Title

First-principles study of hydrogen- and oxygen-related complexes in ScN

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First-principles study of hydrogen- and oxygen-related complexes in ScN

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Scandium nitride (ScN) is an attractive material for electronic applications due to its high n-type conductivity. Native defects and unintentional impurities may limit the electron concentration and reduce the mobility; therefore, it is important to control their formation and incorporation. Hydrogen and oxygen are unintentional impurities that are commonly present during growth and processing. They act as shallow donors in ScN and hence may be regarded as harmless or even favorable to achieving n-type conductivity. Here we show, using state-of-the-art first-principles calculations, that these impurities can be detrimental because they readily form complexes with scandium vacancies (V_{Sc}). Isolated V_{Sc} have relatively high formation energies and thus have low concentrations and little impact on electronic properties. However, complexes between V_{Sc} and either hydrogen or oxygen form more readily than the pristine vacancy and will act as both compensating and scattering centers. Our results point to the importance of controlling the incorporation of hydrogen and oxygen in ScN (and AlScN alloys) to avoid degradation of the electronic properties.

I. INTRODUCTION

Rocksalt scandium nitride (ScN) is a semiconducting transition-metal nitride that has received significant attention due to the demonstrated synthesis of high-quality thin films[1–3] and their potential applications in thermoelectric[4–7] and electronic[8] devices. It exhibits high mobility and carrier concentrations[9–11] and ambipolar dopability.[12] It can also be integrated in heterostructures with other nitride semiconductors, including GaN.[13–16]

Given the importance of high conductivity for many of these applications, it is important to understand what factors may affect the carrier concentration and mobility. These include the possibly detrimental effects of point defects and impurities. Kumagai *et al*.[17] performed an analysis of point defects using density functional theory (DFT). They found the nitrogen vacancy, which acts as a shallow donor, to be the lowest-energy native defect. Scandium vacancies, on the other hand, were found to have very high formation energies and are thus unlikely to be present. Kumagai *et al*. also studied oxygen and hydrogen and found them to be shallow donors that can readily incorporate.[17] Hydrogen is commonly present as an unintentional impurity, and it may also incorporate due to the use of NH_3 during ScN growth.[18–21] Oxygen has also been recognized as an unintentional impurity that is difficult to avoid.[8,12]

The prior study by Kumagai *et al*.[17] did not identify any species that would act as compensating centers in n-type ScN. In the present work, we focus on the formation of complexes between the unintentional impurities, hydrogen and oxygen, and the cation vacancies. Hydrogenated vacancies have been shown to be relevant in GaN[22–24] and several oxides,[25] and they often have lower formation energies than do the isolated defects. In the nitrides, complexes between cation vacancies and oxygen have similarly been shown to be relevant.[23,24,26,27] The formation of such complexes is plausible in n-type material based on the Coulomb attraction between the cation vacancies, which are negatively charged, and H and O, which act as donors and hence are positively charged. The presence of such complexes would lead to compensation as well as the introduction of scattering centers that would degrade the mobility.

Here, we use first-principles calculations based on DFT[28,29] with a hybrid functional[30,31] to study the formation and properties of a number of complexes in ScN involving hydrogen, oxygen, and scandium vacancies. Oxygen-hydrogen complexes are found to be unfavorable, but complexes between either hydrogen or oxygen and cation vacancies have low formation energies. Complexes with one or two H atoms remain acceptors, while those with four or more H atoms behave as donors. We also investigate the energy needed to dissociate these complexes. To that end, we examine the migration of interstitial protons in bulk ScN, finding a migration barrier of 0.91 eV. Overall, we find that once the complexes are formed, they are unlikely to dissociate. We find complexes between oxygen and V_{Sc} to be similarly robust. Our results indicate that, when hydrogen or oxygen are present, formation of complexes with V_{Sc} is very likely, and these complexes can reduce the electron concentration and the mobility.

We note that these conclusions may also have relevance for AlScN alloys, which have recently received much attention because they exhibit piezoelectricity larger than AlN,[32,33] ferroelectric switching,[34] and large dielectric permittivity.[35] We suggest that the stabilization of cation vacancies due to complex formation with H or O will also occur in AlScN alloys, drawing attention to the importance of controlling H and O incorporation during growth.

