Cation diffusion in polycrystalline thin films of monoclinic HfO$_2$ deposited by atomic layer deposition

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I. INTRODUCTION

Crystalline ion conductors generally consist of a sublattice of mobile ions and one or more sublattices of immobile ions. The latter form a stable framework through which the mobile ions can migrate. In reality, however, no ion is completely immobile in a crystalline solid: the "immobile" ions are merely considerably less mobile than the "mobile" ions. In addition, this has to be the case if the stable phase is a solid and not a liquid. The issue, therefore, is actually one of the relative diffusion rates.
Studying the diffusion of a crystal’s “immobile” ions experimentally is difficult because the number of defects responsible for diffusion is generally low and the activation enthalpy of defect migration is generally high, which means that diffusion coefficients are necessarily very small. High temperatures and long diffusion times are thus needed to achieve measurable diffusion lengths, conditions that are often accompanied by complicating effects (e.g., diffusion specimens showing morphological changes). If one manages to obtain diffusion data of sufficient quality, one faces the further problem of interpreting the measured activation enthalpy of diffusion, \( \Delta H_D \). Even in the simplest case, \( \Delta H_D \) is the sum of two individual enthalpies, \( \Delta H_{\text{mig}} \), the activation enthalpy of defect migration, and \( \Delta H_{\text{gen}} \), the enthalpy of defect generation,

\[
\Delta H_D = \Delta H_{\text{mig}} + \Delta H_{\text{gen}}.
\]

(1)

\( \Delta H_{\text{gen}} \) describes how the concentration of the defect responsible for diffusion, \( c_{\text{def}} \), changes with temperature \( T \),

\[
\Delta H_{\text{gen}} = -k_B \ln c_{\text{def}}/d(1/T).
\]

(2)

For minority defects, neither \( \Delta H_{\text{mig}} \) nor \( \Delta H_{\text{gen}} \) is independently accessible from experiment.

Simulation techniques, based either on Density-Functional-Theory (DFT) calculations or on calculations with Empirical Pair Potentials (EPP), can prove helpful by providing both \( \Delta H_{\text{mig}} \) and the relevant defect energies entering \( \Delta H_{\text{gen}} \). Help is not always guaranteed, however, in the case of cation diffusion in Gd-doped CeO\(_2\), for example, the experimental value of \( \Delta H_D \approx 5.5 \) eV is substantially lower than the sum of the (DFT) computational values for vacancy migration, with \( \Delta H_{\text{mig},v} = 4.4 \) eV and \( \Delta H_{\text{gen},v} = 6.9 \) eV.\(^\text{3,20,21}\) Similarly for UO\(_2\), the experimental value of \( \Delta H_D \approx 5.6 \) eV is substantially lower than the (EPP) computational values of \( \Delta H_{\text{mig},v} = 6 \) eV and \( \Delta H_{\text{gen},v} = 6.5 \) eV.\(^\text{18}\) Values for cation interstitials show even larger discrepancies.

The interpretation of the experimental values of \( \Delta H_D \) would be simplified if the concentration of the defects responsible for diffusion could be fixed over a proper range of temperatures so that \( \Delta H_{\text{gen}} \) goes to zero. For majority defects, a suitable dopant and suitable thermodynamic conditions may serve to fix \( c_{\text{def}} \) (e.g., in Gd-doped CeO\(_2\) under oxidizing conditions, the concentration of oxygen vacancies is fixed by the gadolinium dopant concentration). For minority defects, however, a variety of intrinsic and extrinsic defect reactions determines \( c_{\text{def}} \). That is, the concentrations of minority defects are dictated by thermodynamics. In general, \( c_{\text{def}} \) will, therefore, vary with temperature, giving rise to non-zero \( \Delta H_{\text{gen}} \). For the case of Gd-doped CeO\(_2\) mentioned above, with gadolinium fixing the oxygen vacancy concentration, \( \Delta H_{\text{gen}} \) for cation vacancies is equal to \( \Delta H_{\text{sch}} \) (the enthalpy of the Schottky disorder). One way to avoid this problem, then, is to study samples that are not in equilibrium so that thermodynamics is removed from the problem. We propose to achieve this by investigating cation diffusion in metastable samples in which the concentration of the minority defects is fixed through kinetics, i.e., through the preparation procedure.

In this study, such samples are fabricated by Atomic Layer Deposition (ALD), the established industrial process for growing nanometer-thin, homogeneous insulating HfO\(_2\) thin films for use in high-permittivity metal gate transistors, flash memory, and also a new type of Random Access Memory (RAM), the one utilizing redox-based Resistive switching (ReRAM). The primary advantage for this study is that this method offers the possibility of producing polycrystalline films of monoclinic HfO\(_2\) (m-HfO\(_2\)) at low temperatures.\(^\text{26}\) The low temperatures provide the sluggish kinetics required so that equilibrium is not achieved for the cation sublattice. An additional advantage is that ALD produces films that are free of Si (whose presence complicates the study of diffusion in AO\(_2\) oxides).\(^\text{27–30}\) The use of HfO\(_2\) also offers the advantage of using Zr as a chemically similar species to study cation diffusion rather than using expensive (and hard to process) Hf isotopes.

