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Mechanisms of nonstoichiometry in HfN_{1-x}

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Density functional theory is used to calculate defect structures that can accommodate nonstoichiometry in hafnium nitride: HfN_{1-x}, $0 \leq \times \leq 0.25$. It is predicted that a mechanism assuming simple distributions of nitrogen vacancies can accurately describe the variation in the experimentally observed lattice parameter with respect to the nitrogen nonstoichiometry. Although the lattice parameter changes are remarkably small across the whole nonstoichiometry range, the variations in the bulk modulus are much greater. © *2009 American Institute of Physics*.
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I. INTRODUCTION

The scaling of complementary metal-oxide-semiconductor technology has led to the conventional poly-Si/SiO_2 gate stack, which unfortunately experiences excessive gate leakage currents and the polydepletion effect.[1] There is consequently a need to replace existing materials with materials of superior performance.[2–12] The use of metal/high-k gate stacks such as TaN/HfN/HfO_2 has been proposed as a solution to these problems.[1] Nitrogen deficient hafnium nitride (HfN_{1-x}) is a material with good thermal and electrical conductivity and would therefore be potentially useful in many technological applications,[13] particularly as a gate metal as its work function can be tuned with respect to composition.[14]

In recent density functional theory (DFT) studies, the structure and defect chemistry of stoichiometric uranium nitrides (UN, U_2N_3, and UN_2) as well as nitrogen deficient titanium nitride (TiN_{1-x}) and zirconium nitride (ZrN_{1-x}) were predicted and compared to the available experimental data (see Refs. 15 and 16, and references therein). The aim of the present study is to identify, with the use of similar electronic structure calculations, the mechanism that accommodates N deficiency stoichiometry and the effect of this on the structure and properties of HfN_{1-x}.

II. THEORETICAL METHODOLOGY

Calculations were performed using the plane wave DFT code CASTEP.[17,18] The generalized gradient approximation corrected density functional of Perdew and Wang (PW91) (Ref. 19) was employed to describe exchange and correlation interactions in conjunction with ultrasoft pseudopotentials.[20] The plane wave basis set cutoff was 450 eV in conjunction with a Monkhorst–Pack grid with a k-point spacing of 0.04 $Å^{-1}$ (Ref. 21). The supercells contained up to 32 atomic sites. This approach has been established by comparing results for both nitrides and other materials, to experiments.[16,22–24]

The concentration of the nitrogen vacancies (V_N) was adjusted by removing a N atom from the cubic unit cell of HfN (i.e. Hf_4N_3) and supercells of the perfect cubic unit cell (a $2\times1\times1$ cell, H_8N_7, or a $2\times2\times1$ cell $Hf_{16}N_{15}$). Alternatively multiple V_N are removed from a single supercell, which provides additional defect configurations. Figure 1 illustrates a $2\times1\times1$ supercell and the multiple distinct configurations of two V_N defects. For every configuration i, the energy minimized lattice parameters (a_i, b_i, and c_i) and lattice energy E_i can be used to calculate a configurationally averaged lattice parameter:

$$a = \frac{\Sigma n_i[e^{-\Delta E_i/k_BT}(a_i \cdot b_i \cdot c_i)^{1/3}]}{\Sigma n_i \cdot e^{-\Delta E_i/k_BT}}, \quad (1)$$

where k_B is Boltzmann's constant, n_i is the degeneracy (i.e. number of symmetry identical ways to arrange the defects in the cell), and T is the temperature. Using Eq. (1) we can effectively average over a number of ordered distributions and predict the effect that a distribution of defects has in hafnium nitride.

The supercell sizes used in this calculation are necessarily small to make the simulations computationally tractable. The predicted energy required to remove a single nitrogen atom from the crystal to infinity for the largest and second largest supercell sizes ($2\times2\times1$ and $2\times1\times1$, respectively)

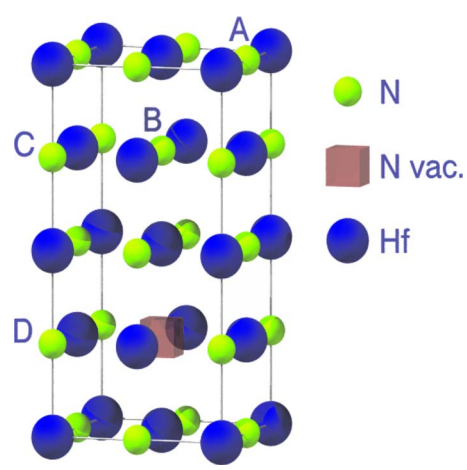

FIG. 1. (Color online) Possible divacancy configurations in a Hf_8N_8 supercell, where blue spheres represent Hf and green spheres N. A single vacancy (shown as a red cube) can be placed at any N site, the second vacancy may be centered at either site A, B, C, or D. Only these four second vacancy configurations give rise to symmetrically distinct divacancy configurations.