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II. METHODS

A. Computational Details

We conduct first-principles calculations based on DFT[28,29] using the Heyd, Scuseria, and Ernzerhof (HSE)[30,31] screened hybrid functional with 25% mixing of exact exchange, as implemented in the Vienna *Ab initio* Simulation Package (VASP).[36,37] We use an energy cutoff of 520 eV for the plane-wave basis set, and the core electrons are described using projector-augmented-wave pseudopotentials,[38,39] with the Sc $4s^2\ 3d^1$, N $2s^2\ 2p^3$, and O $2s^2\ 2p^4$ electrons treated as valence states. For defect calculations, we use 64-atom supercells, which are constructed by doubling the eight-atom conventional cubic unit cell in each direction. Supercell calculations use a single special k point, located at (0.25, 0.25, 0.25). Spin polarization is included. To calculate proton migration barriers, we used the nudged elastic band (NEB) method with climbing images,[40,41] using three intermediate images.

B. Defect Formalism

We calculate the formation energy of point defects as[42]

$$E^f(D^q) = E(D^q) - E_{\text{bulk}} +$$
$$\sum n_E \mu_E + qE_F + \Delta_{\text{corr}}, \quad (1)$$

where $E^f(D^q)$ is the formation energy of defect D in charge state q; $E(D^q)$ is the total energy of a supercell containing the defect; E_{bulk} is the total energy of the pristine supercell; n_E is the number of atoms of species E added to ($n_E < 0$) or removed from ($n_E > 0$) the supercell to create the defect; E_F is the Fermi level, which can lie between the valence-band maximum (VBM) and conduction-band maximum (CBM); and Δ_{corr} is a finite-supercell-size correction term.[43] The calculated band gap of ScN is 0.79 eV,[11] similar to the experimentally measured gap of 0.9±0.1 eV.[44] In thermodynamic equilibrium, the formation energy determines the defect concentration via a Boltzmann expression, meaning that defects with lower formation energies will be exponentially more abundant than those with higher formation energies.

The chemical potential μ_E is related to the abundance of element E. We can express μ_E as the sum of the total energy of E in its elemental phase, $E_{\text{tot}}(E)$, and a deviation, $\Delta\mu_E$, from that energy:

$$\mu_E = E_{\text{tot}}(E) + \Delta\mu_E. \quad (2)$$

For scandium, the elemental phase is bulk Sc, while for nitrogen, oxygen, and hydrogen, the elemental phases are molecular N_2, O_2, and H_2.

Assuming thermodynamic stability of ScN, the values $\Delta\mu_{\text{Sc}}$ and $\Delta\mu_N$ are related to the enthalpy of formation ΔH^f by:

$$\Delta\mu_{\text{Sc}} + \Delta\mu_N = \Delta H^f(\text{ScN}). \quad (3)$$

We calculate $\Delta H^f(\text{ScN}) = -4.03$ eV/(formula unit). We refer to the conditions corresponding to $\Delta\mu_{\text{Sc}} = 0$ [$\Delta\mu_N =$

$\Delta H^f(\text{ScN})$] as "Sc-rich", where Sc metal is equally favored relative to ScN. Similarly, for $\Delta\mu_N = 0$ [$\Delta\mu_{\text{Sc}} = \Delta H^f(\text{ScN})$], we refer to "N-rich" conditions. For the purposes of presenting our results we will focus on the N-rich limit; results for other conditions can easily be obtained by referring back to Eq. (1).

For impurities—in this case, oxygen and hydrogen—we reference chemical potentials to the formation enthalpies of the most relevant secondary phases. For oxygen, this is Sc_2O_3, and we relate chemical potentials to its enthalpy of formation as:

$$2\Delta\mu_{\text{Sc}} + 3\Delta\mu_O \leq \Delta H^f(\text{Sc}_2\text{O}_3), \quad (4)$$

where we calculate $\Delta H^f(\text{Sc}_2\text{O}_3) = -18.54$ eV/(formula unit) For hydrogen, molecular NH_3 is the limiting phase:

$$\Delta\mu_N + 3\Delta\mu_H \leq \Delta H^f(\text{NH}_3), \quad (5)$$

where we calculate $\Delta H^f(\text{NH}_3) = -1.20$ eV/(formula unit). For presentation purposes we will use the chemical potential values at the upper bounds of these expressions, where the impurity elements are present at their solubility limit. Our approach and results are consistent with those of Kumagai *et al.*,[17] who found very similar formation energies to those we report for V_{Sc}^{3-}, H_i^+, and O_N^+.

