

# Local Epitaxial Templating Effects in Ferroelectric and Antiferroelectric ZrO<sub>2</sub>

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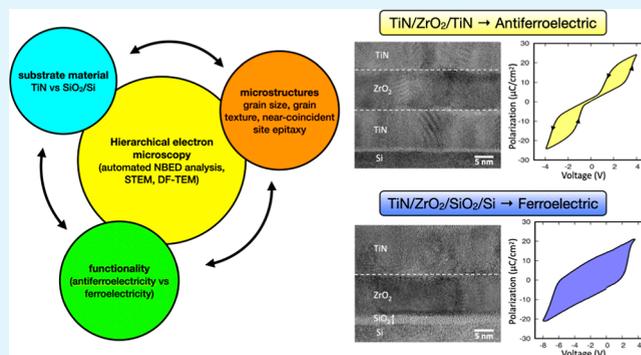
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**ABSTRACT:** Nanoscale polycrystalline thin-film heterostructures are central to microelectronics, for example, metals used as interconnects and high-K oxides used in dynamic random-access memories (DRAMs). The polycrystalline microstructure and overall functional response therein are often dominated by the underlying substrate or layer, which, however, is poorly understood due to the difficulty of characterizing microstructural correlations at a statistically meaningful scale. Here, an automated, high-throughput method, based on the nanobeam electron diffraction technique, is introduced to investigate orientational relations and correlations between crystallinity of materials in polycrystalline heterostructures over a length scale of microns, containing several hundred individual grains. This technique is employed to perform an atomic-scale investigation of the prevalent near-coincident site epitaxy in nanocrystalline ZrO<sub>2</sub> heterostructures, the workhorse system in DRAM technology. The power of this analysis is demonstrated by answering a puzzling question: why does polycrystalline ZrO<sub>2</sub> transform dramatically from being antiferroelectric on polycrystalline TiN/Si to ferroelectric on amorphous SiO<sub>2</sub>/Si?

**KEYWORDS:** nanobeam electron diffraction, high-throughput material characterization, nanocrystalline interface, scanning transmission electron microscopy, hafnium–zirconium oxides



## INTRODUCTION

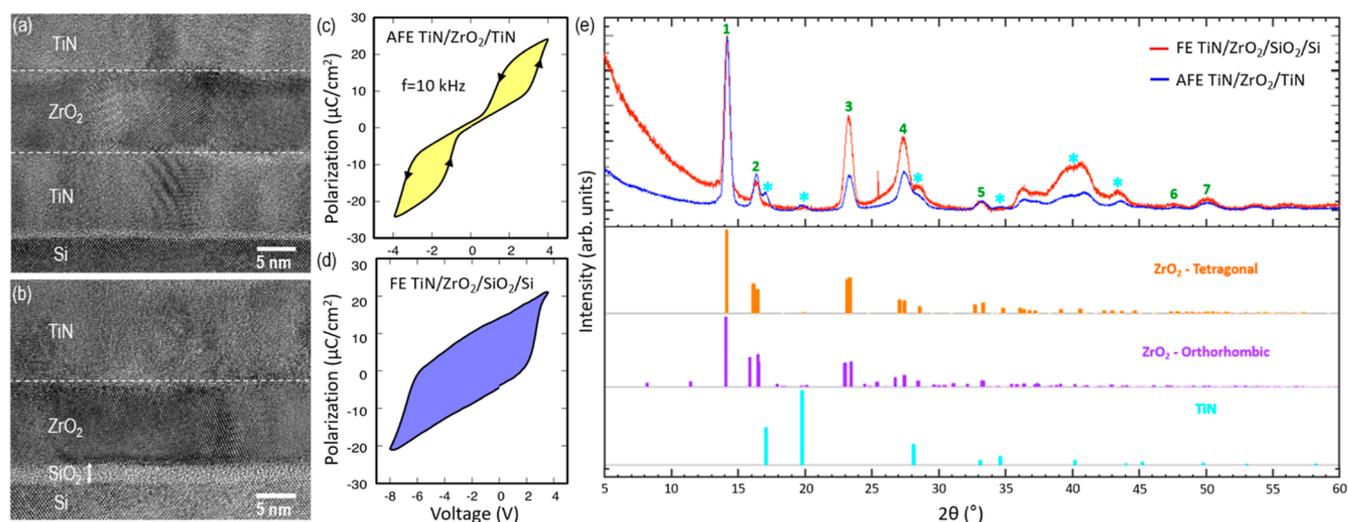
ZrO<sub>2</sub> is an incipient ferroelectric (FE) material, wherein a polar, FE orthorhombic *Pca*2<sub>1</sub> phase is in close energetic competition with an antipolar, antiferroelectric (AFE) tetragonal *P4*<sub>2</sub>/*nmc* phase.<sup>1</sup> Consequently, relative phase stability can be altered due to subtle changes in growth conditions, that is, substrate materials. Some of the previous works reported the effects of the substrate on the electrical properties of thin-film hafnia–zirconia alloys.<sup>2,3</sup> However, these FE oxides are nanocrystalline when deposited as thin films on practical substrates such as nanocrystalline TiN, complicating the fundamental understanding between the microstructure and process optimization. For nanocrystalline growth, the microstructure shows a wide variety of grain sizes and subgrain features, such as domain walls and interphase boundaries, intricately convoluting the relationship between the structure and electronic properties.<sup>4–7</sup>

In the nanocrystalline, heterogeneous interface between ZrO<sub>2</sub> and TiN, the microstructural evolution of both materials is known to be codependent on grain growth and

crystallization, which mostly occur during postdeposition annealing at elevated temperatures. Due to the large lattice mismatch (~18%) between ZrO<sub>2</sub> and TiN, conventional lattice matching epitaxial growth would be allowed only for specific orientation relationships. ZrO<sub>2</sub><sup>8</sup> or Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> (HZO)<sup>9</sup>(111) grown on TiN(001) would be most favorable due to the lowest level of epitaxial strain. However, other orientations of HZO, such as (100) and (110), are frequently reported on TiN electrodes with mixed TiN orientations of (111) and (001),<sup>10</sup> resulting in a large lattice mismatch. This large lattice mismatch leads to interfacial dislocations for which additional HZO atomic planes match the integral widths of multiple TiN atomic planes. Such a near-coincident site

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**Figure 1.** Antiferroelectricity and ferroelectricity in  $\text{ZrO}_2$ . HR-TEM images for (a)  $\text{TiN}/\text{ZrO}_2/\text{TiN}$  and (b)  $\text{TiN}/\text{ZrO}_2/\text{SiO}_2/\text{Si}$  thin-film stacks. Electrical characteristics of polarization–voltage curves show the (c) AFE and (d) FE behaviors for 10 nm thick  $\text{ZrO}_2$  on  $\text{TiN}$  and  $\text{SiO}_2$ . (e) A comparison of normalized GIXRD patterns obtained at an incident angle of  $0.15^\circ$  for a  $2\theta$  range of  $5\text{--}60^\circ$  is shown for 10 nm  $\text{ZrO}_2$  MIM (blue) and 10 nm  $\text{ZrO}_2$  MIS (red). Diffraction peaks are observed at the expected positions of either tetragonal or orthorhombic, with  $\text{TiN}$  peaks present for the MIM case. The numbered peaks are those at which the  $d$ -spacings of MIM and MIS samples have been compared to those of orthorhombic and tetragonal reference peaks (see the Supporting Information).

epitaxial growth<sup>11</sup> has been widely observed in a variety of materials with relatively large lattice mismatch such as semiconductor oxides<sup>12</sup> and oxide–oxide interfaces.<sup>13–16</sup> Note that lattice epitaxy is a special case of 1/1 near-coincident site epitaxy, where each of the atomic planes in both materials matches with each other at the interface, and the epitaxial relationship between the substrate and deposited film extends for large distances (nearly single crystal).

