FERROELECTRICS

Highly enhanced ferroelectricity in HfO₂-based ferroelectric thin film by light ion bombardment

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Continuous advancement in nonvolatile and morphotropic beyond-Moore electronic devices requires integration of ferroelectric and semiconductor materials. The emergence of hafnium oxide (HfO₂)-based ferroelectrics that are compatible with atomic-layer deposition has opened interesting and promising avenues of research. However, the origins of ferroelectricity and pathways to controlling it in HfO₂ are still mysterious. We demonstrate that local helium (He) implantation can activate ferroelectricity in these materials. The possible competing mechanisms, including He ion-induced molar volume changes, vacancy redistribution, vacancy generation, and activation of vacancy mobility, are analyzed. These findings both reveal the origins of ferroelectricity in this system and open pathways for nanoengineered binary ferroelectrics.

rogress toward ultradense oxide electronics and applications, including nonvolatile memories and beyond-Moore devices, necessitates the introduction of improved device paradigms and the development of strategies that utilize the wealth of functionalities of complex materials at extremely reduced dimensions. These include a wide range of emergent properties, such as magnetoelectricity, ferroelectricity, flexoelectricity, and electrochromicity, that result from the intrinsic competition (or cooperation) of charge, spin orbital, and lattice degrees of freedom (1). The switching, logical, and memory devices require a special role for ferroelectricity, which refers to a material property of spontaneous electrical polariza-

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tion that is reversible when an electric field is applied. Ferroelectricity has been studied for the application of next-generation electronic devices, such as ferroelectric field-effect transistors (2, 3) and nonvolatile memories (4, 5), for over 40 years owing to their desirable physical properties, including a fast-switching speed and long-term stability (6). However, despite these superior properties, ferroelectrics have practical limitations owing to scaling effects (7, 8) and a low compatibility with complementary metal-oxide semiconductor (CMOS) processes (9). In particular, the ferroelectricity of conventional perovskite ferroelectrics substantially drops at thicknesses below 50 nm, limiting their application in ultralarge-scale integrated electronics (7). Second, integration between classical ferroelectrics and Si and other semiconductors is limited by intrinsically high oxygen chemical potential in the former, leading to formation of parasitic SiO_x layers and degradation during classical processing. Hence, despite much effort, the goal of ferroelectric-semiconductor integration has remained elusive.

The discovery of HfO_2 -based ferroelectrics with a fluorite structure in 2011 (10), e.g., $Hf_{0.5}Zr_{0.5}O_2$ (HZO), broke the traditional paradigm and offers the promise of nonvolatile and morphotropic beyond-Moore electronic devices (10–13). Unlike conventional ferroelectrics, HfO_2 -based ferroelectrics maintain robust ferroelectricity (14), which would be viable even down to a fundamental barrier restricted by a unit cell dimension, and are highly compatible with the existing CMOS processes (15). However, the nature of ferroelectricity in these materials remains poorly understood owing to the complexity that arises from undefined structural and chemical factors. This poor understanding has in turn hindered the rapid development of facile controllability and large-scale uniformity. From a phenomenological perspective, HfO_2 -based ferroelectrics demand a "wake-up" process to increase ferroelectricity by electric field cycling (16–20), suggesting the nonconventional nature of ferroelectric responses. Furthermore, the deposition parameters, such as doping, oxygen partial pressure and annealing conditions (21–24), and engineering perspective after surface modifications such as plasma treatment (25, 26), were found to have a strong effect on the resulting ferroelectricity.

Ferroelectricity in HfO2-based ferroelectrics can originate from multiple mechanisms, such as intrinsic ferroelectricity (27), electret-like responses associated with charge trapping at internal interfaces and intrinsic electrostriction (28). Moreover, recent studies have illustrated the important role of oxygen vacancies (29). This has gained particular attention in HfO₂-based ferroelectrics because the vacancies stabilize the metastable ferroelectric orthorhombic $(Pca2_1)$ phase over the entire polycrystalline HZO thin film, resulting in an enhancement of ferroelectricity (23, 30). Oxygen vacancy redistribution has been suggested as a possible mechanism for enhancement of the ferroelectricity driven by the wake-up effect (16-19). Despite these findings, controlling the ferroelectric response in HfO2-based ferroelectrics has remained elusive.

We propose a strategy for highly enhanced and precisely controlled ferroelectricity in HfO_2 -based thin films by point defect engineering through light-ion bombardment. We also report possible competing mechanisms that include molar volume changes, vacancy distribution, number of vacancies, and vacancy mobility. We provide evidence for vacancy generation as the dominant mechanism behind the emergence of ferroelectric behavior in these materials.