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differed by 1.6%. The interaction of the defects with periodic images of themselves is therefore not entirely negligible. However the use of configurationally averaged values over a sample of nearest and next nearest neighbor configurations (of which the periodic images may form part) is expected to accurately account for the effects of defect image interactions for a given stoichiometry.

III. RESULTS AND DISCUSSION

The DFT approach predicts the lattice parameter of stoichiometric HfN to be 4.644 Å compared to a reported lattice parameter for hafnium nitride (of unspecified stoichiometry) of 4.525 Å.[25,26] Similarly, the bulk modulus is predicted to be 280 GPa compared to an experimental value of 306 GPa.[27] Using a similar DFT approach, Zhao and Wu[28] predicted that the rock salt structure of HfN is the most thermodynamically stable. Consistently with the study of Zhao and Wu[28] we predict that HfN is metallic.

Nonstoichiometry can have a significant impact on the physical properties of materials and has been systematically studied in oxides but less so in nitrides.[16] Nonstoichiometry in HfN_{1-x} can be accommodated by three distinct mechanisms. The first involves V_N and in what follows, will be termed the vacancy mechanism,

$$N_N \rightarrow V_N + \frac{1}{2}N_2, \tag{2}$$

where N_2 represents a molecule of N liberated by the reaction. The second mechanism, the interstitial mechanism, involves the formation of Hf interstitial defects, Hf_i,

$$HfN \rightarrow Hf_i + \frac{1}{2}N_2. \tag{3}$$

The third mechanism involves the formation of antisite defects, which are common and important in semiconductors (for example in GaSb, Refs. 29 and 30, and references therein) and oxides (for example in $MgAl_2O_4$, Ref. 31 and references therein). So that, if Hf_N represents a Hf atom accommodated at a N lattice site,

$$HfN + N_N \rightarrow Hf_N + N_2. \tag{4}$$

Figure 2(a) presents the predicted lattice parameter of HfN_{1-x} as a function of composition for all three mechanisms. The vacancy mechanism in particular shows only a small change in lattice parameter as a function of nitrogen deficiency. It has previously been established experimentally that the rock salt structured nitrides ZrN and TiN can accommodate substantial nitrogen deficient nonstoichiometry with only limited effect on their lattice parameter (see for example Ref. 32 and references therein). DFT simulations of ZrN and TiN nonstoichiometry also showed only a small change in lattice parameter with the vacancy mediated mechanism.[16] Here there is only one established experimental lattice parameter for a nonstoichiometric composition, that is for $HfN_{0.74}$, which shows a reduction in lattice parameter of only 0.006 Å compared to stoichiometric HfN.[32] As with ZrN_{1-x} and TiN_{1-x} only the vacancy mechanism can reproduce this observation. This implies that nonstoichiometry in HfN_{1-x} is