Atomic-resolution scanning transmission electron microscopy (STEM) is often used to probe atomic-scale epitaxial relationships at the interface of crystalline materials. However, large-scale microstructural analysis over many locations remains a challenge due to the localized nature of STEM data acquisition and the amount of time required to analyze STEM data. It is even more demanding to probe the interface of nanocrystalline materials, which are prevalent in technologically useful material systems such as  $\text{TiN}\text{--}\text{HZO}\text{--}\text{TiN}$  capacitors as aligning grains along zone axes for imaging becomes increasingly difficult with a decreasing grain size. In a previous study, nanobeam electron diffraction (NBED) was employed to efficiently investigate the microstructure at the atomic level over a large area for HZO grown on  $\text{TiN}$ .<sup>9</sup>

NBED provides a series of electron diffraction patterns from evenly spaced grid points, which yields a four-dimensional (4D) stack of data, that is, two-dimensional (2D) scans of 2D patterns. NBED is particularly suitable for high-throughput microstructural characterization because each scan allows for electron diffraction patterns to be collected every few nanometers over micron-sized areas in much less time compared to standard STEM imaging, reducing thermal drift and beam damage effects. However, NBED data can in turn be overwhelming to analyze manually since a single scan may produce thousands of electron diffraction patterns, motivating the development of automated analysis techniques.

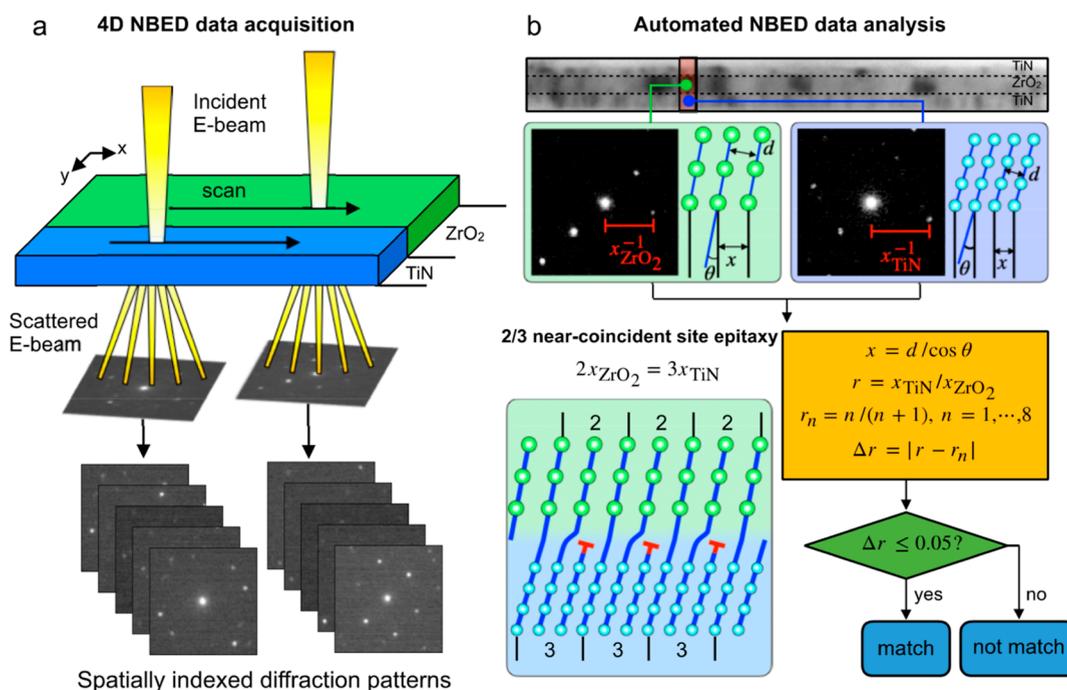
Here, a fully automated workflow is demonstrated to determine various epitaxial relations over the polycrystalline interfaces based on NBED data. Starting from individual diffraction patterns, coordinates of each diffraction spot are

obtained to reconstruct the real-space atomic planes at the interface, which are utilized to determine the possible near-coincident site epitaxial growth at each location probed by the electron beam. Using this technique, various types of near-coincident site epitaxies are frequently observed at the  $\text{ZrO}_2\text{--}\text{TiN}$  interfaces, revealing consistent structure-directing effects of the nanocrystalline  $\text{TiN}$  electrode on the  $\text{ZrO}_2$  film. Atomic-resolution images obtained by STEM confirm the dominant 3/4 (i.e., matching between three  $\text{ZrO}_2$  and four  $\text{TiN}$  atomic planes) and 2/3 near-coincident site epitaxy at the  $\text{ZrO}_2\text{--}\text{TiN}$  interface, consistent with statistics from NBED data.