To quantitatively evaluate the effective enhancement of ferroelectricity after ion beam treatment, we explore the remnant polarization states and the hysteretic behavior via piezoresponse force microscopy (PFM) combined with various advanced techniques, such as the band excitation (BE) method and laser Doppler vibrometer (LDV). To understand the origin of the enhanced ferroelectricity, we examined the atomic structure-chemistry relationship in the polycrystalline HZO thin films before and after the light-ion treatment based on scanning transmission electron microscopy (STEM) combined with energy dispersive x-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS). We revealed that oxygen vacancies are homogeneously distributed over the optimally treated HZO thin film without the intervention of structural defects, which eventually leads to a global phase transition



Fig. 1. Design of experiments and spontaneous polarization properties. (**A**) Schematic representation of ion bombardment process. (**B**) Scheme for dose of He ion bombardment; inserted texts indicate the He ion doses (ions/cm²). (**C**) R-PFM amplitude image of HZO thin film after ion bombardment; greendotted box in (B) indicates the measurement position of (C). (**D**) R-PFM amplitudes as a function of He ion dose extracted from (C) except for the central part of 10¹⁸ ions/cm². (**E**) R-PFM, (**F**) BE-PFM, and (**G**) LDV-PFM amplitude images for 10¹⁷ ions/cm² corresponding to the orange dotted box in (C). The PFM image is rotated 90° counterclockwise to align according to (B) and (C).

(H) Spatial map of effective d_{33} after ion bombardment in (B); the orange and blue dashed boxes serve as visual guides corresponding to the positions with the He ion dose of 5×10^{14} to 5×10^{15} and 10^{16} to 10^{17} ions/cm², respectively. (I) BE-PFM amplitude versus V_{ac} depending on the He ion dose; BE-PFM amplitude was calibrated via the force–distance curve–based static calibration method (55). (J) Effective d_{33} as a function of He ion dose; the green line and area indicate the mean \pm SD deviation of the effective d_{33} in the pristine region, respectively. The effective d_{33} results of (H) and (J) were extracted using least-squares linear fitting, except for the noise floor region.

to the ferroelectric orthorhombic phase whereas the nontreated or unoptimized thin films present a mixture of nonferroelectric and ferroelectric phases. This result implies a strong coupling of the oxygen vacancy and the resulting ferroic behavior of the HZO thin film. Thermodynamical interpretation can elucidate the phenomenological observation as possible competing mechanisms, including molar volume changes, vacancy distribution, number of vacancies, and vacancy mobility. The method that we propose to modulate the density of the point defects could be a breakthrough for the practical application of ferroelectrics to next-generation memory devices via enhanced ferroelectricity.

Piezoresponse-dependent light ion bombardment

We chose He ion bombardment as a strategy to explore the emergence of ferroelectricity, where He ions can become trapped by the lattice, leading to an increase in the molar volume, as well as generating oxygen vacancies. We performed ion bombardment on the HZO thin film as a function of the He ion dose using focused-beam He ion microscopy (Fig. 1A). To observe the change in the electric polarization as a function of defect density, we bombarded the thin film with various He ion doses (Fig. 1B). We determined the changes in the local polarization associated with the He ion dose using resonance PFM (R-PFM), which was measured with an AC voltage of a single frequency near the contact resonance (Fig. 1, C and D) (*31*).

The regions with He ion doses below 10^{16} ions/cm² do not demonstrate noticeable changes in the R-PFM amplitude, which represents the magnitude of the piezoresponse signal that in turn is related to polarization. Instead, these regions present a slight decrease in the piezoresponse. This reduction may result from the defect formation by ion bombardment. However, it may be also associated with carbon contamination at the surface because carbon deposition can be easily induced by the surface adsorbates of hydrocarbon molecules during ion bombardment (32–34) and, furthermore,



Fig. 2. Switchable polarization properties. (A) FORC-PFM hysteresis loop depending on the He ion dose. (B) Positive and (C) negative remnant piezoresponse versus $V_{dc,max}$ depending on the He ion dose. (**D**) Average piezoresponse hysteresis loop and the fitting result by the Preisach

model. (E) Distribution of Preisach density depending on the He ion dose. (F) Dependence of the irreversible amplitude and the ratio of the interaction and coercivity widths extracted by the Preisach model on the He ion dose.

the atomic force microscopy (AFM) measurements can be sensitive to carbon contamination. However, the regions with He ion doses above 10¹⁶ ions/cm² show an increase in the R-PFM amplitude with an increase in the He ion dose. In particular, the R-PFM amplitude in the region with the He ion dose of 10¹⁷ ions/cm² increased by approximately two times compared with the pristine region, indicating substantial enhancement of ferroelectricity. Meanwhile, the central part of the region with the He ion dose of 10^{18} ions/cm² shows a rapid decrease in the R-PFM amplitude and the milled surface (fig. S1) because an excessive He ion dose can lead to a crystallographic collapse via material sputtering.