II. METHODOLOGY

A. Experimental

As noted above, previous studies have shown that silica impurities severely impact the oxygen diffusion behavior in m-HfO\(_2\).\(^\text{31–33}\) For this reason, the industrial standard, silicon wafers are omitted for this study. While ALD makes use of Si-free precursors and, thus, yields Si-free samples, the film substrates remain as a possible source of Si, particularly due to silica residues remaining on the surface after polishing. For this reason, the amount of Si impurities was examined on different substrates [DyScO\(_3\), (LaAlO\(_3\))\(_{3/2}\)(Sr\(_2\)TaAlO\(_3\))\(_{1/2}\), NdGaO\(_3\), SrTiO\(_3\), Al\(_2\)O\(_3\), and YSZ] with Secondary Ion Mass Spectrometry (SIMS). DyScO\(_3\) delivered the best results, with the least amount of Si at the interface of the film and substrate. We attribute this behavior to the self-cleaning effect of perovskite-type systems.\(^\text{1,1–3}\) Reactive ion beam etching on the substrate surface followed by HfO\(_2\) deposition showed no discernible influence on the amount of Si. Thus, polished DyScO\(_3\) single crystals were used as substrates for the HfO\(_2\) thin films.

For the plasma assisted ALD process, tetrakis(ethylmethylamino) hafnium (TEMAH, ≥99.99% trace metal basis excluding ~2000 ppm Zr, SAFC Hitech\(^\text{®}\)) was used as a precursor to deposit HfO\(_2\) at \( T = 573 \) K as a thin, amorphous layer with embedded m-HfO\(_2\) nanocrystals of about 3 nm in diameter.\(^\text{26}\) An oxygen plasma was used as a co-reactant. The ALD process was performed in a Flexal\(^\text{TM}\) ALD tool (Oxford Instruments Plasma Technologies, Bristol, United Kingdom). Then, a thin layer of ZrO\(_2\) was employed as a diffusion source, deposited by RF-magnetron sputtering (an output power of 60 W) from a Zr-target at room temperature under 0.01 mbar pressure in a mixture of 38 sccm Ar and 2 sccm O\(_2\). These conditions resulted in a deposition rate of 0.82 nm/min. Our aim was to deposit 40 nm of ZrO\(_2\) on 100 nm of HfO\(_2\).

Diffusion anneals were carried out in a MoSi\(_2\) furnace in air inside a closed Al\(_2\)O\(_3\) vessel. The heating rate was 500 K/h for all temperatures. Samples were quenched after the anneal by removing them from the MoSi\(_2\) furnace and transferring them to another furnace with a temperature of 873 K. They were then cooled to room temperature with a cooling rate of 500 K/h. This procedure was employed to avoid cracking of the samples through very rapid cooling.

Grazing incidence x-ray diffractograms obtained with a X’Pert MRD system (PANanalytical, Almelo, The Netherlands) indicated the existence of a single monoclinic phase after annealing the sample in air at 1273 K for 20 h. After 20 h at 1373 K, both monoclinic and cubic phases were found. After 10 h at 1423 K, only the cubic phase
was found. We assume that the phase transition occurs as a result of Dy$^{3+}$ and Sc$^{3+}$ diffusing in from the substrate (detected by ToF-SIMS analysis; see below), similar to the stabilization of the cubic phase of ZrO$_2$ upon Y$^{3+}$ doping. To ensure that cation diffusion data refer to the monoclinic phase of HfO$_2$, only samples annealed at temperatures below 1373 K were subjected to analysis.

Scanning electron microscopy (SEM) images of the thin-film samples after the analysis were taken with an SU8000 system (Hitachi, Tokyo, Japan). From these images, we determined that the grain size varied between 20 nm and 90 nm, depending on the annealing temperature. Interference microscopy (NT1100, Veeco Instruments, Inc., NY, USA) indicated a roughness of ±2 nm for the areas relevant to ToF-SIMS analysis (100 × 100 μm$^2$).

ToF-SIMS depth profiles were obtained on a TOF-SIMS IV machine equipped with a ToF-SIMS V analyzer (ION-TOF GmbH, Münster, Germany). 25 keV Ga$^{+}$ ions, rastered over an area of 100 × 100 μm$^2$, were used to generate secondary ions. Measurements were performed with a ToF cycle time of 60 μs in the bunched mode, and negative secondary ions were detected. Preliminary studies indicated that the secondary-ion intensities of MeO$^-$ species (Me = Hf/Zr) under Cs$^+$ bombardment were higher than those of Me$^+$ species under O$_2$ + bombardment. Therefore, 2 keV Cs$^+$ ions were used for sputter etching the sample surface, typically over an area of 400 × 400 μm$^2$. Charge compensation was accomplished with a beam of low-energy (<20 eV) electrons. Secondary-ion intensities of MeO$^-$ species were normalized to the intensity of $^{18}$O$^-$ and to the maximum intensity of the profiles. Crater depths were determined post-analysis by interference microscopy.