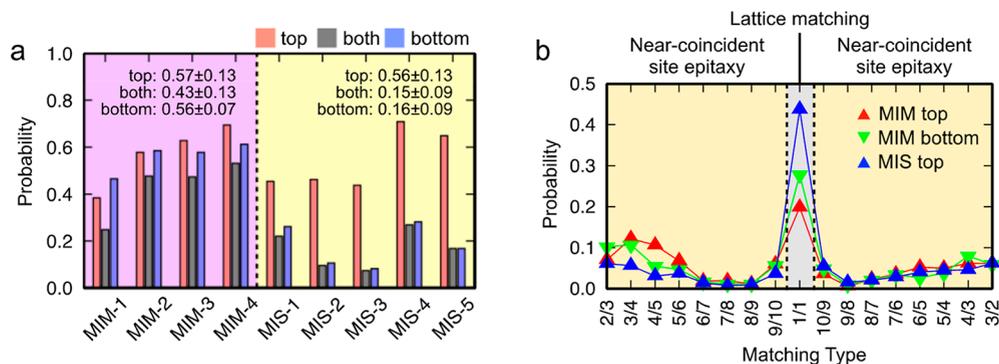
Applying the developed technique, thin films of  $\text{TiN}/\text{ZrO}_2/\text{TiN}$  [metal–insulator–metal (MIM)] and  $\text{TiN}/\text{ZrO}_2/\text{SiO}_2/\text{Si}$  [metal–insulator–semiconductor (MIS)] stack structures are compared to investigate the effects of local domain epitaxial growth and their influences on microstructural evolution and functional response. For  $\text{TiN}/\text{ZrO}_2/\text{TiN}$ , the  $\text{ZrO}_2$  microstructure shows active near-coincident site epitaxy at both top and bottom interfaces and has a small grain-to-grain variation in the size with no apparent interfacial layers. In contrast, for  $\text{TiN}/\text{ZrO}_2/\text{SiO}_2/\text{Si}$ ,  $\text{ZrO}_2$  grains have predominant lattice matching the top  $\text{TiN}$  and a large grain size distribution. These changes in the microstructure should alter the relative stability of the polar and the antipolar phases in  $\text{ZrO}_2$ , resulting in the observed functional AFE and FE responses on  $\text{TiN}$  and  $\text{SiO}_2/\text{Si}$  layers, respectively. Density functional theory (DFT) calculations confirm the dominant role of interfacial free energy in phase stability due to the electrode materials, explaining the AFE to FE functional change of the film with the change in the underlying electrode.

## RESULTS AND DISCUSSION

**Electrical Responses in  $\text{ZrO}_2$ .** Figure 1a,b shows the cross-sectional high-resolution TEM (HR-TEM) images of the MIM and MIS samples, with distinct interfaces between all layers. The MIM sample exhibits prototypical AFE double-hysteresis loops in its polarization (P) versus voltage (V) characteristics (Figure 1c). Conversely, the MIS sample shows



**Figure 2.** Microstructural analysis based on NBED. (a) Schematic diagram of NBED data acquisition. An electron beam with a nanometer-sized diameter is scanned over a >500 nm length of the cross-sectional samples, producing a series of spatially indexed diffraction patterns. (b) Automated NBED data analysis flowchart. Diffraction patterns across the interface are investigated at each location of the sample to determine the type of near-coincident site epitaxy. Horizontal spacing ( $x$ ) is computed from the interplanar spacing ( $d$ ) and the angle of the atomic planes ( $\theta$ ), and the ratio of  $x$  in  $\text{ZrO}_2$  and  $\text{TiN}$  ( $r$ ) is compared with the references ( $r_n$ ). If the absolute error ( $\Delta r$ ) is less than the criterion of 0.05, the corresponding stack is categorized as having a match. Depending on the  $r$  value, the type of near-coincident site epitaxy differs, indicating the number of  $\text{ZrO}_2/\text{TiN}$  atomic planes within a domain. An atomic model of the  $\text{ZrO}_2$ – $\text{TiN}$  interface showing  $2/3$  near-coincident site epitaxy is shown. Note the additional atomic plane shown in red ( $\perp$ ) in the  $\text{TiN}$  region.



**Figure 3.** Statistical analysis of the near-coincident site epitaxy from NBED. (a) Probability of near-coincident site epitaxy for each sample. A total of 2064 and 2014 diffractograms are used to analyze the near-coincident site epitaxy in four MIM ( $\text{ZrO}_2$  on  $\text{TiN}$ ) and five MIS ( $\text{ZrO}_2$  on  $\text{SiO}_2$ ) regions, respectively. All  $\text{ZrO}_2$ – $\text{TiN}$  interfaces regardless of the structure (MIM or MIS) show an average probability of 0.56, while a much lower probability of 0.16 is observed for the  $\text{ZrO}_2$ – $\text{SiO}_2$  interface, which is consistent with the thin amorphous  $\text{SiO}_2$  layer shielding the crystalline substrate. Considering some grains have their zone axes misaligned relative to the electron beam direction, a 56% probability of matching at the top interface is consistent with atomic scale matching being prevalent at the  $\text{ZrO}_2$ – $\text{TiN}$  interfaces. (b) Distribution of the match types at the  $\text{ZrO}_2$ – $\text{TiN}$  interfaces. Lattice matching, a special case of  $1/1$  near-coincident site epitaxy, is most prevalent in all cases, while near-coincident site epitaxy of  $2/3$  and  $3/4$  is the next most prevalent at the  $\text{ZrO}_2$ – $\text{TiN}$  interface. The MIS  $\text{ZrO}_2$ –amorphous  $\text{SiO}_2$  interface is not shown due to the weak signal-to-noise ratio.

a robust, single-loop FE response (Figure 1d). Note that the near-zero remnant polarization is at 0 V for  $\text{ZrO}_2$  on  $\text{TiN}$  (Figure 1c), and a uniform polarization difference in the hysteresis loop is seen throughout the voltages for  $\text{ZrO}_2$  on  $\text{SiO}_2$  (Figure 1d). The characteristic FE and AFE hysteresis loops shown in Figure 1c,d indicate a substantial difference in the degree of FE versus AFE phases present in the MIS versus MIM samples.

Grazing incidence X-ray diffraction (GIXRD) patterns are shown in Figure 1e for the MIM and MIS samples, from which phase analysis is performed. The fixed incident angle of the GI geometry renders any analysis on the intensities of the reflections meaningless as the orientation of the different diffracted planes would have their normal oriented along different directions. Unless the sample is extremely isotropic, the texture cannot be directly inferred from the intensity ratios.

Similarity scores are obtained between experimental peak positions and those in the reference by considering the respective  $d$ -spacings (see the [Supporting Information](#)), where a score of 0 indicates a complete match with that particular phase. Here, it can be seen that the MIS film possesses a score close to the orthorhombic phase, and the MIM film is close to the tetragonal phase. Since the two films have a nonzero similarity score, the possibility of a phase mixture of orthorhombic and tetragonal phases cannot be ignored. However, from the analysis, it can be said with certainty that the MIS film is predominantly orthorhombic and the MIM film is predominantly tetragonal. Additional GIXRD measurements ([Figure S1](#)) show a slight shift of the (111) peak ( $2\theta \sim 30^\circ$ ) to a higher value for  $\text{ZrO}_2$  grown on TiN compared to  $\text{ZrO}_2$  grown on  $\text{SiO}_2/\text{Si}$ , consistent with the reference peak positions for the AFE tetragonal  $P4_2/nmc$  and FE orthorhombic  $Pca2_1$  phases.<sup>17</sup> Note that while the (111) peak around  $2\theta \sim 30^\circ$  is analyzed for the FE versus AFE peak positions, this is not the exclusive texture of the films as shown below in the STEM analysis.