R-PFM can be affected by other contributions, such as a resonance shift or nonferroelectric contributions (35-38), so we measured BE-PFM and LDV-PFM (Fig. 1, F and G) in addition to R-PFM (Fig. 1E). Because BE-PFM can track the resonance frequency, it allows one to minimize the error from the resonance shift (39), which can be associated with carbon contamination. Similar to the R-PFM results. BE-PFM amplitude also indicates an increase in the piezoresponse after ion bombardment. In addition, we confirmed that there was little change of mechanical properties in the ionbombarded HZO thin film through BE-PFM (fig. S2). Meanwhile, recent studies have reported that nonferroelectric factors, such as the electrostatic effect, can be attributed to the PFM signal (35, 36). The difference in the surface potential according to the ion bombardment may affect the PFM signal due to electrostatic effects (40).

Therefore, we conducted LDV-PFM measurements in the same region (Fig. 1G) to evaluate the PFM signal, excluding the longrange electrostatic effect because LDV-PFM is less sensitive to the electrostatic effect (40, 41). We observed a higher PFM amplitude in the region with a He ion dose of 10^{17} ions/cm². Furthermore, although the surface potential in the ion-bombarded region relaxed to the same value as that in the pristine region after a sufficient time elapsed, the R-PFM amplitude still exhibited a strong response in the ion-bombarded region (see fig. S3, 1017 ions/ cm^2), indicating that the highly increased PFM signal originated primarily from the enhanced polarization by the ion bombardment. In addition, to verify the reproducibility of the thin films deposited by another method, we measured R-PFM images after ion bombardment on the HZO thin film deposited by the atomic layer deposition (fig. S4). We observed that light-ion bombardment continues to enhance the polarization in the HZO thin film, regardless of the deposition method used. Overall, the R-PFM results indicate that ion bombardment can be used to control the polarization by controlling the He ion dose.

We measured the effective d_{33} to explore the change in the polarization of HZO after ion bombardment, which may indicate the out-of-plane piezoelectric constant of spontaneous polarization, through an alternatingcurrent voltage $(V_{\rm ac})$ amplitude sweep in the HZO thin film. We determined the variation of the effective d_{33} obtained from the mapping result of the $V_{\rm ac}$ amplitude sweep, i.e., the BE-PFM amplitude according to $V_{\rm ac}$, after ion bombardment (Fig. 1H). The regions that we measured correspond to the regions of 5 \times 10¹⁴ to 10¹⁷ ions/cm² (Fig. 1, I and J). We excluded the regions of 5×10^{17} to 10^{18} ions/cm² because of topographic variations, including beam damage (fig. S1). The regions with He ion doses of 5 \times 10^{16} to 10^{17} ions/cm^2 clearly have a higher effective d_{33} compared with that of the other regions (Fig. 1, H and I), although the difference according to the He ion dose was not observed owing to the equipment background noise below 0.3 $V_{\rm ac}$. We averaged the effective d_{33} results for a quantitative comparison as a function of the He ion dose (Fig. 1J). The regions with He ion doses below 10¹⁶ ions/cm² show a slight decrease in the effective d_{33} . This decrease may be due to the defect formation by ion bombardment or the carbon contamination at the surface of the HZO thin film after ion bombardment (32-34). When the He ion dose is increased to 5×10^{16} ions/cm² or more, the effective d_{33} is substantially increased compared with that of the pristine region. In particular, the effective d_{33} value of the 10¹⁷ ions/cm² region increased by 99% compared with that of the pristine region. Therefore,

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Fig. 3. Chemical and structural analysis of crystal phases and defects.

(A) STEM-EDX chemical maps of the constituent elements Hf, Zr, O, and Si in the HZO samples with different He ion dose conditions: P-HZO, L-HZO, and H-HZO, respectively. For elemental mapping, characteristic x-ray peaks of Hf L (7.898 keV), Zr K (15.744 keV), O K (0.525 keV), and Si K (1.739 keV) were selected. The weak Si contrast shown in the HZO thin film is attributed to the peak overlap of Si K and Hf M (1.644 keV) peaks. Scale bars, 10 nm. (B) Representative HAADF images of the three HZO samples. One of the nanograins in the three samples was aligned to a crystal zone-axis for atomic resolution imaging.
(C) (Left) Enlarged atomic structure images for the regions marked by white boxes in (B): (right) simulated HAADF images corresponding to the experimental images. The Hf and Zr lattice models used for the HAADF image simulations were overlaid

on each image for comparison. The aligned nanograins in the three HZO samples were identified to be [001]-oriented monoclinic and [110]-oriented orthorhombic structures, respectively. (**D**) Comparison between the experimental and the simulated PACBED patterns obtained from each nanograin in the three HZO samples. The simulated PACBED patterns were calculated from the three identified atomic structures. (**E**) Maps of *a/b* ratio in O K EELS for the three HZO samples. The maps were reconstructed by NLLS fitting process for the obtained EELS SI datasets. Insets represent O K EELS spectra averaged over the HZO film regions, respectively. The outside regions shaded with dark gray in each HZO sample were not considered for the evaluation of the *a/b* ratio because those regions are unrelated to the HZO film. The color scale bar on the rightmost side indicates the range of the measured *a/b* ratio in O K edge.

the PFM results indicate that light-ion bombardment can enhance the polarization of HZO; furthermore, it can be used to locally control these enhancements. However, considering the applicability of ferroelectrics to next-generation electronic devices, the switching characteristics of the polarization rather than a spontaneous polarization are more important.

