Optimal stoichiometry for nucleation and growth of conductive filaments in HfO$_x$

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Abstract

We present a first principles based investigation into the nucleation and growth of metal-rich precipitates in substoichiometric hafnium dioxide with relevance to applications in resistive switching memories. We identify an optimal HfO$_x$ stoichiometry, with $x$ in the range 1.50–1.75, for efficient nucleation and growth of stable Hf-rich clusters which may serve as precursors for the growth of conductive filaments during forming. We also show that filaments with sub-nm diameter possess remarkably metallic character. These results provide invaluable atomistic insight into forming in resistive switching films and demonstrate that precise regulation of stoichiometry is essential in order to ensure uniformity in the nucleation and subsequent growth of a conductive filament during the forming process.

Keywords: metal oxides, density functional theory, resistive switching

1. Introduction

Resistive switching memories based upon hafnium dioxide (HfO$_2$) are receiving increasing interest due to their compatibility with current transistor technology and their demonstrated exceptional performance [1–12]. For HfO$_2$, and similar oxides like NiO, TaO and CoO, there is increasing evidence that resistive switching can be understood in terms of the so-called filament model [2, 8, 11–17]. Briefly, the idea is that application of a forming voltage across a thin insulating metal oxide film leads to the growth of a conducting filament between the electrodes which lowers the resistance of the junction. The actual atomistic mechanism of the
forming process still remains a subject of considerable speculation and debate [8, 12, 14–17], however, it is likely to involve diffusion of oxygen ions away from the growing filament, assisted by the electric field, electron trapping and Joule heating. Once the film has been formed, oxidation and reduction of parts of the conductive filament by application of voltage pulses is responsible for the resistive switching effect [8]. While reversible resistance switching devices have been demonstrated [2, 4, 12, 18], there remain many open questions concerning the nature of the conductive filament, the mechanisms of forming and switching, and the material parameters which influence device performance. Understanding these issues is essential in order to overcome the challenges associated with implementation and future scaling of this technology [2, 4].

For HfO2 based resistive switching films some degree of oxygen deficiency in the as grown oxide appears to be important for producing devices with good switching characteristics [3, 5]. This can be achieved either by deliberately growing a substoichiometric oxide film or by inserting an oxygen scavenging metal layer such as Ti or Hf [9]. There is evidence that in polycrystalline HfO2 films oxygen deficiency is enhanced near extended defects, such as grain boundaries, which subsequently serve as precursors for filament growth [11, 12, 19, 20]. This observation is also supported by theoretical predictions which show that oxygen vacancies can be up to 0.8 eV more stable at m-HfO2 grain boundaries relative to the bulk crystal [21]. However, the composition and structure of the conductive filament that is formed (i.e. pure metal, oxidized metal or highly defective oxide) remains unclear. It is also not known how variations in stoichiometry of the as grown film could affect the formation and growth of metal-rich filaments. These questions present serious obstacles to gaining better control over the forming process and thereby ensuring better uniformity in the properties of formed resistive switching devices.

In this article, we employ first principles methods to provide atomistic insight into these issues. First, we show that crystalline HfOx is thermodynamically unstable to phase separation into a slightly oxidized Hf metal phase (HfO0.2) and a fully stoichiometric oxide phase (HfO2). We then develop a simple homogeneous nucleation model to investigate how the initial oxide stoichiometry affects the precipitation and growth of metal-rich phases within the substoichiometric hafnium dioxide host. On this basis, we identify an optimal level of oxygen deficiency for rapid nucleation of a stable metal rich cluster (x = 1.50–1.75). We also show that subsequent growth of the cluster by oxygen diffusion from its surface is thermodynamically favourable demonstrating that it could serve as a precursor for filament growth during forming. Finally, we characterize the electronic properties of a metal-rich filament and show it possesses substantial metallic character even for sub-nm diameter. These theoretical models can be extremely useful for providing guidance into which materials parameters control the forming process.