### B. Computational

All DFT calculations were performed within the generalized gradient approximation after Perdew, Burke, and Ernzerhof (PBE). The potentials generated by the projector augmented wave method were used with an energy cutoff of 500 eV. Calculations were performed for a periodic 2 × 2 × 2 supercell of m-HfO$_2$ containing 31 Hf atoms and 64 O atoms (since a Hf$^{4+}$ species was removed, the behavior of a charged vacancy is considered). k-points were generated by a 2 × 2 × 2 Monkhorst–Pack mesh. For convergence criteria, electronic convergence was set to 1 × 10$^{-4}$ and ionic convergence was set to 1 × 10$^{-3}$. The Climbing-Image Nudged Elastic Band (CI-NEB) method was used to determine the energy of the transition state over three images along the cation jump. The Vienna ab initio simulation package was used.

### III. RESULTS

#### A. Experimental

The sample geometry and the investigated length-scale of the diffusion samples are indicated in Fig. 1(a). Figure 1(b) shows the intensity profiles for ZrO$^-$ and HfO$^-$ secondary ions across the structure obtained prior to the diffusion anneal by SIMS depth profiling. The two different layers are well-defined and homogeneous. Examining the interface region, we find that the range of depths over which the ZrO$^-$ signal decreases is approximately equal to the range of depths over which the HfO$^-$ signal increases. This suggests that the broadening of the signals comes from the samples, i.e., it is due to the roughness of the ZrO$_2$ surface and/or the ZrO$_2$/HfO$_2$ interface. If direct recoil and ion beam mixing (SIMS effects) were responsible, the two ranges of depths would not be similar. At a depth of ~140 nm, the hafnia layer ends and the substrate layer begins, which is the expected result according to the process specifications.
After diffusion annealing, the intensity profile of ZrO\(^2^+\), as shown in Fig. 1(c), still displays a constant plateau in the ZrO\(_2\) layer; at the ZrO\(_2\)/HfO\(_2\) interface, the broadening is less steep than in the sample prior to the diffusion anneal, suggesting cation diffusion; and a long profile, extending from \(\sim 45\) nm up to the substrate at \(\sim 135\) nm, has developed. The position of the HfO\(_2\)/DyScO\(_3\) interface has apparently shifted slightly, but careful examination revealed that it is actually a shift of the ZrO\(_2\)/HIO\(_2\) interface. The thickness of the HIO\(_2\) layer has not changed. We ascribe this shift to the densification of the ZrO\(_2\) layer due to thermal treatment (since it was sputtered at room temperature) and a consequent reduction in film thickness. Near the substrate, an upturn in the ZrO\(^2^+\) intensity profile is observed. We attribute this upturn to a SIMS artifact that arises as the sputter front passes through the interface from the HfO\(_2\) film to the DyScO\(_3\) substrate. Simulations of diffusion (see below) did not reproduce this upturn. The obvious interpretation of the profile is that the broadening is due to diffusion in bulk m-HfO\(_2\) and the long profile is due to a combination of fast grain-boundary diffusion and slow diffusion out of the boundary. Given that the area of the ToF-SIMS analysis was 100 \(\mu\)m\(^2\) and the area of a single grain is of the order of 10\(^5\) nm\(^2\), the profile refers to the average over \(\sim 10^4\) grains and their grain boundaries. The diffusion profile obtained for HfO\(^-\) shows similar, though not identical, behavior.

Going from the substrate toward the surface, one sees a constant plateau of HfO\(^-\) in the HfO\(_2\) layer, a decrease corresponding to diffusion and to the broadening arising from interfacial roughness, but then, an increase in HfO\(^-\) intensity toward the surface. This suggests surface diffusion of Hf from the film to the external ZrO\(_2\) surface and diffusion inward from this surface. In the following, we do not consider the HfO\(^-\) profiles further, but focus on the ZrO\(^2^+\) profiles in HfO\(_2\).

Given the complexity of the diffusion problem—diffusion along two different paths (bulk and grain boundary) in a medium of finite extent from a non-trivial initial distribution—we chose to solve the diffusion equation numerically in two dimensions in order to obtain the relevant diffusion coefficients. To this end, Finite-Element-Method (FEM) simulations were implemented in COMSOL Multiphysics® (COMSOL AB, Stockholm, Sweden) for a simulation box of length \(l_{\text{sim}}\) and of width \(d_{gr} + d_{gb}\) (of which \(d_{gb}\) is the region within which slow grain-boundary diffusion takes place). Bulk and grain-boundary diffusion coefficients were assumed to be isotropic and the same for both ZrO\(_2\) and HfO\(_2\) layers. The assumption of isotropic diffusion coefficients for non-isotropic m-HfO\(_2\) is reasonable since each diffusion profile is an average over \(\sim 10^3\) grains (and the grains show no preferred orientation according to XRD scans). In the simulations, \(l_{\text{sim}}\) was set to the film’s thickness, \(d_{gr}\) was chosen to be 1 nm, and \(d_{gb}\) was assumed to be constant at each temperature (i.e., grain growth was assumed to take place faster than in diffusion), with values taken from the SEM images. The intensity profile prior to the diffusion anneal [e.g., Fig. 1(b)] was used as the initial condition.