III. RESULTS

A. Hydrogen and Oxygen

1. Hydrogen

Figure 1 displays the formation energy of interstitial hydrogen, which acts as a shallow donor with only the positive charge state (H_i^+) being stable throughout the band gap. H_i^+ binds to a lattice N atom with a bond length of 1.03 Å, and the N–H bond is oriented in a $\langle 111 \rangle$ direction. In principle, we can also stabilize a negative charge state, H_i^-. H_i^- is tetrahedrally coordinated with four neighboring Sc atoms, from each of which it is separated by 1.92 Å. Its presence also causes a distortion in the N sublattice, as the nearest-neighbor N atoms are repelled slightly away from it. However, H_i^- has a very high formation energy (2.89 eV at the CBM), so it will not be stable unless the Fermi level is above the (+/−) thermodynamic transition level, which is at 0.84 eV above the CBM. Due to the relatively large conduction-band density of states of ScN, such a high Fermi-level position will never be reached, even at extremely high electron concentrations,[11,17] and thus H_i^- will never be present. However, knowledge of the position of the (+/−) level is useful in the context of band alignments.[45]

2. Hydrogen Migration

Interstitial protons are known to be quite mobile in materials, and it is important to assess their diffusion properties. We
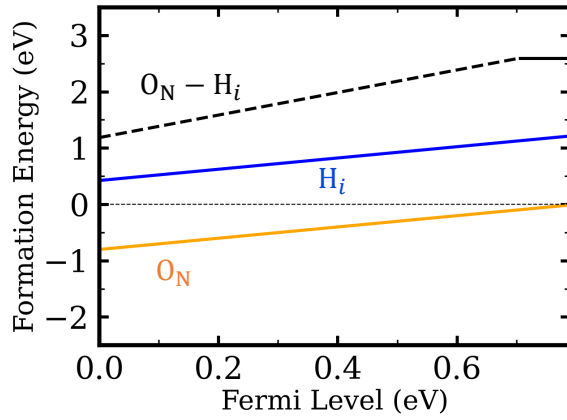
FIG. 1. Formation energies of interstitial H (H_i), substitutional oxygen O_N, and O_N–H complexes as a function of Fermi level under N-rich conditions in ScN. The dashed line indicates the complex is unstable.
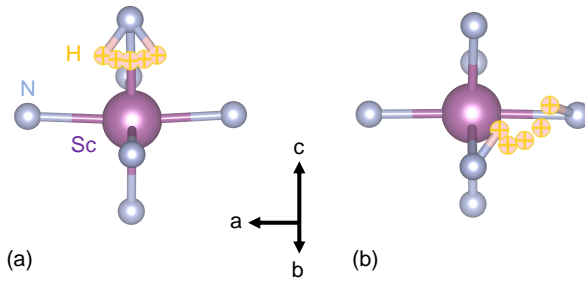

FIG. 2. Pathways for H_i^+ motion in ScN: (a) rotation around a nitrogen atom; (b) jumping between two nitrogen atoms. Images were produced using the VESTA3 software.[47]

performed NEB calculations for two possible pathways for H_i^+ motion, depicted schematically in Fig. 2: rotation around a single N anion (panel a) and jumping between two N anions (panel b). Rotation can proceed with a barrier of $E_b = 0.16$ eV. The jumping step, on the other hand, requires a larger migration barrier of $E_b = 0.91$ eV. This barrier is very similar to the migration barrier for H_i^+ in GaN, which was calculated to be ~ 0.9 eV.[46] For H_i^+ to move throughout the material, both steps are necessary, with the larger of the two barriers ($E_b = 0.91$ eV) being the rate-limiting step.

Knowledge of the migration barrier allows us to estimate the temperature at which the impurity becomes mobile. Within transition state theory,[48] the rate Γ at which an impurity hops to a neighboring equivalent site can be expressed as:

$$\Gamma = \Gamma_0 \exp\left(-\frac{E_b}{k_B T}\right), \quad (6)$$

where k_B is the Boltzmann constant. The prefactor Γ_0 is related to a typical vibrational frequency, which can be approximated as 10^{14} s^{-1}. An estimate for the "annealing temper-

ature" T_a at which the impurity becomes mobile can then be obtained as the temperature at which the rate $\Gamma = 1$ s^{-1}, which leads to $T_a \approx E_b \times 360$ K/eV. With $E_b = 0.91$ eV for H_i^+, we obtain a temperature of 328 K, i.e., hydrogen will become mobile at temperatures slightly above room temperature.

3. Oxygen

The most stable configuration for oxygen in ScN is as a substitutional species on an anionic site, O_N. As shown in Fig. 1, O_N is present exclusively in the positive charge state, O_N^+, indicating that it acts as a shallow donor. O_N has a negative formation energy over the entire range of Fermi levels, which indicates that ScN would be unstable relative to formation of Sc_2O_3. Actual growth will of course use conditions that avoid oxidation, but the result does point to the tendency for oxygen to incorporate very easily in ScN.