The rest of this paper is organized in the following way. In section 2 we describe the first principles based methodology we employ to model the nucleation and growth of precipitates in HfOx before presenting our results in section 3. In sections 4 and 5 the results are discussed and summarized with particular attention to their relevance to improving the performance of resistive switching memories.

2. Methodology

2.1. Density functional theory calculations

The structure and stability of substoichiometric oxide phases and the parameters entering the homogeneous nucleation model are calculated using density functional theory (DFT) and the
projector augmented wave (PAW) method as implemented in the Vienna Ab-initio simulation package [22, 23]. For the calculations presented in this article the 5p, 6s and 5d electrons of Hf, and the 2s and 2p electrons of O are treated as valence electrons and expanded in a plane wave basis with energies up to 300 eV (400 eV for cell optimization). Exchange and correlation are described using the Perdew–Burke–Ernzerhof (PBE) functional. For the conventional cell of monoclinic HfO$_2$ ($m$-HfO$_2$), which is most stable phase in ambient conditions, an $8 \times 8 \times 8$ Monkhorst–Pack $k$-point grid is used and structural optimization is performed until forces are less than 0.01 eV Å$^{-1}$. Similar $k$-point densities are used for all other phases considered. These approximations have been employed in previous studies of HfO$_2$ and predict lattice parameters within 1% of experimental values ($a = 5.14$ Å, $b = 5.19$ Å, $c = 5.25$ Å and $\beta = 99.7^\circ$) [24].

2.2. Nucleation model

The nucleation and growth of precipitates in oxides is a highly non-equilibrium process, however, one can often learn a lot about the material parameters which control such effects purely from thermodynamic considerations. In particular, if one can determine the free energy barrier to the formation of stable precipitates one can determine how likely they are to form. Directly modelling this process at an atomistic level, for example using molecular dynamics, would be an extremely challenging problem as one would need to consider systems containing many thousands of atoms for very long timescales in order to observe the relatively infrequent atomic rearrangements that result from thermal vibrations. Furthermore, one would need to repeat such simulations many times over in order to investigate how a given material parameter, e.g. the stoichiometry, affects the rate of nucleation and growth. An alternative approach is not to consider the atomic scale dynamics of the nucleation process explicitly, but instead to consider a more coarse grained model of the thermodynamics driving it. This is the essence of nucleation theory which has proved a very powerful approach for modelling processes as diverse as biomineralization [25], precipitation in solid solutions [26] and the formation of droplets in water vapour [27].

As we will show below, HfO$_x$ (for $x$ in the range 0.2 to 2.0) is thermodynamically unstable to phase separation into a slightly oxidized metallic Hf phase and fully stoichiometric $m$-HfO$_2$. The thermodynamic driving force for this is that the free energy of the metallic phase is lower than that of the partially oxidized phase. However, nucleation of a finite sized precipitate within the partially oxidized host phase also introduces surface atoms which are less well bound, reducing the relative stability of the precipitate. In addition a finite precipitate of a second phase will introduce strain which further reduces stability. The usual approach in simple nucleation models is to try to separate these contributions so that they can be evaluated separately and this is the approach we take here.

We consider the precipitation of a spherical HfO$_x$ cluster containing $N$ formula units within a substoichiometric HfO$_x$ host (shown schematically in figure 1). The change in free energy associated with formation of the cluster relative to that of the homogeneous oxide phase can be decomposed into three terms,

$$\Delta G(N) = \Delta G_b + \Delta G_i + \Delta G_s,$$

where $\Delta G_b$ is the change in free energy associated with taking $N$ formula units of HfO$_x$ from the bulk HfO$_x$ phase and putting them in the bulk HfO$_x$ phase, $\Delta G_i$ is the change in free energy associated with formation of the interface between HfO$_x$ and HfO$_x$, and $\Delta G_s$ is the change in free energy associated with strain induced both within the cluster and in the surrounding oxide phase.
Figure 1. The stability of a spherical metallic precipitate embedded in HfO$_x$ relative to a homogeneous HfO$_x$ phase depends on its radius, $r_{\text{Hf}}$. Further growth of the precipitate by outward diffusion of oxygen becomes thermodynamically favourable only beyond a critical radius, $r^*$. 