Figure 2(a) shows a 2D concentration heat map obtained from an FEM simulation of zirconium diffusion in the layer structure. The different regions and grain boundaries of the model are clearly visible in the heat map. The concentration heat map was averaged parallel to the surface to obtain a simulated diffusion profile that was compared visually with the experimental data. \(D_{gr}\), \(D_{gb}\), and \(D_{gb}\) were varied until good agreement was found, as shown in Fig. 2(b).

(Note that only small adjustments to \(d_{gb}\) from the SEM values were necessary.) Unlike the standard analysis of grain-boundary diffusion,\(^{43-46}\) which yields the grain-boundary diffusion product \(D_{gb}D_{gb}\), these simulations give the grain-boundary diffusion coefficient \(D_{gb}\) since \(D_{gb}\) is explicitly specified. This means that the values of \(D_{gb}\) are specific to the value of \(d_{gb}\); if accelerated diffusion takes place within a region wider or narrower than \(d_{gb} = 1\) nm, then the values we obtained for \(D_{gb}\) will change (see later). Diffusion coefficients of zirconium obtained for the m-HfO\(_2\) films as a function of annealing temperature are plotted in Fig. 3. \(D_{gb}\) is seen to be \(\sim 3\) orders of magnitude higher than \(D_{gr}\) at all temperatures. For bulk diffusion of zirconium in m-HfO\(_2\), an activation enthalpy of \(\Delta H_b = (2.1 \pm 0.2)\) eV is obtained. The activation enthalpy of zirconium diffusion in the grain boundary is the same at \(\Delta H_{gb} = (2.1 \pm 0.3)\) eV.

**B. Computational**

Cations in the cubic \(A_2O_5\) fluorite structure (\(c\)-AO\(_2\)) sit on a single crystallographic site and have 8 oxygen ions as the nearest neighbors and 12 cations as the next-nearest neighbors. (Oxide ions are fourfold coordinated by \(A\) cations and are also located on a single crystallographic site.) For cation migration by a vacancy mechanism, cations jump along the (110) directions to vacant sites.\(^{47-49}\) The high degree of symmetry in \(c\)-AO\(_2\) leads to all 12 possible jumps being symmetry equivalent. This is not the case in m-HfO\(_2\), however, where (because of the monoclinic distortion) hafnium is sevenfold coordinated by oxygen and two different oxygen sites exist, half of which are threefold and half are fourfold coordinated. Although the number of next-nearest neighboring hafnium ions and, thus, the
number of possible jumps remain to be twelve (i.e., the same as in $c$-$\text{AO}_2$), many of these jumps are no longer symmetry equivalent. In fact, only four of these jumps are symmetry equivalent, leaving eight distinct possible jumps [see Fig. 4(a)], in contrast to the single, unique jump of the cubic structure. We used CI-NEB calculations to calculate the migration barriers by a vacancy mechanism for these hafnium ion jumps in the monoclinic structure. The results are plotted in Fig. 4(b).

The activation barriers are seen to vary from 1.8 eV to 4.8 eV. This range of values does not seem to be consistent with those from the experiments. One critical point, however, is the combinations of jumps that are required so that hafnium can migrate through the cell from one side to the other. In this regard, jumps 3 and 8, with 2.1 eV and 1.8 eV, together provide a path through the cell in the $(001)$ direction. The second critical point concerns the jump rates at the temperatures of the experiments, $\Gamma_v = \nu_0 e^{\Delta S_{\text{mig},v}}/k_B e^{\Delta H_{\text{mig},v}/k_B T}$. Assuming that the attempt frequencies ($\nu_0$) and the activation entropies of migration ($\Delta S_{\text{mig},v}$) do not vary much for the various jumps, one finds that, at $T = 1100$ K, jumps over the other barriers occur far less frequently in comparison (for 3 eV, a factor of $10^4$ less; for 4.8 eV, a factor of $10^{12}$ less). Hence, hafnium migration in other directions will not be observed at the temperatures of the experiments because those paths have substantially higher barriers. We thus conclude that the activation energy of hafnium-vacancy migration at the temperatures of interest in a polycrystal with randomly oriented grains will be given by the (largest) migration barrier in the $(001)$ direction, $\sim 2$ eV.