Influence of light-ion bombardment on polarization switching

To observe the changes in the polarization switching characteristics owing to He ion bombardment, we performed PFM hysteresis loops based on the first-order reversalcurve (FORC) method (42). We measured the polarization switching behavior depending on the maximum direct-current voltages $(V_{dc,max})$ as a function of the He ion dose (Fig. 2A). Whereas the coercive voltages related to the polarization switching were in a similar range regardless of the ion bombardment and He ion dose, the piezoresponse indicating the intensity and direction of polarization was substantially increased at



Fig. 4. Polarization charge after ion bombardment. Normalized polarization P(E) on the electric field *E* calculated for (**A**) normalized spontaneous polarization *p* versus relative film thickness h/h_d calculated for different $N_{do} = (2, 1.5, 1, 0.5) \cdot N_0$ (black, red, blue, and green curves, respectively) where $N_0 \cong 10^{25} \text{ m}^{-3}$ and h_d is the decay factor of the defect concentration. (**B**) Normalized spontaneous polarization *p* versus vacancy concentration N_{do} calculated for different film thicknesses $h = (2, 5, 10, 20) h_d$ (black, red, blue, and green curves, respectively). Parameters: T = 300 K, $\frac{1}{k_0} = -10 \text{ K}$, $q_{33}W_{33}^dN_0 = -5 \cdot 10^6 \text{ m J/C}^2$ corresponds to, e.g., $N_0 \cong 10^{25} \text{ m}^{-3}$ at $W_{33}^d \cong -10^{-29} \text{ m}^{-3}$ and $q_{33} = 5 \cdot 10^{10} \text{ m J/C}^2$. (**C**) Topographic image of HZO thin film with top electrodes. Red and blue circles indicate the points where *P*-*V* curve measurements by AFM-PUND were performed for the pristine and bombarded regions, respectively. The slightly larger height with rectangular shape indicates the region bombarded with $10^{17} \text{ ions/cm}^2$. (**D**) *P*-*V* curve measurements were performed before He ion bombardment.

He ion doses above 10^{16} ions/cm². These results can be more clearly observed through the remnant piezoresponse (Fig. 2, B and C). The positive remnant piezoresponse increases more steeply in the He ion doses of 5×10^{16} and 10^{17} ions/cm² than that of other doses with an increasing $V_{dc,max}$ as the polarization direction shifts downward in the HZO thin film, except for the result at 1 $V_{dc,max}$, where switching does not occur (Fig. 2B). In the region with a He ion dose of 10^{17} ions/ cm^2 , the positive remnant piezoresponse at 8 $V_{\rm dc,max}$ was increased by ~42% compared with that in the pristine region. The ion bombardment in the present case does not substantially affect leakage current (fig. S5). The piezoresponse was slightly decreased at He ion doses below 10¹⁶ ions/cm², indicating that the slight decrease in both R-PFM amplitude and remnant piezoresponse may have resulted from the defect formation by ion bombardment as well, rather than the carbon contamination.

The PFM hysteresis loops that we obtained by the FORC method were well-fitted by the generalized Preisach model (Fig. 2D) (31). Our analysis suggests that He ion bombardment yields broader distribution of coercive fields than the internal bias fields for the average result, suggesting the nonuniform nature of the material. However, the distributions of the Preisach density for the He ion dose of 5×10^{16} to 10¹⁷ ions/cm² are clearly distinguished from those for the other doses by the narrower distribution of the coercive voltages and higher Preisach density than the coercive fields (Fig. 2E), indicating more uniform and strengthened polarization switching responses. In addition, because of the increasing defect density, the interaction between charged defects and the spontaneous polarization is enhanced, leading to an extended distribution of internal bias voltages for the He ion dose of 5×10^{16} to 10^{17} ions/cm². Apparently, a threshold value exists for the He ion dose to induce strengthened polarization switching and strong interactions. The ratio of the internal bias voltage width to the coercive voltage width and the irreversible amplitude both present an abrupt increment between the He ion doses of 10^{16} and 5×10^{16} ions/cm² (Fig. 2F).

Overall, these results indicate the possibility of using light-ion bombardment to highly enhance the ferroelectric polarization in HZO through defect engineering. Furthermore, an increase in the number of defects can occur owing to light-ion bombardment (figs. S6 and S7). Presumably, the enhanced ferroelectricity of the HZO thin film could be ascribed to the increased defect density inside the HZO thin film by the posttreatment of the He ion bombardment. Regardless, because the enhancement of ferroelectric polarization through defect engineering can be associated with several mechanisms, such as phase transition to the ferroelectric phase (16), we explored the origin of the ferroelectric polarization enhancement.