The first term in equation (1) can be written in terms of the Hf and O chemical potentials of the respective bulk phases,

$$\Delta G_b = -N [\Delta \mu_{\text{Hf}} + y \Delta \mu_{\text{O}}] = -N \Delta \mu_{\text{HfO}_y}$$

where,

$$\Delta \mu_{\text{Hf(O)}} = \mu^{(\text{HfO}_x)}_{\text{Hf(O)}} - \mu^{(\text{HfO}_y)}_{\text{Hf(O)}}$$

$\mu^{(\text{HfO}_x)}_{\text{Hf(O)}}$ is the chemical potential of Hf (O) in the bulk HfO$_x$ phase and $\mu^{(\text{HfO}_y)}_{\text{Hf(O)}}$ is the chemical potential of Hf (O) in the bulk HfO$_y$ phase.

A simple model for the second interfacial term in equation (1) is,

$$\Delta G_i = 4\pi r^2 \gamma,$$

where $\gamma$ is the HfO$_y$/HfO$_x$ interface formation energy and $r$ is the radius of the metallic cluster. Here, for simplicity we consider a perfectly spherical precipitate and a single parameter $\gamma$ representing the average interface formation energy. More realistic treatments could consider the angular dependence of $\gamma$ and nucleation of non-spherical precipitates. A simple expression for the elastic strain contribution to the free energy (third term in equation (1)) can be obtained using linear elasticity theory in terms of the elastic constants of HfO$_y$ and HfO$_x$. Here we use the model described by Lee et al (see equation (12) in [28]).

3. Results

3.1. Thermodynamic stability of HfO$_x$

To assess the thermodynamic stability of substoichiometric hafnia we calculate the free energy of formation of HfO$_x$ for varying levels of oxygen deficiency ($x = 0$–$2$). For each stoichiometry oxygen ions (or equivalently, oxygen vacancies) are distributed homogeneously and we consider monoclinic, tetragonal and cubic HfO$_2$, as well as oxygen intercalated Hf as...
The most stable phase is found to be hcp-HfO$_0$ indicating that it is thermodynamically favourable for HfO$_x$ ($x = 0.2–2.00$) to phase separate into a mixture of pure $m$-HfO$_2$ and hcp-HfO$_{0.2}$.

Candidate crystal structures. In the latter case we find that the octahedral interstitial oxygen site is favoured over the tetrahedral one in agreement with previous studies [29]. The formation energies are calculated with respect to the pure hcp-Hf phase and the pure monoclinic HfO$_2$ phase in the following way,

$$
\Delta G_f(HfO_x) = \mu(HfO_x) - \frac{x}{2} \mu(hcp-Hf) - \frac{x}{2} \mu(m-HfO_2),
$$

where $\mu(HfO_x)$ is the free energy per formula unit of HfO$_x$, $\mu(hcp-Hf)$ is the free energy per formula unit of hcp-Hf and $\mu(m-HfO_2)$ is the free energy per formula unit of $m$-HfO$_x$. In this work we neglect the configurational and vibrational entropic contributions and approximate free energies by total energies obtained by DFT corresponding to zero temperature. The results are summarized in figure 2. We find that the monoclinic structure is the most stable for $x = 1.25–2.00$ and oxygen intercalated hcp-Hf is the most stable for $x < 0.75$. The tetragonal structure is found to be most stable only in a narrow range close to $x = 1$. Importantly hcp-Hf with approximately one fifth of octahedral sites occupied by oxygen (i.e. hcp-HfO$_{0.2}$) is the most stable phase across the entire range. This means that for $x = 0.2–2.00$ it is thermodynamically favourable for HfO$_x$ to phase separate into a mixture of pure $m$-HfO$_2$ and hcp-HfO$_{0.2}$.