IV. DISCUSSION

A. Bulk diffusion

The good agreement between $\Delta H_D$ obtained experimentally and $\Delta H_{\text{mig},v}$ obtained computationally for cation transport in $m$-$\text{HfO}_2$ strongly suggests [see Eq. (1)] that $\Delta H_{\text{gen},v}$ for our non-equilibrium samples was zero and, hence, that the concentration of hafnium vacancies does not vary with temperature, in accord with our initial premise. The investigation of non-equilibrium samples thus opens a new avenue to studying the migration of slow-moving minority defects.
Compared with the values obtained computationally for cation-vacancy migration in other AO₂ systems—\( \Delta H_{\text{mig},v} \) is over 4 eV for CeO₂ and over 5 eV for UO₂—one observes in cubic B. Grain-boundary diffusion activation barrier of migration (being monoclinic rather than cubic samples having a higher site fraction of cation vacancies and a lower \( Y \Delta v \) reported that fusion in Er et al. also two substantially lower values (\( \approx 2 \) eV). The difference between these three oxides and HfO₂ is the crystal symmetry: CeO₂ and UO₂ adopt the high-symmetry cubic form (and ZrO₂ was considered in the computer simulations as a hypothetical cubic structure), whereas HfO₂ has a strongly distorted monoclinic structure.

Metlenko et al. proposed a general rule for the effect of structural perturbations on ion migration. They hypothesized that, for ions that are highly mobile in a given structure, structural perturbations lead to a decrease in ion mobility, whereas for ions that are immobile, structural perturbations lead to an increase. Indeed, isothermal rates of oxide-ion transport in monoclinic and tetragonal ZrO₂ and HfO₂ are found to be much lower than in the cubic form. We would expect, therefore, the strong structural perturbation of \( m\)-HfO₂ to lead to higher rates of cation diffusion than in the cubic counterparts. In the present case, one could argue more specifically in terms of the oxygen coordination of the cations. A sevenfold coordination of hafnium by oxygen increases their mobility compared to that in an eightfold coordination; for CeO₂ and UO₂, such an enhancement of cation mobility is found in the presence of oxygen vacancies (specifically, an increase in grain-boundary mobility was observed in an oxygen-poor atmosphere). If we understand oxygen vacancies in a cubic fluorite lattice as a perturbation of the eightfold coordination of the A cation toward a sevenfold coordination, then the sevenfold coordination of hafnium in the monoclinic crystal structure might increase the cation mobility and explain the low migration enthalpies.

Another benefit of our approach is that it allows us to estimate \( n_v \), the site fraction of cation vacancies in our samples. Since we can express the bulk diffusion coefficients in terms of \( n_v \), a jump distance \( d_s \), and the jump rate \( \Gamma_v \),

\[
D_b = n_v d_s^2 \Gamma_v,
\]

we find, with \( d_s = 0.36 \text{ nm}, v_0 = 10^{13} \text{ s}^{-1}, \) and \( \Delta S_{\text{mig},v}/k_B = 0, n_v = 10^{-8} \). This is consistent with cation vacancies being the minority defects in acceptor-doped AO₂ systems.

In Fig. 5, we compare our bulk cation diffusion coefficients with selected experimental data reported in the literature. If one considers the datasets B, C, and D together and extrapolates the data to the lower temperatures of our experiments, one finds that our bulk cation diffusivities are significantly higher than the ones found in similar fluorite-structured systems and the activation enthalpy is significantly lower. Beschnitt and De Souza reported that \( \Delta H_b = (5.5 \pm 0.4) \text{ eV} \) for Zr diffusion in Gd-doped (0.5%) CeO₂ (cubic); Tesch et al. reported that \( \Delta H_b = (8.0 \pm 0.3) \text{ eV} \) for Hf diffusion in Er₂O₃-stabilized (10%) HfO₂ (cubic); and Swaroop et al. reported that \( \Delta H_b = (5.3 \pm 0.9) \text{ eV} \) for Hf diffusion in 3 mol. % Y₂O₃-stabilized ZrO₂ (tetragonal). We attribute the difference to our samples having a higher site fraction of cation vacancies and a lower activation barrier of migration (being monoclinic rather than cubic or tetragonal).

B. Grain-boundary diffusion

Fast grain-boundary diffusion of cations has also been previously observed in cubic AO₂-type oxides. Ref. 20, the ratio of the activation enthalpies was also found to be \( r = \Delta H_{\text{gb}}/\Delta H_b \approx 1, r = 0.5 \). This would suggest that the traditional picture of fast grain-boundary diffusion taking place along the grain-boundary core does not hold here (as it requires \( r \approx 0.5 \)). The alternative possibility is fast diffusion along space-charge layers. In addition, the presence of such layers at grain boundaries is well established for various acceptor-doped AO₂-type oxides in which positive grain-boundaries are compensated by negative space-charge layers in which (positive) oxygen vacancies are depleted and (negative) acceptor dopants are accumulated. The important point in this case is that cation vacancies, as negatively charged defects, are also accumulated in the space-charge layers. It is this accumulation that gives rise to the enhanced rates of cation diffusion. In the following, we show that this picture is consistent with the experimental data and we extract the space-charge potential. The comparison is made on the basis of the grain-boundary diffusion product, \( D_{\text{gb}}d_{\phi} \), for three reasons. First, it is the quantity that is usually extracted from diffusion experiments in Harrison-type B kinetics. Second, it avoids the arbitrary specification of \( d_{\phi} \) used Sec. III A. Third, it is the quantity that comes out of the space-charge analysis.

