# Clustering of oxygen point defects in transition metal nitrides

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## ABSTRACT

Point defects create exotic properties in materials such as defect-induced luminescence in wide-bandgap semiconductors, magnetism in nonmagnetic materials, single-photon emission from semiconductors, etc. In this article, oxygen defect formation in metallic TiN and semiconducting rock salt-(Al,Sc)N is investigated with a combination of first-principles density functional theory, synchrotron-based x-ray absorption spectroscopy (XAS) analysis, and scanning transmission electron microscopy–energy-dispersive x-ray spectroscopy mapping. Modeling results show that oxygen in TiN and rock salt-(Al,Sc)N prefers to be in the defect complex of substitutional and interstitial oxygen ( $nO_N + O_i$ ) types. While in TiN, the preferential interstitial sites of oxygen in  $O_N + O_i$  are at the tetrahedral site, in rock salt-(Al,Sc)N, a split interstitial site along the [111] direction was found to be energetically preferable. Simulations performed as a function of the oxygen partial pressure show that under experimental growth conditions, four oxygen atoms at the substitutional sites of nitrogen ( $4O_N$ ), along with four Ti atoms, decorate around an interstitial oxygen atom at the tetrahedral site ( $O_i$ ) in the energetically favored configuration. However, in rock salt-(Al,Sc)N, n in  $nO_N + O_i$  was found to vary from two to four depending on the oxygen partial pressure. Theoretical predictions agree well with the experimentally obtained XAS results. These results are not only important for a fundamental understanding of oxygen impurity defect behavior in rock salt nitride materials but will also help in the development of epitaxial metal/semiconductor superlattices with efficient thermionic properties.

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#### INTRODUCTION

Defect engineering in crystals enables the tailoring of their properties and imparts novel functionalities that are otherwise missing. Intentional and controlled defect engineering in materials enhances their application space such as in defect-induced luminescence in wide-bandgap semiconductors for optical communications, enhanced optical absorption for efficient photo-catalysis, magnetism in otherwise nonmagnetic materials for spintronics, single-photon emission from defect states in wide-bandgap semiconductors, <sup>1,2</sup> etc. On the other hand, unintentional and uncontrolled defects (impurities) significantly affect the material and device performances<sup>3–6</sup> such as reduction of electron mobility and conductivity, quenching of luminescence, scattering of electrons, phonons, spins, etc. Moreover, the site preference of point defects plays a major role in determining the overall properties of many materials. For example, when Mg occupies the Ga atomic site in GaN, it acts as a *p*-type dopant, while in the interstitial site, it behaves as an *n*-dopant.<sup>7,8</sup> Similar observations were also made on the Li doping in ZnO<sup>9</sup> and other examples of amphoteric dopants.<sup>10,11</sup> Therefore, from a device application point of view, controlling the types and nature of point defects as well as their

concentrations is extremely important for achieving optimum performance, and careful experiments and meticulous modeling analysis are required to understand the complete nature of various kinds of defects and their impacts on the physical properties of materials.