### 3.2. Effect of stoichiometry on precipitate nucleation

To determine the change in free energy associated with nucleation of metal-rich clusters in HfO$_x$ we first compute the parameters entering the equations outlined in section 2.2. For each stoichiometry, $x$, we calculate the oxygen chemical potential by calculating the change in energy on adding or removing oxygen atoms. We take an average over several sites in order to define $\mu_O$ and use the relation,

$$
\mu_{Hf}^{(HfO_x)} + \mu_{O}^{(HfO_x)} = \mu(HfO_x)
$$

(6)

to determine $\mu_{Hf}$. In this way we calculate $\Delta \mu_{HfO_x}$ (equations (2) and (3)) for each stoichiometry (summarized in table 1).

To estimate the interface formation energy, $\gamma$, we constructed a model interface between a Hf(0 0 0 1) surface and a (1 × 2) oxygen terminated HfO$_2$(0 0 1) surface similar to that recently
Table 1. Calculated HfO$_x$ formation energy ($\Delta G_f$) and the change in chemical potential ($\Delta \mu_{\text{HfO}_y}$). The most stable crystal structure is indicated in brackets. The calculated critical radius, $r^*$, activation barrier, $\Delta G^*$, and diffusion radius, $r_d$, is also given for each composition.

| $x$  | $\Delta G_f$ (meV) | $\Delta \mu_{\text{HfO}_y}$ (eV) | $r^*$ (Å) | $\Delta G^*$ (eV) | $r_d$ (Å) |
|------|-------------------|-------------------------------|----------|------------------|---------|
| 2.000 | 0 (m)           | —                             | —        | —                | —       |
| 1.991 | 9 (m)           | 1.79                          | 3.2      | 4.5              | 22.1    |
| 1.750 | 249 (m)         | 1.53                          | 3.9      | 6.5              | 9.0     |
| 1.500 | 396 (m)         | 1.37                          | 4.4      | 8.3              | 8.0     |
| 1.250 | 687 (m)         | 1.22                          | 5.2      | 11.5             | 8.3     |
| 1.000 | 416 (t)         | 0.52                          | 14.3     | 85.5             | 19.8    |
| 0.750 | 400 (t)         | 0.26                          | 43.0     | 775.0            | 54.5    |

Figure 3. The structure of the Hf(0 0 0 1)/HfO$_2$(0 0 1) interface. Grey spheres represent Hf ions and red spheres represent O ions. The periodic supercell is indicated by the outline.

reported for the TiN/m-HfO$_2$ interface [30]. We consider pure metallic Hf rather than HfO$_{0.2}$ as it allows us to neglect the effect or different spatial arrangements of interstitial O atoms. Although this is a simplified model we believe it should provide an approximate estimate of the interface energy. The model (figure 3) consists of 4 monolayers of m-HfO$_2$ (96 atoms) and 8 monolayers of hcp-Hf (48 atoms) adjoined to form a periodically repeating bi-layer in the direction perpendicular to the interface (supercell dimensions 10.29 × 5.19 × 41.37 Å$^3$). The Hf layers were strained in the directions parallel to the interface to match the lattice parameters of HfO$_2$. The interface formation energy was calculated with respect to bulk hcp-Hf and bulk m-HfO$_2$. The presence of sub-oxide layer near the interface and ionic distortions is responsible for a relatively large interface formation energy, $\gamma = 1.6$ J m$^{-2}$.

We also computed the elastic bulk moduli using DFT in order to model the long range elastic strain contribution to the change in free energy (equation (1)). We note that short range strain effects localized near the interface are already included in the definition of the interface formation energy above. Again we approximate the elastic properties of HfO$_{0.2}$ by those of Hf since the large cells required to calculate the elastic properties of HfO$_{0.2}$ would make the calculations computationally prohibitive. We obtained $B_{\text{Hf}} = 108$ GPa and $B_{\text{HfO}_2} = 237$ GPa.