Incidently, one can easily discount the alternative explanation that the observed behavior is simply due to more cation vacancies being present in the grain-boundary core. This ignores that space-charge layers are present at grain boundaries in acceptor-doped AO₂ systems. In addition, it requires the migration barrier for cation vacancies at the boundary to be the same as in the bulk: this is extremely unlikely. In addition, it requires the cation vacancies to be neutral (if they were charged, the question of space-charge zones raises its head).

Measurements of leakage currents and subsequent analysis in line with the discussion of Gritsenko et al. give a range for the concentration of acceptor concentrations \( c_{\text{acc}} \) in the HfO₂ thin films, which amounts to \( 10^{20} \text{ cm}^{-3} \). Using a range of \( \epsilon_r = 15–25 \).
for the relative dielectric permittivity of $m$-HfO$_2$, we found that a space-charge potential $\Phi_0 \approx 0.82$ V is consistent with the experimental data (see Fig. 6). The impact of the range in acceptor concentration and dielectric permittivity is rather small, and the space-charge potential is neither unreasonably high nor low.

V. CONCLUSION

Studying experimentally the diffusion of “immobile” minority species, widely considered as very challenging, is achieved by utilizing a low-temperature preparation method, ALD, to prepare non-equilibrium samples in which the concentration of the minority defects is constant. The behavior of these defects was probed subsequently by performing cation diffusion experiments. The measured diffusion profiles display two features, are analyzed by solving the diffusion equation numerically, and yield bulk diffusion coefficients and grain-boundary diffusion coefficients.

The activation enthalpy of bulk diffusion is $\Delta H_b \approx (2.1 \pm 0.2)$ eV and significantly lower compared to other oxide systems of comparable structures. DFT calculations for the individual cation jumps in $m$-HfO$_2$ give mostly migration enthalpies of $3$ eV–$5$ eV, which agree with the values obtained for the other $AO_2$ systems. However, two jumps have significantly lower values ($\approx 2$ eV) and allow long-range diffusion through the bulk. We argue that the other jumps occur far less frequently and the DFT results, thus, agree with our experiments. The difference in the activation enthalpy of bulk diffusion between other $AO_2$ systems and $m$-HfO$_2$ is attributed to the structural perturbations in the monoclinic system, which are hypothesized to increase the ion mobility for immobile ions (such as cations in oxide-ion conducting $AO_2$ systems).

The observed grain-boundary diffusion activation enthalpy is the same as the activation enthalpy for bulk diffusion with $\Delta H_{gb} = (2.1 \pm 0.3)$ eV. This contradicts the traditional picture of fast grain-boundary diffusion along the grain-boundary core, and we, instead, suggest fast cation diffusion along space-charge layers. This theory is supported by the prediction of a reasonable space-charge potential for our investigated system.

FIG. 6. Comparison of $D_{gb}$ values obtained experimentally (red circles) and predicted from a space-charge potential of $\Phi_0 \approx 0.82$ V (gray area). The predicted range of $D_{gb}$ is obtained for $10^{15} \leq c_{gb} \leq 10^{25}$ and $15 \leq \epsilon_i \leq 25$.

SUPPLEMENTARY MATERIAL

See the supplementary material for the x-ray diffractograms of the HfO$_2$ films and SEM images of the annealed samples.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