**High-Throughput NBED Analysis Workflow.** An automated analysis method for NBED data was developed to investigate near-coincident site epitaxy in heterogeneous interfaces over large sample areas with statistical significance. Electron diffraction patterns were analyzed to determine any epitaxial relations between nanocrystalline  $\text{ZrO}_2$  and TiN or Si. For statistical analysis, four TiN/ $\text{ZrO}_2$ /TiN (MIM) and five TiN/ $\text{ZrO}_2$ / $\text{SiO}_2$ /Si (MIS) sample areas with widths over 500 nm were probed. The process is composed of three stages as shown in [Figures 2 and 3](#): (1) NBED data acquisition, (2) automated NBED data analysis, and (3) statistical analysis.

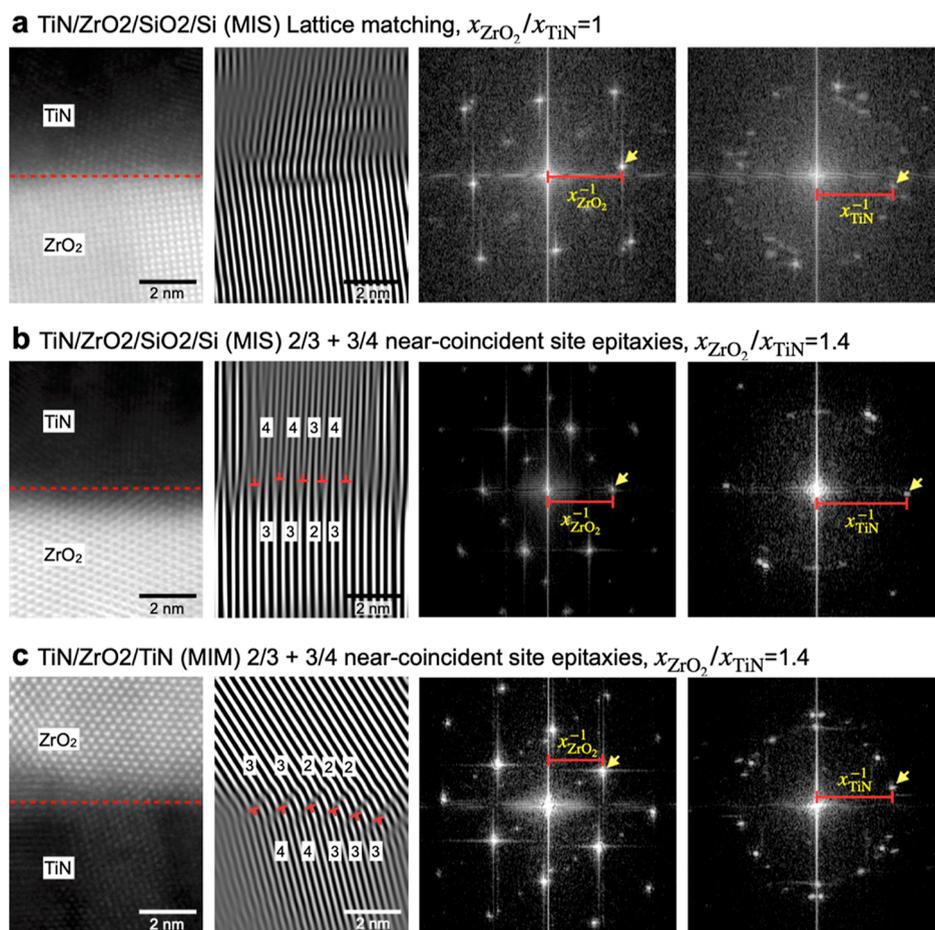
In the data acquisition stage, the nanoscale electron beam probes the focused ion beam (FIB)-processed samples on an evenly spaced grid to generate a series of electron diffraction patterns as shown in [Figure 2a](#). In these experiments, an electron beam with a diameter of approximately 5 nm was scanned on an even grid with a step size of 2 nm in all directions. A total of 2064  $\text{ZrO}_2$ -TiN diffraction pattern pairs and 2014  $\text{ZrO}_2$ - $\text{SiO}_2$  diffraction pattern pairs along the interfaces of  $\text{ZrO}_2$  samples grown on TiN and  $\text{SiO}_2$ , respectively, were recorded. Note that for NBED, the electron beam direction is fixed with respect to the sample, so additional near-coincident site epitaxy could occur at locations with no crystalline diffraction peaks at the fixed detection angle. Thicknesses of the FIB samples in this study range from 50 to 100 nm, which creates a possible over-counting of the near-coincident site epitaxy due to multiple through-thickness grains being present. It is important to note that a well-known complementary advanced microscopy technique, precession electron diffraction, can offer three-dimensional statistical crystallite analysis in the form of phase and orientation mapping.<sup>18,19</sup> However, the lamella through thickness compared to the crystallite size may likely result in overlapping of grains, leading to low reliability, and a smaller through thickness with a 10 nm film of interest can result in a poor signal-to-noise ratio. The NBED analysis used here shows statistically significant differences between samples even with the possible presence of over-counting (see the [Supporting Information](#) for detailed discussion).

Electron diffraction patterns can be used to reconstruct the crystal lattice structures of the probed area; microstructural information such as the crystal symmetry, crystallographic orientation, and interplanar spacing can be explicitly obtained

by inspecting the diffraction patterns. Here, an image processing workflow to automatically identify the coordinates of diffraction peaks is developed as follows. By using the electron diffraction data (i.e., intensity distribution in the diffraction pattern) as a 2D potential energy landscape, subsequent Monte Carlo simulations on noninteracting fictitious particles are performed so that clusters of the fictitious particles form around each of the diffraction peaks, as shown in [Figure 2b](#). A density-based spatial clustering of applications with noise (DBSCAN) algorithm,<sup>20</sup> as implemented in a Sci-Kit Python library,<sup>21</sup> is used to separate individual clusters of the fictitious particles to compute the center of mass positions of each diffraction peak. The details and pictorial descriptions of the process can be found in the [Supporting Information](#). After listing all the diffraction peak positions for both  $\text{ZrO}_2$  and TiN, located along the same interfacial position within the NBED scan, near-coincident site epitaxy is tested based on the diffraction peak positions. The horizontal distance ( $x$ ) is varied by the interplanar spacing ( $d$ ) and rotation angle ( $\theta$ ) as  $x = d/\cos \theta$ . The ratios of the  $x$  values from  $\text{ZrO}_2$  and TiN ( $r = x_{\text{TiN}}/x_{\text{ZrO}_2}$ ) are compared at each location along the  $\text{ZrO}_2$ -TiN interface and designated as matching if the error ( $\Delta r$ ) is less than 5%. Comparing the  $x$  values in  $\text{ZrO}_2$  and TiN ensures the identification of the matching conditions at the interface regardless of the combination of  $d$  and  $\theta$  resulting in  $x$  of each layer, as long as the interface is completely horizontal, which is hypothesized in this present study. Coincidental matching, if any, should be approximately the same for all interfaces. The example in [Figure 2b](#) shows 2/3 near-coincident site epitaxy, where the coherence length is equal to the horizontal distance of two  $\text{ZrO}_2$  and three TiN atomic planes. Note the additional atomic plane in the TiN layer marked by a red symbol ( $\perp$ ).