4. Oxygen-Hydrogen Complexes

Since protons are known to bond favorably with oxygen,[49] and since we found H_i^+ to be quite mobile, we investigate the potential formation of O_N–H complexes. As shown in Fig. 1, this complex can be formed in either the 2+ or neutral charge state. For complexes it is important to calculate the binding energy, expressed relative to its constituents. For a defect complex A–B, the binding energy is defined as:

$$E_{\text{bind}}(A\text{–}B) = -E^f(A\text{–}B) + E^f(A) + E^f(B). \quad (7)$$

A positive value of E_{bind} indicates a stable complex. For (O_N–H)$^{2+}$ we calculate $E_{\text{bind}} = -1.56$ eV, which indicates that such complexes will not be stable in ScN (hence the dashed line in Fig. 1). This result is not surprising, in light of the Coulomb repulsion between H_i^+ and O_N^+. For Fermi levels closer to the CBM, the complex forms in a neutral charge state; referenced to O_N^+ and H_i^-, the binding energy of (O_N–H)^0 is 0.28 eV. This relatively small binding energy indicates that the complex is likely to be dissociated at modest temperatures.

B. Scandium Vacancy Complexes

1. Complexes with Hydrogen

Next, we explore the formation of complexes between V_{Sc} and hydrogen. In this case, we expect Coulomb attraction to favor complex formation, since V_{Sc} occurs in the 3− charge state in n-type ScN.[17] The sixfold coordination in rocksalt implies that V_{Sc}^{3-} is surrounded by six N atoms, each of which can potentially bind with a H atom; we therefore consider complexes with up to six H atoms.

In Fig. 3, we plot our calculated formation energies for complexes containing one, two, three, or four H atoms, denoting them V_{Sc}–nH, where n is the number of H atoms. Clearly, the complexes have lower formation energies than V_{Sc}^{3-}, and

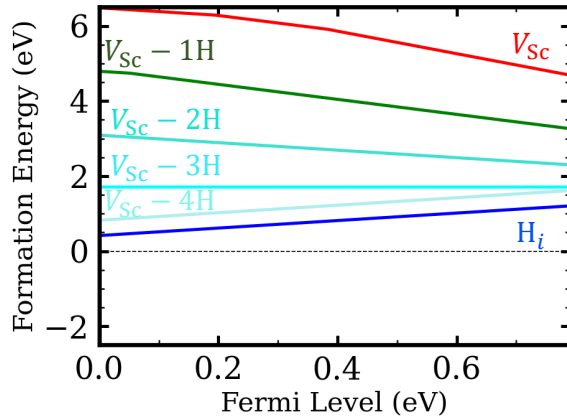FIG. 3. Formation energies of V_{Sc}, H_i, and V_{Sc}–nH complexes under N-rich conditions in ScN.

the charge state in n-type material changes from $3-$ in the bare vacancy to $2-$ in V_{Sc}–H, $1-$ in V_{Sc}–2H, neutral in V_{Sc}–3H, and $1+$ in V_{Sc}–4H.

We also examined complexes containing five or six H atoms, but found that their formation energy at the CBM is higher than for V_{Sc}–4H. This result is not surprising, given that adding an H_i^+ to a complex that is already positively charged is expected to be unfavorable. We therefore did not include the formation energies for complexes involving more than four H atoms in Fig. 3. We also note that complexes with large numbers of H atoms are unlikely, since in those cases entropy favors the isolated species.

To describe binding in complexes involving more than one hydrogen, we need an additional quantity other than the binding energy defined in Eq. 7. We could still define a binding energy by looking at the energy difference between the (V_{Sc}–nH)$^{3-n}$ complex on the one hand and the sum of the energies of isolated V_{Sc}^{3-} and n H_i^+ on the other; dividing by n then yields an average binding energy per H.[22] However, it is more informative to define a "removal energy" E_r, defined as the energy necessary to remove one H_i^+ from a given complex:

$$E_r(n \to n-1) = -E^f[(V_{Sc}-n\mathrm{H})^{-3+n}]$$
$$+ E^f[\mathrm{H}_i^+] + E^f[(V_{Sc}-(n-1)\mathrm{H})^{-4+n}]. \quad (8)$$

For $n = 1$, Eq. 8 coincides with the definition of the binding energy [Eq. 7]. Removal energies for each complex are listed in Table I. As can be seen, these energies are large and positive, consistent with the fact that when H is added to V_{Sc}, a new bond is formed between N and H, and the N–H bond strength is large. The large removal energies suggest that, once formed, the complexes will be difficult to dissociate.