1. K. Ando and Y. Oishi, J. Nucl. Sci. Technol. 20, 973 (1983).
2. C. Sari, J. Nucl. Mater. 78, 425 (1978).
3. B. Beschoten, T. Zacherle, and R. A. De Souza, J. Phys. Chem. C 119, 27307 (2015).
4. W. Busch, W. H. Schulte, E. Garfunkel, T. Gustafsson, W. Qi, R. Nieh, and J. Lee, Phys. Rev. B 62, R13290 (2000).
5. H. Inaba and H. Tagawa, Solid State Ionics 83, 1 (1996).
6. C. Rovin and G. Mairesse, Chem. Mater. 10, 2870 (1998).
7. J. A. Kilner, Solid State Ionics 129, 13 (2000).
8. A. Orera and P. R. Slater, Chem. Mater. 22, 675 (2010).
9. M. Vilo, C. Zambralli, P. Olivo, E. Pérez, M. K. Mahadevaiah, O. G. Ossorio, C. Wenger, and J. Delmín, J. Appl. Mater. 7, 081120 (2019).
10. F. Cúppers, S. Menzel, C. Bengel, A. Hardtdegen, M. von Witzleben, U. Böttger, R. Wasert, and S. Hoffmann-Eielf, J. Appl. Mater. 7, 091105 (2019).
11. G. H. Kim, H. Ju, M. K. Yang, D. K. Lee, J. W. Choi, J. H. Jang, S. G. Lee, I. S. Cha, B. K. Park, J. H. Han, T.-M. Chung, K. M. Kim, C. S. Hwang, and Y. K. Lee, Small 13, 1701781 (2017).
12. S. Clima, Y. Y. Chen, C. Y. Chen, L. Goux, B. Govoreanaeu, R. Degraeve, A. Fantini, M. Jurczak, and G. Pourtois, J. Appl. Phys. 119, 225107 (2016).
13. P. Calka, M. Sowinska, T. Bertaud, D. Walczyk, J. Dabrowski, P. Zaussmeil, C. Walczyk, A. Glokovskii, X. Cartoixà, J. Sufet, and T. Schroeder, ACS Appl. Mater. Interfaces 6, 5056 (2014).
14. M. Lanza, K. Zhang, M. Porti, M. Nafría, Z. Y. Shen, L. F. Liu, J. F. Kang, D. Gilmer, and G. Bersuker, Appl. Phys. Lett. 100, 123508 (2012).
15. B. Govoreanaeu, G. S. Kar, Y. Y. Chen, V. Paraschiz, S. Kubicek, A. Fantini, I. P. Radu, L. Goux, S. Clima, R. Degraeve, N. Jossart, O. Richard, T. Vandeweyer, K. Seo, P. Hendrickx, G. Pourtois, H. Bender, L. Altimime, D. J. Wouters, J. A. Kitti, and M. Jurczak, in IEEE International Electron Devices Meeting (IEDM), 2011 (IEEE, Piscataway, NJ, 2011), pp. 31.6.1–31.6.4.
16. S. Abolhassani, G. Bart, and A. Jakob, J. Nucl. Mater. 399, 1 (2010).
17. B. Mihalka, M. Stan, J. Ramírez, A. Zubelewicz, and P. Cristea, J. Nucl. Mater. 394, 182 (2009).
18. H. Matzke, J. Chem. Soc., Faraday Trans. 2, 83, 1121 (1987).
19. S. Beschoten and R. A. De Souza, Solid State Ionics 305, 23 (2017).
20. T. Zacherle, A. Schriver, R. A. De Souza, and M. Martin, Phys. Rev. B 87, 134104 (2013).
21. G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. 89, 5243 (2001).
22. J. Robertson, Appl. Surf. Sci. 190, 2 (2002).
23. J. Robertson, O. Sharia, and A. A. Demkov, Appl. Phys. Lett. 91, 132912 (2007).
25 W. Li, J. Zhou, S. Cai, Z. Yu, J. Zhang, N. Fang, T. Li, Y. Wu, T. Chen, X. Xie, H. Ma, K. Yan, N. Dai, X. Wu, H. Zhao, Z. Wang, D. He, L. Pan, Y. Shi, P. Wang, W. Chen, K. Nagashio, X. Duan, and X. Wang, Nat. Electron. 2, 563 (2019).
26 A. Hardtdegen, H. Zhang, and S. Hoffmann-Effert, ECS Trans. 75, 177 (2016).
27 M. de Ridder, A. G. J. Vervoort, R. G. van Welzenis, and H. H. Brongrersma, Solid State Ionics 156, 255 (2003).
28 M. P. Mueller and R. A. De Souza, Appl. Phys. Lett. 112, 051908 (2018).
29 L. G. Goncharova, M. Dalponte, D. G. Starodub, T. Gustafsson, E. Gafunkel, P. S. Lysaght, B. Foran, J. Barnett, and G. Bersuker, Appl. Phys. Lett. 89, 044108 (2006).
30 P. S. Waldow, H. Wardenga, S. Beschnitt, A. Klein, and R. A. De Souza, J. Phys. Chem. C 123, 6340 (2019).
31 Z. Shen, S. J. Skinner, and J. A. Kilner, Phys. Chem. Chem. Phys. 21, 13194 (2019).
32 D. J. Druce, T. Ishihara, and J. A. Kilner, Solid State Ionics 262, 893 (2014).
33 D. J. Druce, H. Téllez, T. Ishihara, and J. A. Kilner, Faraday Discuss. 182, 271 (2015).
34 H. Yokokawa, N. Sakai, T. Kawada, and M. Dokiya, in Science and Technology of Zirconia V, edited by S. P. S. Badwal and M. J. Bannister (Technomnic Publishing Co., Lancaster, Pa., 1993), pp. 59–68.
35 R. A. De Souza, J. Zehnpfennig, M. Martin, and J. Maier, Solid State Ionics 176, 1465 (2005).
36 R. A. De Souza and M. Martin, MRS Bull. 34, 907 (2009).
