals, which have the potential to greatly contribute to the breakdown leakage current with the help of grain boundary twisting, temperature, the transformation from monoclinic ZrO2 to cubic ZrO, etc. Such understanding is critical to probing the breakdown mechanism of the metal oxide and advantageous for the development of future device applications.

Experimental Section

**Device Fabrication:** The metal gate was made of 200 nm TiN. The transistor channel was made of a 30 nm InGaAs layer. The gate stack consisted of atomic layer deposition (ALD)-grown 2 nm Al2O3/5 nm ZrO2 films. FIB In Situ TEM Preparation: First, a 1 μm thick Pt layer was deposited on the sample to protect the device surface. Second, two rectangular cross-section patterns were used to cut “U” shaped with an ion beam, and the distance between the edge of the Pt layer and the rectangular pattern was typical ∼0.5 to 1 μm. Then, the thickness of the TEM lamella was reduced to ≈1.5–2 μm by ion milling. Third, a Pt layer was used to connect the TEM lamella to the nanotip. Then, the nanotip was moved to lift out the TEM lamella. Fourth, after the lift-out process, the lamella was mounted on top of a TEM grid by depositing Pt to attach the lamella to the Cu grid. Finally, the thickness of the TEM lamella was reduced to ≈50 nm by FIB cutting.

**In Situ TEM Characterization:** The device was fabricated by the FIB technique using a gallium beam in a dual beam Helios 600i system from FEI Co. The TEM instrument was a Cs-corrected TEM (FEI Titan 80-300) with an operation acceleration voltage of 200 kV. The e-beam was carefully spread out to avoid any e-beam-induced structural damage while maintaining atomic resolution. For EELS analysis, the probe size was set to be ≈3 Å in diameter, and the EELS energy resolution was 0.7 eV with a 0.5 eV per channel dispersion (1000 eV energy range). The EELS spatial resolution was 0.3 nm.

**Simulation Method:** First, the defect density distribution in space and energy was extracted by fitting the experimental C–V and I–V curves of fresh devices. Then, based on this extracted initial defect profile, time-dependent dielectric breakdown (TDDB) simulations were performed to investigate the temperature distribution during stressing. Both the C–V/I–V and TDDB simulations were performed using the Cinestra simulation software package,[40] which was based on a statistical kinetic Monte-Carlo model with multiphonon TAT and considered field- and temperature-induced defect generation.[41]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

breakdown, in situ transmission electron microscope, interfacial defects, oxygen vacancies, III–V semiconductors

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