The actual dissociation energy to remove hydrogen from a V_{Sc}–nH complex could be calculated by tracing a migration pathway and performing NEB calculations. However, a reasonable estimate for this energy barrier can be obtained by adding the migration barrier for H_i^+ in bulk (which we calculated to be 0.91 eV) to the removal energy. This leads to values which are at least as large as $1.76 + 0.91 = 2.67$ eV

Complex	E_r (eV)			
	$n=1$	$n=2$	$n=3$	$n=4$
$(V_{Sc}-n\mathrm{H})^{-3+n}$	2.66	2.19	1.76	2.04
$(V_{Sc}-n\mathrm{O})^{-3+n}$	1.30	1.10	0.71	0.47

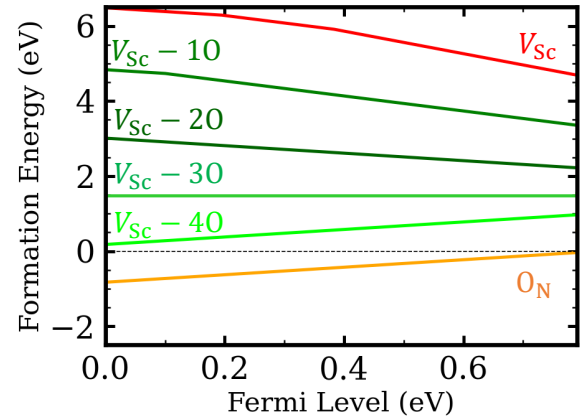TABLE I. Calculated removal energies for complexes of V_{Sc} with up to four H or O.

FIG. 4. Formation energies of V_{Sc}, O_N, and V_{Sc}–nO complexes under N-rich conditions in ScN.

for the V_{Sc}–nH complexes considered here. Combined with our estimate for an annealing temperature, as discussed in Sec. III A 1, this means that temperatures of at least $360 \times 2.67 = 960$ K would be required to remove H from the complex. To remove the last H_i^+ from the complex would require an even greater temperature of $360 \times (2.66 + 0.91) = 1285$ K. We can conclude that, once formed, it is quite unlikely that the hydrogenated complexes will dissociate.

2. Complexes with Oxygen

In much the same manner as with hydrogen, we can consider the formation of complexes between V_{Sc} and various numbers of oxygen atoms on neighboring nitrogen sites. We denote these complexes as V_{Sc}–nO and we again consider complexes with up to four O_N^+. Our results in Fig. 4 show that, as with complexes involving hydrogen, the formation energy decreases as n increases, and the charge state becomes less negative, consistent with the fact that O_N acts as a shallow donor.

Following a similar definition as shown in Eq. 8, Table I lists the removal energies for separating one O_N^+ from each of the V_{Sc}–nO complexes complexes. The removal energies are positive but considerably smaller than for the hydrogen complexes. Still, once formed, the V_{Sc}–nO complexes are unlikely to dissociate, because the barrier for moving oxygen atoms is high (much higher than the migration barrier for hydrogen).

IV. CONCLUSION

In summary, we have presented a comprehensive investigation of hydrogen and oxygen impurities and their complexes with scandium vacancies in ScN. Interstitial H_i^+ and substitutional O_N^+ act as shallow donors that are easily incorporated. They readily bind to V_{Sc}, forming complexes that are lower in energy than the bare vacancy. Once formed, these complexes are hard to dissociate. Since hydrogen and oxygen are often unintentionally present (or, in the case of hydrogen, may actually be part of the growth precursors), the presence of these $V_{Sc}–n$H and $V_{Sc}–n$O complexes is thus quite likely. Complexes with one or two H or O atoms act as compensating acceptors, and since they are negatively charged, they also act as scattering centers that degrade the mobility. We suggest that our conclusions also have relevance for AlScN alloys, where stabilization of cation vacancies due to complex formation with H or O could also degrade the properties. When hydrogen is part of the precursors, for instance in the form of NH$_3$, incorporation of hydrogen can probably be reduced by moving to more N-rich conditions. Incomplete dissociation of NH$_3$ molecules should be particularly avoided, since it may lead to nonequilibrium incorporation of N–H species that, when formed next to a vacant cation site, will be extremely difficult to remove.

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AUTHOR DECLARATIONS

Conflicts of Interest

The authors have no conflicts to disclose.

AUTHOR CONTRIBUTIONS

A.J.E.R.: Methodology, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing. **S.M.**: Investigation, Writing - Original Draft, Writing - Review & Editing. **C.V.d.W.**: Conceptualization, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

DATA AVAILABILITY

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

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