As shown in figure 4 we use the parameters obtained above to calculate the change in free energy as a function of cluster radius using equation (1) for each stoichiometry. For $x \leq 1.00$, nucleation of a stable metallic cluster is found to be highly unfavourable, with critical radii $r^* > 14$ Å and barriers to nucleation $\Delta G^* > 85$ eV. However, for $x > 1.00$ we find that nucleation is much more favourable. Generally, as the hafnia oxygen deficiency increases the free energy barrier to nucleation and the critical radius also increase (see Table 1). On these grounds one would conclude that $x \sim 2$ would be optimal for forming. However, nucleation of a stable precipitate in a nearly stoichiometric oxide is likely to be kinetically limited as
there are few vacant lattice sites available to accommodate the oxygen that is expelled from the growing metal-rich cluster. One way to quantify this is to consider the smallest radius within which all oxygen expelled from cluster could be accommodated, \( r_d \) (see table 1). An optimal material for forming would be characterized by small \( r_d \) and small \( \Delta G^\ast \). On this basis, \( x = 1.50-1.75 \) appears to be optimal, for which the activation barrier is of the order 6–8 eV and the critical radius is about 4 Å.

3.3. Electronic properties of a metal-rich filament

The results above suggests that above a critical radius a cluster of HfO_{0.2} embedded in HfO_3 is stable against dissolution and that subsequent growth by outward diffusion of oxygen ions from its perimeter is endothermic. In order to test this prediction we modelled the properties of a HfO_{0.2} filament of \( \sim 3 \) Å radius embedded within a m-HfO_2 host using DFT. The initial structure was obtained by cutting an approximately cylindrical Hf wire from bulk hcp-Hf and inserting it into a 324 atom m-HfO_2 supercell. Any atoms overlapping atoms were removed and we performed simulated annealing to find a low energy configuration. We consider a Hf wire within HfO_2 rather than a Hf cluster as it allows us to use a much smaller supercell making the calculation computational feasible. The simulated annealing consisted of 15 ps equilibration at 1800 K, followed by a gradual reduction in temperature to 100 K over 9 ps, finally the structure was fully optimized using a conjugate gradients algorithm. Figure 5(a) shows the optimized structure. Bader analysis shows that Hf inside the filament varies from a fully metallic state in the centre of the filament to fully oxidized outside [31]. To assess the stability of the filament against further growth formation energies for oxygen vacancy defects at various position in the supercell were also calculated. Typically oxygen vacancies near the surface of the filament are found to be easier to form than in the bulk oxide by about 0.9 eV suggesting filament growth by outward diffusion of oxygen ions is thermodynamically favourable. Calculating the relevant kinetic barrier to filament growth during forming is more challenging as one should include the effects of electron trapping and local electric fields. However, a simple linear interpolation procedure suggests that transferring an oxygen ion from near the filament into an interstitial site in the oxide requires overcoming an energy barrier of about 2 eV. Since we model a extended wire rather than a finite cluster for reasons of computationally efficiency we consider diffusion of oxygen laterally away from the surface. However, we stress that oxygen could diffuse in
Figure 5. Top: hafnium-rich filament inside HfO$_2$. Large grey spheres indicate metallic Hf atoms. Bottom: electronic density of states showing separated contributions from oxygen, Hf filament and bulk Hf atoms.