Mechanism of highly enhanced ferroelectricity based on defect engineering

To determine the dominant defect formed and the cause of the enhanced ferroelectricity in the treated HZO thin film, we performed a chemical analysis on the HZO samples with He ion doses of 5×10^{15} and 10^{17} ions/cm², respectively, and compared those with the case of the pristine HZO thin film. The pristine HZO and the two HZO thin films with different He ion doses are denoted as pristine (P-HZO), 5×10^{15} ions/cm² (L-HZO), and 10¹⁷ ions/cm² (H-HZO), respectively. We constructed EDX elemental maps of Hf (red), Zr (yellow), O (green), and Si (cyan) for the three HZO samples of P-HZO, L-HZO, and H-HZO, respectively (Fig. 3A). The annular dark field (ADF) STEM images and the corresponding EDX maps confirm that the thicknesses of the HZO thin films are ~10 nm but appear to become larger with an increasing dose of He ions, which indicates an increase in molar volume. Comparing the high-resolution high-angle (HA)ADF STEM images of the three HZO samples (Fig. 3B), we observed layer thickening and structural disorder (seen as the increased fuzzy contrast in the image) in the H-HZO sample. This characteristic volume change is also apparent at the atomic scale in the comparison of planar spacings of the orthorhombic phase observed in the three HZO samples (fig. S8). The EDX maps of the three samples revealed that Hf and Zr are sufficiently mixed without elemental segregation, and the distribution of oxygen is wider than

that of Hf and Zr, extending into the Si substrate. This result indicates that a portion of oxygen in the HZO thin film was consumed to form a thin SiO_2 bottom layer on the Si substrate due to the interface reaction during the growth. Thus, the bottom part of the HZO layer would be oxygen deficient as compared to the upper part.

To clarify the structural transition of the HZO thin films to the ferroelectric orthorhombic phase by He ion bombardment, we obtained atomic-scale HAADF STEM images for the three HZO samples and compared them with the simulated counterparts (Fig. 3C). Because the signal contrast in the HAADF imaging mode is approximately scaled to the atomic number squared (Z^{-2}) , heavy Hf atoms (Z = 72) appear as bright dots, whereas light oxygen atoms (Z = 8) are hardly observed (43). Owing to the polycrystalline nature of the grown HZO thin films, we only observed the atomic structures of the thin films for nanograins aligned along an arbitrary crystal zone axis. Hence, we conducted multiple STEM observations for each sample to determine the polymorphic phase distribution over the film of investigation. As a result, the P-HZO and L-HZO thin films present a mixture of monoclinic and orthorhombic phases, maintaining the monoclinic structure as the dominant phase. We identified the two atomic structures as orthorhombic and monoclinic phases observed in both HZO thin films (figs. S9, A and B). By contrast, we identified the nanograins in the H-HZO thin film as the ferroelectric orthorhombic $(Pca2_1)$ phase in all the observations (fig. S9C). We collected an extra dataset confirming this behavior (fig. S10). Interphase boundaries between orthorhombic and monoclinic domains were occasionally spotted in P-HZO films (fig. S11A) but were seldom observed in the orthorhombic grains in H-HZO films. Statistical size measurements indicate that the average grain size was slightly increased by ~2 nm after the He ion bombardment-induced transition to orthorhombic phase (fig. S11B). The HAADF STEM images of the P- and L-HZO samples show the [001]-oriented monoclinic structure, whereas that of the H-HZO samples represents the [110]-oriented orthorhombic structure (Fig. 3C). Position-averaged convergent beam electron diffraction (PACBED) analysis (44) was correspondingly performed on the regions of STEM observations to confirm those structures. Consistently, the experimental PACBED patterns show a good match with the simulated PACBED patterns that were derived from the structures identified by the STEM observations (Fig. 3D). Considering the multiple structural observations, we conclude that the He ion bombardment into the pristine HZO thin film readily induces a homogeneous distribution of the ferroelectric orthorhombic phase over the film. These results suggest that atomic defects such as oxygen vacancies and the structural disorder that were induced by He ion bombardment could play an important role in the favorable structural transition to the ferroelectric orthorhombic phase, thus resulting in the notable enhancement of ferroelectricity.