[Figure 3a](#) shows the probability of epitaxial matching throughout the 2064 and 2014 diffraction pattern pairs at the  $\text{ZrO}_2$  interfaces in the MIM and the MIS structures, respectively. [Figure 3a](#) shows a 56% probability of near-coincident site epitaxy for the bottom  $\text{ZrO}_2$ -TiN crystalline interface, which is more than 3 $\times$  higher than the probability of near-coincident site epitaxy for the bottom  $\text{ZrO}_2$ - $\text{SiO}_2/\text{Si}$  interface (16%). Note that the  $\text{SiO}_2$  layer is a thin amorphous layer formed on top of Si; therefore, near-coincident site epitaxy of  $\text{ZrO}_2$  to  $\text{SiO}_2/\text{Si}$  is essentially near-coincident site epitaxy of  $\text{ZrO}_2$  to Si through the  $\text{SiO}_2$  layer, for which the templating effect by remote Si is expected to be minimal. It is hypothesized that the observed near-coincident site epitaxy of  $\text{ZrO}_2$  to the bottom  $\text{SiO}_2/\text{Si}$  is due to the extremely flat surface promoting the aligned growth of  $\text{ZrO}_2$ . Interestingly, all the  $\text{ZrO}_2$ -TiN interfaces at both the top and bottom TiN in the MIM structure and the top TiN in the MIS structure show a consistent probability of  $\sim 56\%$  matching regardless of the location of the TiN layer with respect to the  $\text{ZrO}_2$  layer. This indicates a close interaction between TiN grains and the  $\text{ZrO}_2$  grains' crystallization over the atomically abrupt interface, which forms mostly in the annealing process at an elevated temperature.

In the MIM structure, it is noted that a significant portion of the matching grains show a simultaneous matching on both interfaces in the same location. Forty-three per cent (43%) of the probed area shows simultaneous matching, which corresponds to over 75% of the grains showing a match to either the top or bottom. Previously, similar correlations between the  $\text{ZrO}_2$  and TiN grains have been reported.<sup>22</sup> Note



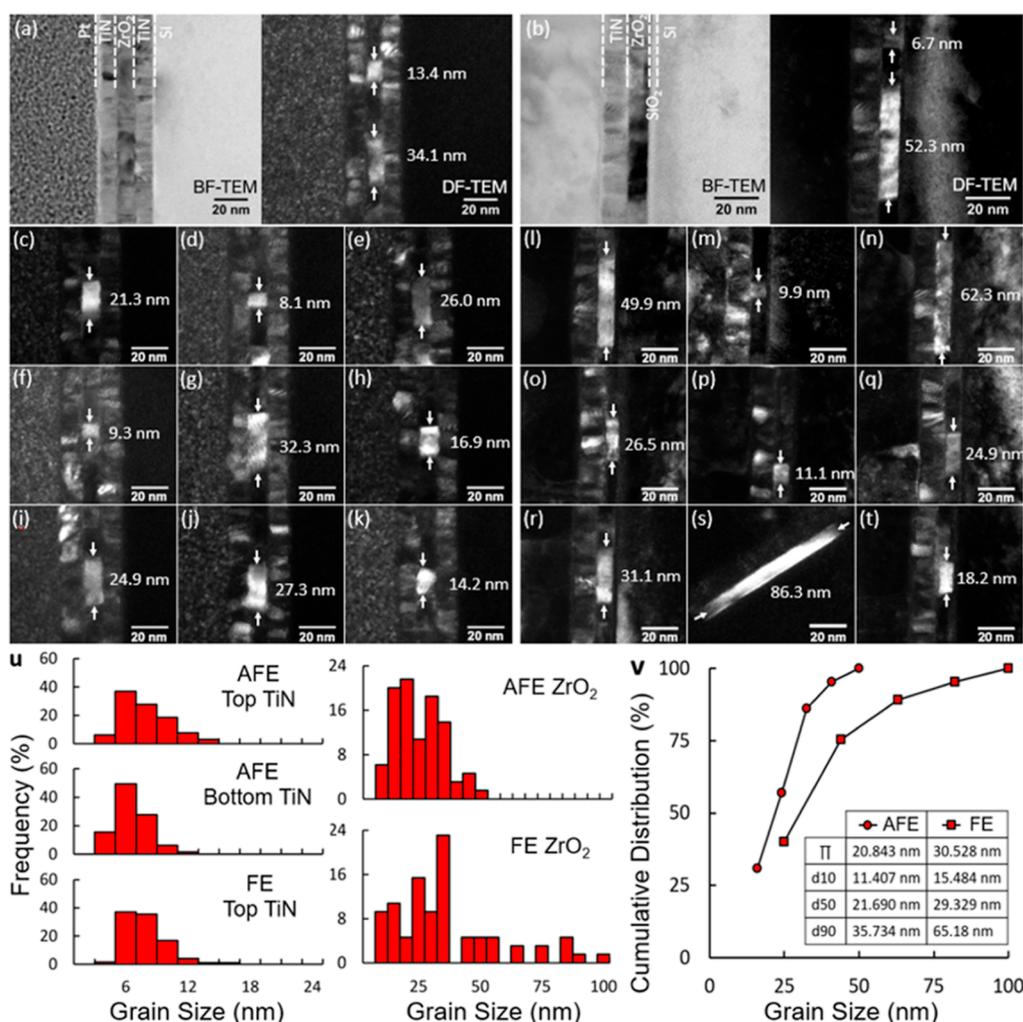
**Figure 4.** Confirmation of near-coincident site epitaxy at the ZrO<sub>2</sub>–TiN interfaces in STEM images. (a) Lattice matching atop the TiN–ZrO<sub>2</sub> interface in MIS, (b) mixture of 2/3 and 3/4 near-coincident site epitaxies at the top TiN–ZrO<sub>2</sub> interface in MIS, and (c) mixture of 2/3 and 3/4 near-coincident site epitaxies at the ZrO<sub>2</sub>–bottom TiN interface in MIM. In each set of data, STEM images, Fourier-filtered images, and diffractograms for ZrO<sub>2</sub> and TiN are provided. The horizontal distance ( $x$ ), inverse of interplanar spacing projected onto the interface, is directly measured from the diffractograms, and the ratio is given in the Fourier-filtered image. The computed ratio agrees well with the near-coincident site epitaxy type observed in the STEM image.

that both the top and bottom TiN layers were deposited by atomic layer deposition (ALD) below 300 °C in the present study (see the [Method](#) section for detailed deposition conditions), while TiN in the other work was deposited by sputtering,<sup>22</sup> indicating that the microstructural correlation can be independent of the deposition method if the interfaces are abrupt.