37 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 78, 1396 (1997).
38 P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
39 M. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
40 G. Henkelman, B. P. Uberuaga, and H. Jónsson, J. Chem. Phys. 113, 9901 (2000).
41 G. Henkelman and H. Jónsson, J. Chem. Phys. 113, 9978 (2000).
42 H. Jönsson, G. Mills, and K. W. Jacobsen, in Classical and Quantum Dynamics in Condensed Phased Simulations, edited by B. J. Berne, D. F. Coker, and G. Cicotti (World Scientific Publishing Co., 1998), pp. 385–404.
43 G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
44 G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
45 H. Mehrer, Diffusion in Solids: Fundamentals, Methods, Materials, Diffusion-Controlled Processes, Springer Series in Solid-State Sciences Vol. 155 (Springer-Verlag GmbH, Berlin, Heidelberg, 2007).
46 K. Aar, Y. Mishin, and W. Gust, Fundamentals of Grain and Interphase Boundary Diffusion, 3rd ed. (Wiley, Chichester, 1995).
47 M. Kilo, C. Argirusis, G. Borchardt, and R. A. Jackson, Phys. Chem. Chem. Phys. 5, 2219 (2003).
48 R. A. Jackson, A. D. Murray, J. H. Harding, and C. R. A. Catlow, Philos. Mag. A 33, 27 (1986).
49 B. Dorado, D. A. Andersson, C. R. Stanek, M. Bertolus, B. P. Uberuaga, G. Martin, M. Freyss, and P. Garcia, Phys. Rev. B 86, 035110 (2012).
50 A. Stukowski, Modell. Simul. Mater. Sci. Eng. 18, 025016 (2010).
51 J. Wang and U. Becker, J. Nucl. Mater. 433, 424 (2013).
52 M. Kilo, R. A. Jackson, and G. Borchardt, Philos. Mag. 83, 3309 (2003).
53 V. Metlenko, A. H. H. Ramadan, F. Gunkel, H. Du, H. Schraknepper, S. Hoffmann-Effert, R. Dittmann, R. Waser, and R. A. De Souza, Nanoscale 6, 12864 (2014).
54 N. Bonanos, unpublished work cited by, M. Mogensen, D. Lybye, P. V. Hendriksen, and F. W. Poulsen, Solid State Ionics 174, 279 (2004).
55 U. Brossmann, G. Knomer, H.-E. Schaefer, and R. Würschum, Rev. Adv. Mater. Sci. 6, 7 (2004).
56 U. Brossmann, R. Würschum, U. Södervall, and H.-E. Schaefer, J. Appl. Phys. 85, 7646 (1999).
57 M. Schie, M. P. Miller, M. Salinga, R. Waser, and R. A. De Souza, J. Chem. Phys. 146, 094508 (2017).
58 P.-L. Chen and I.-W. Chen, J. Am. Ceram. Soc. 77, 2289 (1994).
59 H. Matzke, J. Phys. Colloq. 34, C9 (1973).
60 R. J. Tesch, C. D. Wirkus, and M. F. Berard, J. Am. Ceram. Soc. 65, 511 (1982).
61 S. Swareoop, M. Kilo, C. Argirusis, G. Borchardt, and A. H. Chokshi, Acta Mater. 53, 4975 (2005).
62 C. Herzig and Y. Mishin, in Diffusion in Condensed Matter, edited by P. Hettijans and J. Karger (Springer-Verlag Berlin Heidelberg, Berlin, Heidelberg, 2005), pp. 337–366.
63 D. L. Beke and G. Erdelyi, in Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, Group III Condensed Matter Vol. 33A, edited by O. Made郎ung and H. Landolt (Springer, Berlin, 1998), pp. 1–26.
64 R. W. Balluffi, Phys. Status Solidi B 42, 11 (1970).
65 X. Tong, D. S. Mebane, and R. A. De Souza, J. Am. Ceram. Soc. 103, 5 (2020).
66 D. van Laethem, J. Deconinck, and A. Hubin, J. Eur. Ceram. Soc. 39, 432 (2019).
67 H. J. Avila-Paredes, K. Choi, C.-T. Chen, and S. Kim, J. Mater. Chem. 19, 4837 (2009).
68 R. A. De Souza, M. J. Pietrowski, U. Anselmi-Tamburini, S. Kim, Z. A. Munir, and M. Martin, Phys. Chem. Chem. Phys. 10, 2067 (2008).
69 X. Guo, W. Sigle, J. Fleig, and J. Maier, Solid State Ionics 154-155, 555 (2002).
70 X. Guo and R. Waser, Prog. Mater. Sci. 51, 151 (2006).
71 J. P. Parras and R. A. De Souza, Acta Mater. 195, 383 (2020).
72 V. A. Gritsenko, D. R. Islamov, T. V. Perevalov, V. S. Aliev, A. P. Yelisseyev, E. E. Lomonova, V. A. Pustovarov, and A. Chin, J. Phys. Chem. C 120, 19980 (2016).
73 J. Robertson, Eur. Phys. J. Appl. Phys. 28, 265 (2004).
74 X. Zhao and D. Vanderbilt, Phys. Rev. B 85, 233106 (2002).
75 Y. Wang, F. Zahid, J. Wang, and H. Guo, Phys. Rev. B 85, 224110 (2012).
76 R. A. De Souza, Phys. Chem. Chem. Phys. 11, 9939 (2009).