To trace the distribution of oxygen vacancies inside the HZO thin films, we conducted an EELS spectrum imaging (SI) analysis of the O K edge for each HZO film (fig. S12). From the EELS SI datasets, we extracted the averaged O K spectra for the three HZO thin films (see insets in Fig. 3E). The O K energy-loss nearedge structure (ELNES) of HZO presents a notable doublet-peak shape denoted as a (peak at ~534 eV) and b (peak at ~538 eV) with an energy difference (ΔE_{b-a}) of ~4 eV, which is attributed to the O 2p orbital hybridized with the Hf (or Zr) d_{e_a} and $d_{t_{2a}}$ orbitals, respectively (45). This characteristic peak splitting of the O K ELNES commonly appears in the HfO₂ polymorphs of monoclinic, tetragonal, and cubic phases with slight differences in the energy shift and peak broadening (45). Characteristically, the peak sharpness and intensity of peak a relative to peak b varies with the crystallinity and content of the oxygen vacancies in the HfO₂ film. Poor crystallinity causes a broadening of the double peak structure and also a decrease in the relative intensity of peak a, which should be considered when HZO thin films are grown at different annealing temperatures (46). Because the HZO samples were grown under the same thermal processing conditions, the most probable origin of the change in the O K ELNES could be the formation of the oxygen vacancies and/or the occurrence of structural disorder due to the He ion bombardment. The notable reduction in the a/b ratio from 0.60 to 0.43 in O K edges (Fig. 3E and fig. S12C) implies that the vacancy defects and structural disorder increased as the dose of He ion bombardment was increased to the optimal value of 10^{17} ions/cm² (H-HZO). Because monoclinic and orthorhombic HZO structures have sevenfold coordinate metal ions, a similar broad doublet peak structure of the O K edges is observed (fig. S13A). However, cubic and tetragonal HfO2 structures with sixfold coordinate metal ions would present substantially sharper double-peaked O K ELNES owing to the higher crystal field symmetry (46). Previous studies reported that the formation of oxygen vacancies reduces the first peak (a) intensity of the O K doublet edge when other factors are held constant (46, 47). Our density functional theory-based O K-edge simulations for the influence of oxygen vacancies represent the same tendency (figs. S13, B and C, and S14) (31).

Therefore, we examined the change in the relative intensity of peak a in the O K ELNES to detect the oxygen vacancies inside the HZO

thin films and mapped the a/b ratios corresponding to the entire film region by nonlinear least squares (NLLS) fitting analysis (Fig. 3E). The resulting a/b ratio maps show that the oxygen vacancy content is gradually increased from P-HZO to H-HZO. Notably, the entire H-HZO thin film is revealed to be populated by oxygen vacancies, whereas the distribution of the oxygen vacancies is localized and nonuniform in the other two HZO samples (P-HZO and L-HZO); these results are similar to those previously obtained for a conventional HfO_2 sample (48). The statistical histograms of the measured a/b ratios for the three HZO samples clearly indicate the varving population behavior of oxygen vacancies from the P- and L-HZO to the H-HZO thin films (fig. S12C). The Gaussian curve fits of the a/b distributions for the three HZO samples demonstrate that the H-HZO thin film is highly oxygen deficient compared with the other two HZO samples. The a/b ratio can also be decreased to some extent as the crystallinity becomes poor (46). Given the increase in structural disorder by the He ion bombardment, it is also expected that the a/b ratio would be correspondingly further reduced, making quantification of the vacancy content by EELS difficult.

Theoretical calculations predicted that the injection of oxygen vacancies and substitutional doping into the HfO_2 thin film can promote a phase transition from the monoclinic $(P2_1/c)$ to the ferroelectric orthorhombic ($Pca2_1$) phase (49, 50). However, this doping was presumably insufficient to stabilize the metastable ferroelectric phase over the predominant monoclinic phase (51, 52). Experimental work demonstrated that the role of oxygen vacancy is more important in stabilizing the ferroelectric phase, prompting efforts for developing a facile route to controlling the concentration of the oxygen vacancy in the hafnia film (23, 30). On the basis of the STEM-EELS results, we confirmed that He ion bombardment into the HZO thin film efficiently triggers the formation of oxygen vacancy and increases its density and distribution with an increasing He ion dose before causing structural damage ($\geq \sim 10^{18}$ ions/cm²). Thus, to explore why the ferroelectric orthorhombic phase is stabilized as the oxygen vacancies are gradually introduced, we surveyed the change in total energy difference between the monoclinic and orthorhombic phases up to the vacancy content of 25% (fig. S13D) (31). Unexpectedly, we found that a threshold concentration (>20%) of oxygen vacancy is required to fully stabilize the ferroelectric orthorhombic phase. Annular bright-field STEM imaging confirmed that the oxygen-deficient ferroelectric orthorhombic structure is stably sustained (fig. S13E). A slight reduction in both R-PFM amplitude and remnant piezoresponse at He ion doses below

 $10^{16}\ \mathrm{ions/cm^2}$ may also be associated with the threshold concentration.

Nevertheless, because ferroelectric behavior can have multiple causes, we further analyze the possible thermodynamic mechanisms, including a direct change in molar volume, emergence of ferroelectricity, vacancy formation, and vacancy redistribution. The free energy contribution $G_{\rm PE}$ describing the ferroelectric order-disorder-type transition can be expressed using the macroscopic polarization vector components (28):

$$G_{PE} = N_d \left\{ -\frac{J}{2} p^2 - \frac{J_{\mathrm{nl}}}{4} p^4 + \frac{k_{\mathrm{B}}T}{2} \sum_{i=1}^3 \left[(1+p_i) \ln(1+p_i) + (1-p_i) \ln(1-p_i) \right] - d \cdot p_i \left(E_i^e + \frac{E_i^d}{2} \right) \right\} + \frac{\delta_{ijkl}}{2} P_d^2 \frac{\partial p_i}{\partial x_k} \frac{\partial p_j}{\partial x_l} \quad (1)$$