Distributions of the type of near-coincident site epitaxy at the ZrO<sub>2</sub>–TiN interfaces are shown in [Figure 3b](#), demonstrating that the conventional lattice matching epitaxy (a special case of 1/1 near-coincident site epitaxy) is most dominant. However, a meaningful portion of near-coincident site epitaxy types is 2/3, 3/4, 4/5, and 5/6, indicating that specific types of non-1/1 near-coincident site epitaxy prevail in the ZrO<sub>2</sub>–TiN interface. It is expected that the specific matching types are favored depending on the lattice mismatch and preferred grain orientations to minimize the mismatch. Some of those near-coincident site epitaxy interfaces are directly confirmed in the STEM analysis, discussed below. It is interesting to note that the probability of near-coincident site epitaxy is higher when the ZrO<sub>2</sub> grains are confined by both the top and bottom TiN interfaces (i.e., MIM), while the probability for the lattice matching is highest in the MIS sample. This implies that the near-coincident site epitaxy on one interface can be influenced

by the other interface across the 10 nm ZrO<sub>2</sub> layer, which could promote grain boundary formation and decrease the average grain size (see below).

**Direct Observations of Near-Coincident Site Epitaxy in STEM Microstructural Analysis.** To confirm the versatile epitaxial relations between ZrO<sub>2</sub> and TiN shown in the NBED analysis, exemplar atomic-resolution STEM analyses are shown in [Figure 4](#). The STEM images are presented in the first column, demonstrating atomically sharp interfaces between ZrO<sub>2</sub> and TiN. The atomic planes showing epitaxy at the interface have finite angles compared to the direction normal to the interface. To highlight those planes, Fourier-filtered images, shown in the second column, are generated using a virtual aperture applied to the Fourier peaks, marked by yellow arrows in the diffractograms. This approach has frequently been used in previous studies to identify the near-coincident site epitaxy.<sup>11–16</sup> The ratio between  $x_{\text{ZrO}_2}$  and  $x_{\text{TiN}}$  (the plane spacing projected onto the interface) is extracted from the images to determine the matching type, as shown in [Figure 2b](#). The ratio obtained at the top interface of the shown MIS structure in [Figure 4a](#) is 1, so lattice matching epitaxy is observed, and the atomic planes of ZrO<sub>2</sub>(100) and TiN(111) are lattice-matched.<sup>9</sup> The same top TiN–ZrO<sub>2</sub> interface in MIS was probed at a different location, showing different



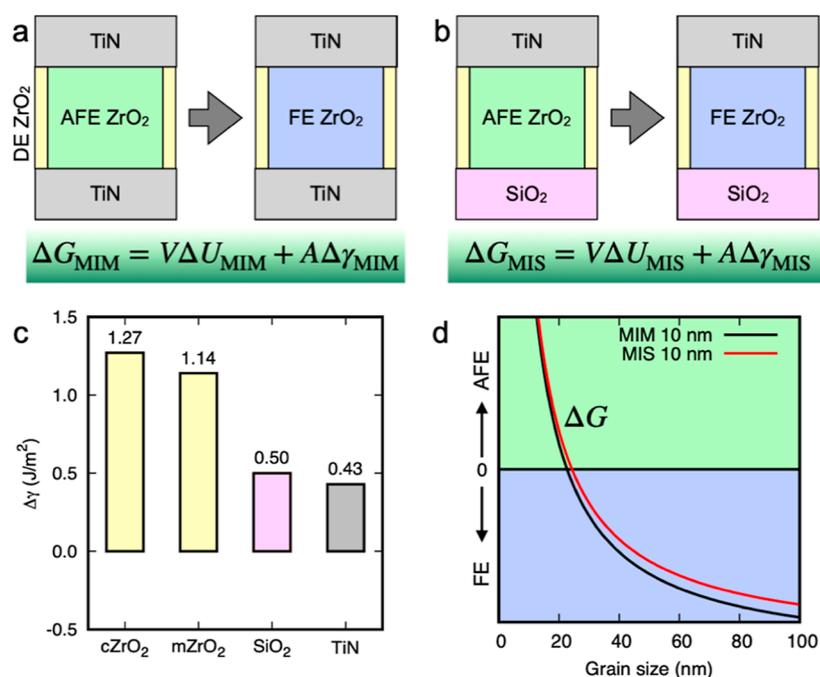
**Figure 5.** Grain size distributions of  $\text{ZrO}_2$  and TiN characterized by TEM. Bright-field (BF) and DF modes of TEM images in (a) MIM and (b) MIS stacks. In the DF mode, the grain size can be measured from the side view due to the high contrast for the grain-to-grain misorientation. DF-TEM images of (c–k) MIM and (l–t) MIS. With a total of 70 measurements per film, grain size distributions for all TiN and  $\text{ZrO}_2$  films are obtained as shown in (u). Cumulative distributions of the  $\text{ZrO}_2$  grain size (v) show larger grains in MIS (FE) than in MIM (AFE).

epitaxial growth. A  $x_{\text{ZrO}_2}/x_{\text{TiN}}$  ratio of 1.4 is observed (Figure 4b), which is best matched to 3/4 (1.33) near-coincident site epitaxy. Compared to ideal ratios, the experimental ratio of 1.4 lies between 3/4 (1.33) and 2/3 (1.5); the difference may be due to stress or strain at the interface. The discrepancy compared to the ideal values is consistent with the coexistence of local domains of 2/3 and 3/4 forming next to each other to compensate the compressive and tensile stresses (Figure 4b). As seen in Figure 4c, atomic planes at the bottom TiN– $\text{ZrO}_2$  interface in MIM also show a mixture of 2/3 and 3/4 near-coincident site epitaxies. In this case, the experimental ratio of 1.4 lies between 2/3 and 3/4, and it can be confirmed that both near-coincident site epitaxy types are observed from the Fourier-filtered image. As mentioned above, microstructures at the  $\text{ZrO}_2$ –TiN interface are independent of the relative location within the  $\text{ZrO}_2$  thin film.

It is evident that near-coincident site epitaxy is prevalent at the  $\text{ZrO}_2$ –TiN interfaces, but elucidating the underlying mechanism is not trivial. First, it is difficult to calculate the free energies of interfaces showing the near-coincident site epitaxy. To develop DFT models, large supercells need to be constructed, and detailed oxygen arrangements at the interface

need to be investigated. Second, at the annealing temperature used in this work (450 °C for 30 s in  $\text{N}_2$ ), the  $\text{ZrO}_2$  layer would be kinetically hindered to find the thermodynamic ground states. Rather, the pre-existing (nano)crystalline TiN would direct the crystallographic orientation of  $\text{ZrO}_2$ .