The above results show that filaments with sub-nm diameter are stable against dissolution and in fact are thermodynamically driven to grow by outward diffusion of oxygen ions. Such filaments are thought to be responsible for the low resistance state in resistive switching devices by providing an electrical connection between the electrodes, therefore, it is interesting to examine their electronic properties. Figure 5(b) shows the calculated electronic density of states (DOS) for the filament in the HfO$_2$ supercell, with contributions from bulk Hf ions, filament Hf atoms and O ions shown separately. The DOS shown here is calculated using the semi-local PBE exchange-correlation functional. We also calculated the DOS using the non-local HSE functional as it gives a much better description of the band gap for wide gap oxides like HfO$_2$ [32, 33]. However, in this case we found that it gave a much poorer description of metallic Hf than PBE. Nevertheless, in both cases the conduction band offset between the Hf filament and HfO$_2$ is about 1 eV. It is noteworthy that the local electronic structure of the filament is very similar to that of bulk hcp-Hf despite its very small radius and distorted structure.
4. Discussion

Although we have demonstrated that nucleation and growth of metal-rich precipitates in substoichiometric hafnium dioxide is thermodynamically favourable it should be stressed that this is not sufficient to describe the non-equilibrium forming process. Indeed to do that one would need to consider the interplay of complex effects such as inhomogeneous local electric fields, electron trapping and local heating (e.g. see [12]). However, the thermodynamic approach we have employed can still provide important insights into the underlying energetics of the process.

We find that partially oxidized \( hcp-Hf \) (close to \( HfO_{0.2} \)) is the most stable phase across the entire oxygen content range. This result is consistent the experimental observation that Hf is able to dissolve high concentrations of oxygen without transformation or phase separation. It is also consistent with theoretical predictions which have recently been made for the very similar material \( ZrO_2 \) (see [34] and references within). Of course, one can question whether the approximate exchange-correlation functional employed in these DFT calculations is able to capture the correct phase stability. Importantly for the present paper, we find the electronic properties and Hf chemical potential of \( hcp-HfO_{0.2} \) differs little from pure \( hcp-Hf \) so we do not expect the precise nature of the ground state to significantly affect the main conclusions. The key point is that there is a thermodynamic driving force for precipitation of metal-rich Hf clusters within substoichiometric hafnium dioxide.

The simple homogeneous nucleation model we present allows us to investigate how the activation energy for nucleation depends on hafnia stoichiometry. The model predicts that there is an optimal \( HfO_{x} \) stoichiometry (in the range \( x = 1.50-1.75 \)) for thermally induced precipitation of metal-rich clusters which could subsequently serve as seeds for filament growth. The estimation of the optimal composition for phase separation is necessarily imprecise. It is a balance between minimizing the thermodynamic activation energy for nucleation (as characterized by \( \Delta G_f \)) and minimizing the parameter \( r_d \) which provides a crude descriptor of the kinetically limited oxygen transport needed to facilitate the precipitation. This nucleation model provides useful insight however should only be considered as a semi-quantitative picture owing to the approximations employed. In particular, the relatively small size of critical clusters means that the free energy decomposition employed in equation (1) may be overly simplistic. However, the subsequent DFT calculations for a finite filament embedded in \( HfO_2 \) support the predictions of the model by demonstrating both the stability Hf-rich precipitates and their tendency for growth by outward diffusion of oxygen ions.

An important prediction of the model is that the activation energy for nucleation depends on the stoichiometry. This may have important consequences for device variability since the probability of forming thermally induced precipitates will depend sensitively on the stoichiometry. Quantitatively estimating rates of nucleation is extremely challenging and often associated with large uncertainties. However, to get some feeling of how stoichiometry affects the rate of nucleation one could use the simple expression proposed by Turnbull et al which is appropriate for thermally induced precipitation [35]. Using the activation energies from table 1 we find that for \( x = 1.75 \) the average time to nucleate a single critical cluster at 2000K in an active device of dimensions \( 10 \times 10 \times 10 \text{ nm}^3 \) is about 0.3 s, whereas for \( x = 1.50 \) it is 1.6 h. This may be the difference between a device containing a metal-rich cluster which may act as a seed for further filament growth or not containing one, possibly leading to significant differences in the characteristics of the post-formed device.

There is some experimental evidence that understoichiometric \( HfO_2 \) films are needed for effective forming and resistive switching. One of the ways this is often achieved is through the introduction of an oxygen scavenging metal layer (e.g. Ti) between one of the electrodes
and the HfO$_2$ film [9]. However, it is difficult to precisely control or indeed measure the local stoichiometry in such films making direct comparison with the theoretical results difficult. It is hoped the predictions in this paper may provide invaluable guidance for the optimization of materials for devices.