where PE denotes electrical polarization; the polarization components are normalized as $p_i = \frac{P_i}{P_d}, P_d \cong N_d d; d$ is the concentrationindependent average value of an elementary dipole moment; the concentration N_d can be related with the average concentration $\langle \delta N_d(r) \rangle$ of different vacancies and/or other defects; J is the effective interaction constant that is negative for the considered case of improper ferroelectricity; J_{nl} is the effective nonlinearity coefficient; δ is the positive gradient coefficient determined by the correlation between the dipole moments and by the contribution of the spatial gradients induced by the surface, as well as by the inhomogeneities inherent to the film; and $k_{\rm B}$ is the Boltzmann constant. We consider that the film surfaces are defect blocking, so all O, Hf, and Zr vacancies inside the film are time independent. Consequently, the average concentration of the vacancies is also time independent and equal to the average value calculated in the initial moment of time. Inserting elastic fields, created by different defects, into the (Hf,Zr)O₂ Gibbs potential and its subsequent expansion on the polarization powers leads to renormalization of the coefficient α by the electrostriction coupling with the Vegard expansion tensor, and the depolarization field effect [see (28, 31)]. Then, a local polar state can emerge for an out-of-plane polarization component $p \equiv \frac{P_3}{P_d}$ when the average concentration of defects $\langle \bar{N}_d \rangle$ is high enough, and the positive terms proportional to $\Lambda/h\epsilon_0$ and $\delta/\lambda h$ are small enough, where Λ is the effective screening length produced by the exposed free surface and/or imperfect bottom electrode; *h* is the $(Hf,Zr)O_2$ film thickness; and ε_0 is the universal dielectric constant.

We show typical dependences of the spontaneous out-of-plane polarization p on the film thickness and vacancy concentration N_{do}

(Fig. 4, A and B). The p value decreases rapidly with increasing film thickness h (Fig. 4A). Further, the *p* value increases rapidly and then saturates with increasing vacancy concentration N_{do} (Fig. 4B). The appearance of ferroelectricity is a typical size-induced effect because the second (positive) and third (negative) terms in eq. S10 for k = 3 are thickness dependent. In particular, the third term increases with has $\frac{1}{h}$, because $\langle \bar{N}_d \rangle = N_{d0} \frac{h_d}{h} (1 - \exp(-\frac{h}{h_d}))$ in accordance with eq. S9, where h_d is the decay factor of the defect concentration. Small second and large third terms are required for the negative $\langle \langle \alpha_{33}^R \rangle \rangle$. Making $\Lambda < 0.1$ nm corresponds to a high screening degree by, e.g., either conducting electrodes or ambient free carriers, and using a small gradient coefficient (i.e., $\delta \le 10^{-10} \text{ C}^{-2} \text{ m}^3 \text{ J}$) makes the positive terms appear smaller than the negative one. Thus, the third term explains the size effect (Fig. 4, A and B). Assuming that the polar state occurs at $N_{do} \cong 10^{25}$ to 10^{26} m⁻³, we need to minimize exposure to He; $N_{\rm He} \simeq 10^{14}$ ions/cm² can create such a defect concentration over the already available defect "background." Our analysis suggests that the emergence of ferroelectricity in He ion-bombarded hafnia can be driven by a synergy of several factors. In accordance with eq. S10, emergence of ferroelectricity via renormalization of $\langle \langle \alpha_{33}^R \rangle \rangle$ requires a dominant third term. This in turn requires high negative values of electrostriction coupling and large product $\langle W_{33}^d \rangle \langle \bar{N}_d \rangle$. Of these, the electrostriction coefficient q_{33} is of the same order for most ferroics. Hence, the product of the defect concentration and Vegard expansion coefficient $\langle W_{33}^d \rangle$ emerges as a predominant factor controlling ferroelectricity in this material. Although we consider a quasiequilibrium static configuration, the modeling charge defect transport in HfO2-based ferroelectrics in a nonequilibrium state could be an interesting further work for electrical cycling.

Finally, although the STEM and theoretical results showed that polarization enhancement based on defect redistribution and phase transition could be one of the possible mechanisms, electrical measurements are still necessary because nonferroelectric factors such as electrostatic effects might contribute to the obtained PFM signal (Figs. 1 and 2). Thus, we directly observed the remnant polarization charge of the electrode sample through an AFM-based positive-up-negative-down (i.e., AFM-PUND) method (*53*, *54*). The remnant polarization charge density clearly increased after the He ion bombardment at a dose of 10^{17} ions/cm² (Fig. 4, C and D).