**Grain Size Statistics by DF-TEM.** To probe the grain size distribution, dark-field TEM (DF-TEM) is used as shown in Figure 5, through which individual grains are identified in both the MIM and MIS structures. Here, the grain size is defined by the maximum width of the grain cross-section. Note that DF-TEM is capable of distinguishing one grain from neighboring grains with a large crystallographic misorientation due to the explicitly distinct diffraction patterns. Typically, oxygens are disordered at the high-angle grain boundaries and therefore should show a nonpolar electric response. Based on the measurement of 70 grains for  $\text{ZrO}_2$  in each of the sets of MIM and MIS samples, the grain size distributions are shown in Figure 5u. The geometric mean for the grain sizes in  $\text{ZrO}_2$  is found to be 20.8 and 30.5 nm for the MIM and MIS samples, respectively. Figure 5v shows the cumulative distribution functions for each case, confirming a wider grain size distribution for the MIS film throughout the 1–100 nm range. This 50% difference in the average grain width



**Figure 6.** Effects of the grain size and substrate. Schematic diagrams of (a) MIM and (b) MIS where ZrO<sub>2</sub> undergoes a phase transition from AFE to FE, which is exothermic ( $\Delta U < 0$ ) in the bulk state. Cubic ZrO<sub>2</sub> (cZrO<sub>2</sub>) or monoclinic ZrO<sub>2</sub> (mZrO<sub>2</sub>), shown in yellow, is hypothesized to form at the grain boundaries just as a model DE for simplicity. (c) Interfacial free energy change ( $\Delta\gamma$ ) for cZrO<sub>2</sub>, mZrO<sub>2</sub>, SiO<sub>2</sub>, and TiN calculated by DFT. DE layers (cZrO<sub>2</sub>, mZrO<sub>2</sub>, and SiO<sub>2</sub>) show significant  $\Delta\gamma$  due to the electrostatic interactions to FE, while TiN shows very small  $\Delta\gamma$  due to its metallic characteristics. (d) Free energy ( $\Delta G$ ) is calculated based on the DFT total energies and interfacial free energies. Overall, AFE is favored for small grains because interfacial effects dominate the overall phase stability, while FE is favored as the grain size increases due to the lower total energy.

corresponds to approximately 2× difference in the grain area and volume.

The smaller average grain size in MIM compared to that in MIS is ascribed to the near-coincident site epitaxy at the interfaces on both sides of the 10 nm ZrO<sub>2</sub> layer, for example, top and bottom TiN interfaces. The MIM near-coincident site epitaxy shown at the ZrO<sub>2</sub>–TiN interfaces, as well as the prevalent triple matching (i.e., TiN–ZrO<sub>2</sub>–TiN) in Figure 3, is consistent with the confinement of the ZrO<sub>2</sub> grain size. Conversely, for MIS, the amorphous SiO<sub>2</sub> provides flexible interfacial bond formation, spontaneously releasing the bond strain and thereby resulting in larger grain sizes. Various textures of the ZrO<sub>2</sub> film, for example, (001), (011), and (111), are observed from STEM analysis (see the Supporting Information).

**Role of the Grain Size in Phase Stability.** The most dramatic change in the microstructure of the ZrO<sub>2</sub> film due to different substrates is in the grain size distribution (Figure 6) and the corresponding electrical characteristics due to the phase transformation (Figure 1). To understand the role of the grain size in relative phase stability, a free energy ( $\Delta G$ ) model is developed, similar to previous study,<sup>23</sup> as a function of total energy ( $\Delta U$ ) and differential interfacial free energy ( $\Delta\gamma$ ) as shown in Figure 6:

$$\Delta G(x) = V(x)\Delta U(x) + \sum A(x)\Delta\gamma(x) \quad (1)$$

where  $x$  refers to the size of each grain.  $A$  and  $V$  represent the interfacial area and volume of the grain, respectively. The details of the model are described in the Supporting Information. The AFE to FE phase transition is thermodynamically exothermic in the bulk state, that is,  $\Delta U < 0$ , but the

change in the interfacial interactions,  $\Delta\gamma = (\text{FE}) - \gamma(\text{AFE})$ , depends on various factors such as electrical characteristics of the phase and bond strains at the interface. The interfacial interactions have crucial effects on the phase stability as the grain size decreases.<sup>24</sup> In the MIS structure, each of the grains has interfaces to either the top or bottom electrodes (TiN or SiO<sub>2</sub>) or neighboring grains, so there are three different interfacial free energies: grain boundary, SiO<sub>2</sub>, and TiN. Here, it is hypothesized that a dielectric (DE) layer is formed at the grain boundaries as was shown previously.<sup>25</sup> This interfacial DE is modeled as the cubic ( $Fm\bar{3}m$ ) ZrO<sub>2</sub> phase to provide computational simplicity since only the electrostatic portion of the interfacial free energy is being considered as in the previous work.<sup>26</sup> Figure 6c shows the comparable interfacial free energies between the cubic phase and the monoclinic phase ( $P2_1/c$ ) due to the same DE responses. The sum of  $A\Delta\gamma$  terms runs over all the interfaces, that is, top, bottom, and sides. Figure 6c shows that  $\Delta\gamma$  is very large for DE ZrO<sub>2</sub> (both cubic and monoclinic phases) and SiO<sub>2</sub> due to the electrostatic interactions with the FE phase. For TiN, even though it has metallic electronic structures,  $\Delta\gamma$  is comparable to that of SiO<sub>2</sub> because of the Ti–O bonds at the interface.

Figure 6d shows  $\Delta G$  as a function of grain size ( $x$ ). For a small grain size, the AFE phase is favored as the interfacial free energy term dominates. In MIS,  $\Delta\gamma$  is greater than that in MIM due to DE SiO<sub>2</sub> on the bottom (Figure 6c). This indicates that a slightly larger grain size is needed to stabilize the FE phase in MIS. The templating effects due to the nanocrystalline TiN electrodes limit the ZrO<sub>2</sub> grain size in MIM where the AFE phase is favored, while larger grains are observed in the MIS structure (Figure 5) favoring the FE phase. Moreover, additional DE interlayer formation such as

TiON at the TiN–ZrO<sub>2</sub> interface would further increase  $\Delta\gamma$ , making the film prefer the AFE phase due to the unfavorable interfacial free energy between FE and DE. If the film thickness is decreased, the critical grain size is further increased due to an increase in interfacial effects, that is, increased surface-to-volume ratio. However, when the film thickness is decreased down to a few nanometers, the strain becomes a dominating factor, changing the relative energy ( $\Delta U$ ) significantly from that of the bulk.<sup>24</sup> In addition to the grain size, the oxygen content also plays a role in the ZrO<sub>2</sub> phase stability, in which oxygen deficiency is observed in the monoclinic and tetragonal phases.<sup>27,28</sup> Since ZrO<sub>2</sub> films grown on SiO<sub>2</sub> do not experience scavenging effects from the bottom substrate, the ZrO<sub>2</sub> film is expected to contain a higher oxygen content than its MIM counterpart, resulting in the orthorhombic phase being a more likely stable phase in the MIS case.