In the current work we have investigated how stoichiometry affects precipitation of metal-rich clusters in bulk HfO$_{x}$. Considering precipitation in the bulk is a simplification that allows us to obtain a simple phenomenological model with parameters which can be estimated from first principles calculations. However, as mentioned in the introduction grain boundaries are important for resistive switching. In polycrystalline films the enhanced segregation of oxygen vacancies to grain boundaries which is predicted theoretically [21] would most likely lead to preferential precipitation at grain boundaries with smaller activation energies. To model this effect one could consider a heterogeneous nucleation model. However, since not all grain boundaries are equivalent the parameters entering such a model would bring an extra layer of complexity. This will be a future direction of research but is beyond the scope of the work reported here. Further work in this area should also consider the role of the electrode interface as a preferential nucleation site for precipitates.

Going beyond the simple nucleation theory level of modelling, one could employ long time scale molecular dynamics simulations as has been successful for mineral nucleation from solution [36]. However, this is more challenging for oxides owing to the limited availability (and significant computational expense) of reactive force fields capable of describing transition metals in intermediate oxidation states [37].

5. Conclusions

The nucleation and growth of a metal-rich filament in the forming of resistive switching devices is one key factors which govern their performance, reliability and variability. Here we show that the free energy barrier to nucleation of a primary precipitate depends sensitively on the hafnia stoichiometry, with the optimal oxygen deficiency of the order 10–25%. The results also show that stable precipitates containing as few as 15 Hf atoms can serve as precursors for filament growth by diffusion of oxygen ions away from its surface. The electronic properties of metallic filaments with diameters as small as 6 Å are found to be remarkably similar to bulk Hf and are characterized by a conduction band offset $\sim$1 eV with respect to hafnia.

Since the nucleation rate of metallic precipitates is (inverse) exponentially dependent on the free energy barrier to nucleation, small variations in stoichiometry between devices may cause significant variations in the structure and properties of the filament that is ultimately formed. For this reason, minimization of device-to-device variability requires precise control of hafnium dioxide stoichiometry. On the other hand, spatial variation of stoichiometry within films can play an important role in determining where the filament initially nucleates and grows. For example, extended defects such as grain boundaries have been shown to be sites of appreciable oxygen deficiency and there is evidence that they are correlated with the location of filaments in resistive switching devices [12, 21, 38–40]. There are already examples where one-dimensional spatial control of stoichiometry has been exploited, for example by growing hafnia adjacent to the anode in oxygen poor conditions [7, 9]. Regulation of stoichiometry in two- or three-dimensions may offer even better control over uniformity of post-formed devices. It would be straightforward to extend the homogeneous nucleation model described above to such inhomogeneous situations, however, the qualitative conclusions described here are expected to be unchanged.
In summary, we have presented a first principles based investigation into thermodynamic driving forces for filament nucleation and growth in HfO$_2$. An advantage of the nucleation model we present is that it does not depend on the precise mechanism of oxygen diffusion but can still make predictions on the key materials parameters governing the process. In particular, we predict an optimal HfO$_x$ stoichiometry, with $x$ in the range 1.50–1.75 for efficient forming. We also show that even sub-nm diameter filaments exhibit remarkably metallic electronic properties. Although this article has focused on hafnia, similar results are expected for other oxides such as NiO, TaO and CoO. We also note that similar phase separation effects have been observed for SiO$_x$ which is also being actively considered as a material for resistive switching memories [41–44]. These results provide invaluable atomistic insight into forming in resistive switching films. Specifically, they show that precise control of hafnium dioxide stoichiometry is essential in order to ensure uniformity in nucleation and subsequent growth of a metallic filament during the forming process. They also point to practical approaches for reducing device variability associated with forming in resistive switching devices.

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