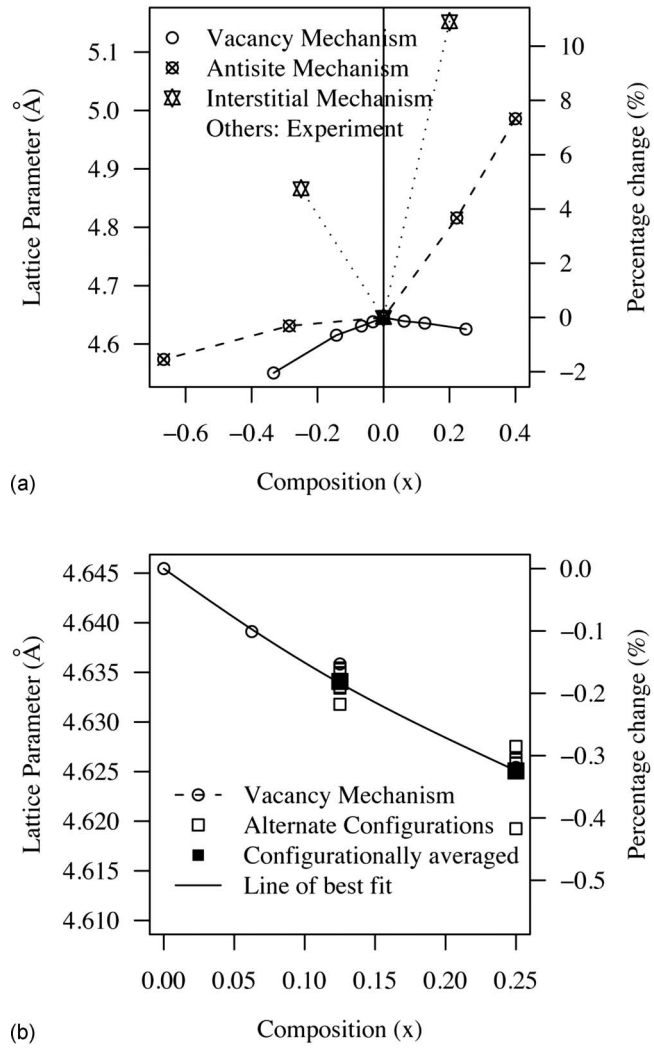

FIG. 2. (a) Lattice parameter dependence on the nonstoichiometry for the vacancy, interstitial, and antisite defect mechanisms in HfN_{1-x} and (b) lattice parameter dependence for the vacancy mechanism including alternate configurations.

accommodated by a vacancy mediated mechanism in a similar manner to other nonstoichiometric nitrides, that is TiN_{1-x} and ZrN_{1-x}.

Figure 2(b) shows in more detail the dependence of the lattice parameter as a function of composition in HfN_{1-x} assuming the vacancy mechanism and including alternate configurations. It is clear that at $x=0.125$ and $x=0.25$ there are a significant number of V_N configurations that can potentially accommodate the nonstoichiometry, each causing only a small reduction in lattice parameter. This is because Hf atoms that are nearest neighbor to a vacancy relax inwardly toward the vacant nitrogen site by only 0.037 Å while the second nearest neighbor N atoms relax away from the defect site by only 0.024 Å. This relaxation is remarkably small compared to, for example, equivalent processes in oxides with the same crystal structure (for example 0.2 Å relaxation of Mg^{2+} away from an oxygen vacancy in MgO, Ref. 33) or in diamond structure semiconductor materials (for example 0.46 Å relaxation of Ge atoms toward a Ge vacancy in germanium, Ref. 34). Furthermore, in the case of HfN, the lattice parameters generated for the various configurations are

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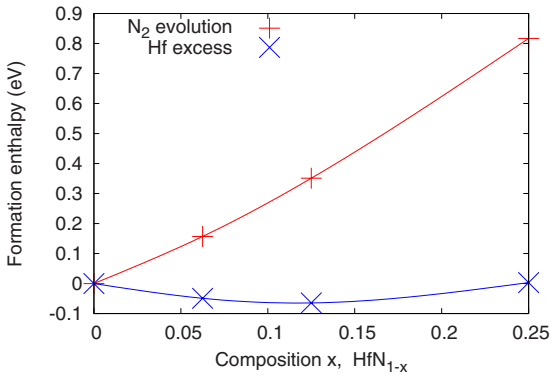

FIG. 3. (Color online) The formation enthalpy of nonstoichiometric HfN_{1-x} with respect to either the evolution of N_2 gas [Eq. (5)] or addition of excess Hf metal [Eq. (6)].

remarkably similar. The energy difference between various configurations can be up to 0.39 eV. Although for most configurations there is remarkably little variation in the predicted energies, within 0.02 eV for the most energetically favorable configurations. As a result, at ambient temperatures and above we do not predict significant clustering of nitrogen vacancies, nor at high concentrations of nitrogen vacancies do we expect significant ordering of the defects. The present study provides a first insight into the disorder processes of HfN_{1-x}.