In summary, the grain size in the 10 nm ZrO<sub>2</sub> thin film interfacing with the nanocrystalline TiN depends critically on the near-coincident site epitaxy, which is shown to exist by using the automated, high-throughput NBED analysis developed in this work. The average grain size is shown to be smaller for the MIM samples with two TiN interfaces when compared with that for the MIS samples with only one TiN interface. The reduced grain size is sufficient to favor the AFE phase over the FE phase, making the ZrO<sub>2</sub> thin film attractive as it can display various electric responses.

## CONCLUSIONS

An automated analysis workflow is presented for state-of-the-art NBED, where local crystalline information can be probed by the nanoscale electron beam throughout the sample. The analysis is used to compute the horizontal distances of atomic planes at the interface revealing prevalent near-coincident site epitaxy. Various types of near-coincident site epitaxies are detected automatically over thousands of diffraction patterns and are confirmed by atomic-resolution STEM images. The technique is tested on TiN/ZrO<sub>2</sub>/TiN and TiN/ZrO<sub>2</sub>/SiO<sub>2</sub>/Si interfaces and reveals that not only dominant lattice matching (1/1) but also finite near-coincident site epitaxy (2/3 and 3/4) exist at the ZrO<sub>2</sub>/TiN interface, verified by real-space STEM imaging. Over 56% of the samples show atomic scale epitaxial matching, and most of the grains show simultaneous epitaxy on both top and bottom interfaces, indicating confinement in the microstructure. To elucidate the correlations between the microstructure and functionality of ZrO<sub>2</sub> thin films grown on TiN and SiO<sub>2</sub>/Si substrates, DF-TEM is used to compute the grain size distribution. Larger grains are observed for ZrO<sub>2</sub> grown on SiO<sub>2</sub>/Si showing ferroelectricity, while grain sizes are smaller for AFE ZrO<sub>2</sub> grown on TiN, consistent with lower strain and less near-coincident site epitaxy at the ZrO<sub>2</sub>–SiO<sub>2</sub> interface compared to that at the ZrO<sub>2</sub>–TiN interface. DFT calculations are used to elucidate the phase stability of the polycrystalline ZrO<sub>2</sub> film on different substrate materials as a function of grain size. It is shown that interfacial free energy plays a crucial role, where the grain size is sensitively influenced by the substrate material. Combined with the high-throughput microstructure analysis technique developed here, statistical analysis of the nanocrystalline interfaces can be done quantitatively, and optimal electrode materials can be investigated for the advancements of emerging microelectronics.

## METHODS

**Fabrication and Electrical Measurements.** 10 nm ZrO<sub>2</sub> thin films were deposited by ALD on a 10 nm TiN layer and on a 1.5 nm chemical SiO<sub>2</sub> layer, both grown on a degenerately doped p+ Si substrate. ALD was performed below 300 °C to ensure the films were nearly amorphous in the as-deposited state. Top TiN layers were subsequently grown on both heterostructures using ALD, followed by sputtering and lithographic patterning of Ti (30 nm)/Au (5 nm) top electrodes for electrical probing; again, TiN ALD was performed below 300 °C to ensure the as-deposited ZrO<sub>2</sub> remained nearly amorphous. Postmetallization annealing was performed at 450 °C for 30 seconds under a N<sub>2</sub> ambient condition for the crystallization of ZrO<sub>2</sub>.

**Structural Characterization Methods.** Cross-sectional samples for imaging were prepared using an FEI Nova Nanolab 200 FIB/scanning electron microscope equipped with a high-energy FIB using Gallium-69 and operated at an accelerating voltage between 5 and 30 kV. The resulting FIB lamellas were approximately 10  $\mu\text{m}$  in length and 50 nm in thickness. BF-TEM, DF-TEM, and HR-TEM images were captured using an FEI Tecnai G2 F30 transmission electron microscope/scanning transmission electron microscope, operated at an accelerating voltage of 300 kV and a beam current of 9  $\mu\text{A}$ . STEM images were collected using a Hitachi HD-2700 aberration-corrected scanning transmission electron microscope/scanning electron microscope, operated at a 200 kV accelerating voltage, 30 mrad convergence angle, and a beam current of 9  $\mu\text{A}$ . Stacks of STEM images were collected to minimize drifting while keeping a reasonable signal-to-noise ratio, each frame taken at integration times between 0.1 and 0.15 s with an image size of 512  $\times$  512 pixels and each stack containing 30–70 frames. The drift correction was performed using a Hitachi-America (HTA) plugin based on local intensity maxima. GIXRD measurements were performed at the SLAC National Accelerator Laboratory using the Beam Line 2-1 station with a PILATUS 100K detector. An X-ray energy of 17 keV (wavelength of 0.729 Å) is used, with X-rays incident to the ZrO<sub>2</sub> film at an angle of 0.15° for both MIM and MIS samples and also using a Bruker D8 Discover diffractometer with an incidence angle of 0.45° (Cu K $\alpha$  radiation,  $\lambda = 0.154$  nm).

NBED scans were collected using an FEI Tecnai G2 F30 transmission electron microscope/scanning transmission electron microscope with an accelerating voltage of 300 kV and a convergence angle of 0.7 mrad. NBED analysis is used to obtain a series of diffractograms from evenly spaced grid points across the TEM cross-sectional samples. Each of the diffractograms is spatially indexed, so the diffraction peak positions from individual grains of ZrO<sub>2</sub> and TiN at the same location can be directly compared. To avoid the overcounting due to the finite size of the electron beam ( $\sim 5$  nm in this study), the diffraction patterns are collected away from the ZrO<sub>2</sub>–TiN or ZrO<sub>2</sub>–SiO<sub>2</sub> interfaces. In each diffractogram, coordinates of the diffraction peaks are found by the Monte Carlo-based optimization method, detailed in the Supporting Information, and are converted to directly compare the width of each domain to determine the matching type.

**Simulation Methods.** DFT calculations were performed as implemented in the Vienna Ab initio Simulation Package.<sup>29,30</sup> Exchange-correlation functional of Perdew–Burke–Ernzerhof<sup>31</sup> was implemented to build the Kohn–Sham Hamiltonian, and the projector augmented wave method was used for the core part of the wave functions.<sup>32</sup> The plane waves were expanded up to a kinetic energy cutoff of 450 eV, and the  $k$ -points were uniformly sampled within the Brillouin zone at a minimum of 0.032 Å<sup>-1</sup> by using the Monkhorst–Pack scheme.<sup>33</sup> The stopping criteria for DFT self-consistent field and conjugate gradient ionic relaxation were 10<sup>-5</sup> meV and 10 meV/Å, respectively.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.2c03151>.

Additional GIXRD analysis for ZrO<sub>2</sub> in MIM and MIS; multiple grains probed by NBED; automated image processing procedures; additional STEM images for ZrO<sub>2</sub> in MIM and MIS; and thermodynamic phase stability for a model polycrystalline thin film (PDF)

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### Notes

The authors declare no competing financial interest.

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