Conclusions

We have demonstrated the high enhancement of ferroelectricity in HZO thin films based on defect engineering by He ion bombardment. Our PFM results indicate that the He ion bombardment substantially enhanced the ferroelectricity in the HZO thin film. In particular, the resonance PFM results indicate that the amplitude of piezoresponse in the ion-bombarded region of 1017 ions/cm2 increased by approximately twofold compared with that in the pristine region. This implies that the fine modulation of light-ion bombardment can substantially enhance the polarization of HZO. Furthermore, the STEM and EELS results show that the large enhancement of ferroelectricity by ion bombardment can be caused by a homogeneous distribution of oxygen vacancies and a phase transition to the ferroelectric phase. Furthermore, the theoretical calculations for thermodynamic mechanism allow us to explore possible mechanisms for the enhancement of the polarization by ion bombardment. These results, regarding the variation of ferroelectricity through defect engineering based on ion bombardment, suggest additional possibilities for ferroelectricity enhancement in HfO2-based ferroelectrics, including HZO. Thus, He ion bombardment can be a facile technique for stabilizing the ferroelectric orthorhombic phase. Furthermore, this study suggests that highly enhanced ferroelectricity can be selectively obtained by controlling light-ion bombardment with a high spatial resolution. Ultimately, this approach can be directly applied to a semiconductor process without structural modification and, thus, can increase its applicability in next-generation electronic devices, such as ultrascaled ferroelectrics-based transistors and memories.

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ACKNOWLEDGMENTS

Funding: This work was supported by the National Research Foundation of Korea (NRF) funded by the Korean government (MSIT) (grant nos. 2021R1A2C2009642, 2020R1F1A1072355, and 2020R1A2C1006207). This work was also supported by the Samsung Advanced Institute of Technology, Samsung Electronics, in Korea, The work of A.N.M. is supported by the National Academy of Sciences of Ukraine (grant no. 1230) and the European Union's Horizon 2020 research and innovation programme under Marie Skłodowska-Curie grant agreement no. 778070. A portion of the work, including He ion exposure, AFM measurements, and data analysis, was conducted at the Center for Nanophase Materials Sciences, which is a US Department of Energy Office of Science User Facility (CNMS2018-219; CNMS2021-B-00917, CNMS2022-R-01082). J.L acknowledges the support of the Korea Basic Science Institute (National Research Facilities and Equipment Center) through a grant funded by the Ministry of Education (no. 2021R1A6C101A429). S.-Y.C. acknowledges the support of the Global Frontier Hybrid Interface Materials of the National Research Foundation of Korea (NRF) funded by the Ministry

of Science and ICT (2013M3A6B1078872). The use of the TEM instrument (ARM300F) was supported by Advanced Facility Center for Quantum Technology at SKKU. Author contributions: Conceptualization: Y.K. Data Curation: S.K., W.-S.J., A.N.M., Y.K. Formal Analysis: S.K., W.-S.J., A.N.M., C.W., E.A.E. Funding acquisition: S.-Y.C., J.L., S.V.K., Y.-M.K., Y.K. Investigation: S.K., W.-S.J., A.N.M., O.K., Y.J., Y.-H.K., H.B., C.W., S.-H.Y., E.A.E., Y.P., K.-J.G., S.-Y.C., J.H.J., J.L., Y.K. Methodology: J.H., S.V.K., Y.-M.K., Y.K. Project administration: S.V.K., Y.-M.K., Y.K. Resources: A.B., S.R., L.C., S.J., M.-H.J., H.W.C., S.K., H.Y.J., O.S.O. Supervision: J.H., S.V.K., Y.-M.K., Y.K. Validation: S.K., W.-S.J., A.N.M., S.V.K., Y.-M.K., Y.K. Writing - original draft: S.K., W.-S.J., C.W., A.N.M., S.V.K., Y.-M.K., Y.K. Writing - review & editing: S.K., W.-S.J., A.N.M., A.B., L.C., O.S.O., J.H., S.V.K., Y.-M.K., Y.K. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are available in the main text or the supplementary materials. The theoretical calculations for thermodynamic mechanisms were performed and visualized in Mathematica 12.2 Wolfram Research software. Mathematica notebook is available per reasonable request.

SUPPLEMENTARY MATERIALS

science.org/doi/10.1126/science.abk3195 Materials and Methods Supplementary Text Figs. S1 to S15 References (56–86) Submitted 6. July 2021: resubmitted 30. Dece

Submitted 6 July 2021; resubmitted 30 December 2021 Accepted 7 April 2022 10.1126/science.abk3195

Science

Highly enhanced ferroelectricity in HfO-based ferroelectric thin film by light ion bombardment

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Science, 376 (6594), • DOI: 10.1126/science.abk3195

Ion enhanced polarization

Hafnium oxide is an exciting material because it has ferroelectric behavior that makes it attractive for various device applications. Kang *et al.* found that the ferroelectric properties improve by bombarding films of hafnium oxide with a beam of helium ions. The ion bombardment creates oxygen vacancies and strain changes from helium implantation that push more of the polycrystalline samples into the ferroelectric orthorhombic phase. This method may become an important tool for stabilizing the ferroelectric phase for the next generation of electronic devices. —BG

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