Having identified the dominant mechanism by which nitrogen deficient stoichiometry is accommodated in HfN, we now examine the energetics of such processes. To achieve this we consider the formation enthalpy of nonstoichiometric HfN from one of two chemical reference processes: evolution of nitrogen gas or the addition of excess Hf metal. The equations for these processes are

$$\mathrm{HfN} \rightarrow \mathrm{HfN}_{1-x} + \frac{x}{2}\mathrm{N}_2, \tag{5}$$

for the nitrogen evolution, and

$$(1-x)\mathrm{HfN} + x\mathrm{Hf} \rightarrow \mathrm{HfN}_{1-x}, \tag{6}$$

for addition of excess Hf metal.

Figure 3 shows the predicted formation enthalpies for each of these processes. While there is no gain in enthalpy to form a nonstoichiometric composition from a stoichiometric material by the evolution of N_2 gas, there is a clear enthalpy gain for the reaction of stoichiometric HfN with excess Hf metal up to a composition of $HfN_{0.875}$.

Despite the small effect on lattice parameter, nonstoichiometry could still have a significant effect on the mechanical properties of hafnium nitride. Mechanical properties can be especially important when considering the stability of thin films, such as those required for the formation of metal/high-*k* gate stacks for microelectronic devices. Here we have considered the effect of nonstoichiometry on the bulk modulus of HfN_{1-x} (see Fig. 4). This figure shows that the predicted changes to the bulk modulus are significant. The results can be used to generate a relationship for the bulk modulus of nonstoichiometric HfN_{1-x} (i.e. $B_{\mathrm{HfN}_{1-x}}$),

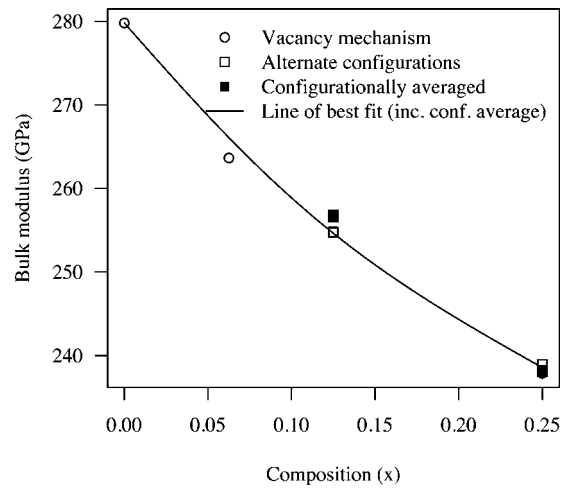

FIG. 4. Dependence of the bulk modulus on nonstoichiometry in HfN_{1-x}.

$$B_{\mathrm{HfN}_{1-x}} = B_{\mathrm{HfN}} + \alpha\Delta x + \beta(\Delta x)^2, \tag{7}$$

where B_{HfN} is the bulk modulus of HfN, Δx is the change in composition x; α and β are constants predicted to be -237.7 and 290.9, respectively. Using Eq. (7) the bulk modulus can be predicted for any composition within the range $0 \leq \times \leq 0.25$.

IV. CONCLUSIONS

In summary, HfN_{1-x} can accommodate an extensive range of nonstoichiometry that has a significant influence on properties such as the density and the bulk modulus but surprisingly little effect on lattice parameter. It is predicted that the only mechanism of nitrogen deficient nonstoichiometry in HfN_{1-x} that can explain lattice parameter variation involves the formation of V_N. Predicting the effect of nonstoichiometry on the lattice parameter and the density, which have an impact on the work function of the gate metal, can aid in the design of more efficient metal/high-*k* gate stacks for microelectronic devices.

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[1]N. Sa, J. F. Kang, H. Yang, X. Y. Liu, Y. D. He, R. Q. Han, C. Ren, H. Y. Yu, D. S. H. Chan, and D. L. Kwong, IEEE Electron Device Lett. **26**, 610 (2005).
[2]P. D. Kirsch, C. S. Kang, J. Lozano, J. C. Lee, and J. G. Ekerdt, J. Appl. Phys. **91**, 4353 (2002).
[3]M. Y. Liao, Y. Gotoh, H. Tsuji, and J. Ishikawa, Appl. Phys. Lett. **83**, 1626 (2003).
[4]A. Dimoulas, G. Mavrou, G. Vellianitis, E. Evangelou, N. Boukos, M. Houssa, and M. Caymax, Appl. Phys. Lett. **86**, 032908 (2005).
[5]M. Naganawa, Y. Shimizu, M. Uematsu, K. M. Itoh, K. Sawano, Y. Shiraki, and E. E. Haller, Appl. Phys. Lett. **93**, 191905 (2008).
[6]S. Brotzmann and H. Bracht, J. Appl. Phys. **103**, 033508 (2008).
[7]A. Chroneos, R. W. Grimes, H. Bracht, and B. P. Uberuaga, J. Appl. Phys. **104**, 113724 (2008).
[8]P. Tsouroutas, D. Tsoukalas, I. Zergioti, N. Cherkashin, and A. Claverie, J. Appl. Phys. **105**, 094910 (2009).
[9]A. Chroneos, H. Bracht, R. W. Grimes, and B. P. Uberuaga, Appl. Phys. Lett. **92**, 172103 (2008).
[10]M. S. Rahman, E. K. Evangelou, A. Dimoulas, G. Mavrou, and S. Galata,

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J. Appl. Phys. **103**, 064514 (2008).
[11]V. V. Afanas'ev, A. Stesmans, G. Mavrou, and A. Dimoulas, Appl. Phys. Lett. **93**, 102115 (2008).
[12]A. Chroneos, R. W. Grimes, and H. Bracht, J. Appl. Phys. **106**, 063707 (2009).
[13]B. O. Johansson, J. E. Sundgren, and V. Helmersson, J. Appl. Phys. **58**, 3112 (1985).
[14]J. A. Rothschild and M. Eizenberg, Appl. Phys. Lett. **94**, 081905 (2009).
[15]E. A. Kotomin, R. W. Grimes, Y. Mastrikov, and N. J. Ashley, J. Phys.: Condens. Matter **19**, 106208 (2007).
[16]N. J. Ashley, R. W. Grimes, and K. J. McClellan, J. Mater. Sci. **42**, 1884 (2007).
[17]M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).
[18]M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, and M. C. Payne, J. Phys.: Condens. Matter **14**, 2717 (2002).
[19]J. P. Perdew, Physica B **172**, 1 (1991).
[20]D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[21]H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[22]A. Chroneos, R. W. Grimes, B. P. Uberuaga, S. Brotzmann, and H. Bracht, Appl. Phys. Lett. **91**, 192106 (2007).
[23]A. Chroneos, H. Bracht, C. Jiang, B. P. Uberuaga, and R. W. Grimes, Phys. Rev. B **78**, 195201 (2008).
[24]A. Chroneos, N. J. Ashley, K. H. Desai, J. F. Maguire, and R. W. Grimes, J. Mater. Sci. **42**, 2024 (2007).
[25]A. N. Christensen, Acta Chem. Scand. **44**, 851 (1990).
[26]S. Yamanaka, K. Hotehama, and H. Kawaji, Nature (London) **392**, 580 (1998).
[27]X. Chen, V. V. Struzhkin, Z. Wu, M. Somayazulu, J. Qian, S. Kung, A. N. Christensen, Y. Zhao, R. E. Cohen, H. K. Mao, and R. J. Hemley, Proc. Natl. Acad. Sci. U.S.A. **102**, 3198 (2005).
[28]E. Zhao and Z. Wu, J. Solid State Chem. **181**, 2814 (2008).
[29]H. Bracht, S. P. Nicols, E. E. Haller, J. P. Silveira, and F. Briones, J. Appl. Phys. **89**, 5393 (2001).
[30]A. Chroneos and H. Bracht, J. Appl. Phys. **104**, 093714 (2008).
[31]S. T. Murphy, B. P. Uberuaga, J. B. Ball, A. R. Cleave, K. E. Sickafus, R. Smith, and R. W. Grimes, Solid State Ionics **180**, 1 (2009).
[32]J. K. Burdett and J. F. Mitchell, Prog. Solid State Chem. **23**, 131 (1995).
[33]R. W. Grimes, C. R. A. Catlow, and A. M. Stoneham, J. Phys.: Condens. Matter **1**, 7367 (1989).
[34]A. Chroneos, B. P. Uberuaga, and R. W. Grimes, J. Appl. Phys. **102**, 083707 (2007).

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