Nitride thin films and their solid-solution alloys are not only the fundamental building blocks of modern optoelectronic devices and hard coating technology, but they also have tremendous potential in solid-state energy conversion applications such as in thermoelectric energy conversion, photo-catalysis, quantum computing, etc.<sup>12-14</sup> More specifically, transition metal nitrides (TMN) have generated significant interest in recent years for their thermoelectric, plasmonic, and solar-energy conversion applications. However, a major challenge for the development of efficient nitride materials has been the incorporation of unwanted impurities such as oxygen that arises either from the source contaminations or from the background O2, H2O, CO2, etc., pressure during the thin film deposition process. The incorporation of oxygen into nitride materials like GaN,<sup>15</sup> InN,<sup>16</sup> and ScN<sup>17,18</sup> results in degenerate n-doping with high electron concentrations when oxygen occupies the nitrogen sites (O<sub>N</sub>). Similarly, the mechanical properties of silicon nitride (Si<sub>3</sub>N<sub>4</sub>) degrade upon oxygen incorporations,<sup>19</sup> while a small fraction of oxygen in AlN drastically changes its piezoelectric properties.<sup>20</sup> In terms of its effects on metallic nitrides, TiN loses its golden color, a manifestation of the degradation of its excellent plasmonic properties upon the incorporation of oxygen,<sup>2</sup> while a high concentration of oxygen in tantalum nitride (TaN) changes the nature of the material from crystalline to amorphous.<sup>2</sup> TiN is a refractory material with a melting point above 2900 °C. But in the presence of oxygen, it starts oxidizing at temperatures as low as 400 °C<sup>23</sup> and completely oxidizes at 800 °C and forms stable TiO<sub>2</sub>,<sup>24</sup> limiting its use at high temperatures in ambient air. Oxygen dissolution in TiN is exothermic.<sup>25,26</sup> Thus, it will spontaneously incorporate itself into TiN samples grown using the sputtering technique.<sup>27-34</sup> Post-growth exposure to ambient air forms an oxide layer at the surface of TiN. Oxygen can also diffuse from the oxide layer to the TiN layer in TiN/oxide heterostructures at high temperatures, limiting their device performance.<sup>35</sup> ScN also has a very high affinity toward oxidation,<sup>36,37</sup> which significantly affects its electronic properties.<sup>37-45</sup> Thus, from both the fundamental and application points of view, studies on oxygen impurities in nitride materials are of great interest.

Epitaxial cubic TMN thin films such as ScN, CrN, and TiN and their multilayers and superlattices such as TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N have generated significant interest in recent years for a range of solid-state energy conversion applications such as in thermionic emission-based waste-heat to electrical energy conversion, plasmon-induced hot-electron solar-energy conversion in photocatalysis, photo-detectors, hot-carrier solar cells, etc., as well as for the fundamental physics studies on the heat, light, and current transport in nanostructured metamaterials.<sup>46,47</sup> TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N is the first demonstration of an epitaxial single-crystalline metal/semiconductor superlattice48-51 that does not exhibit much extended defects but instead exhibits lattice-matched atomically sharp interfaces with minimal interface roughness. These superlattices have exhibited excellent optical properties with a hyperbolic dispersion of iso-frequency surfaces<sup>50</sup> and large enhancement in its photonic densities of states that could be useful for designing quantum

electronic devices. Moreover, these superlattices have been utilized to demonstrate phonon wave-effects and a large reduction of thermal conductivity<sup>52</sup> that is necessary for thermoelectric applications.

While these important developments in TMNs and metal/ semiconductor superlattices have aroused significant interest, oxygen impurities have become a major concern for thermionic energy conversion applications.<sup>53</sup> Unwanted oxygen impurities in ScN and (Al,Sc)N lead to a high n-type carrier concentration of ~ $(1-5) \times 10^{20}$  cm<sup>-3</sup>, which results in a small depletion width at the metal/semiconductor interfaces (of the order of 1-3 nm) and prevents the observation of thermionic emission necessary for device applications.<sup>54</sup> Though intentional hole-doping of nitride semiconductors has been developed successfully to compensate for the heavy *n*-type doping, and a *p*-type ScN has been demonstrated, a reduction of the oxygen impurities and an understanding of their effects on the physical properties of nitride multilayers are extremely important. Therefore, in order to better understand the effects of oxygen incorporation into the structural and electronic properties of TiN, (Al,Sc)N, and their superlattices, in this article, the oxygen site preference, formation energies, and their effects on the electronic properties are determined by a combination of firstprinciples density functional theory (DFT) based simulations and soft x-ray absorption near edge spectroscopy (XANES). Scanning transmission electron microscopy (STEM) based energy-dispersive x-ray spectroscopy (EDS) mapping is performed to further elucidate the structural and electronic properties of oxygen impurities in such materials.

#### METHODS

#### Material synthesis

Epitaxial TiN,  $Al_{0.72}Sc_{0.28}N$  thin films, and a TiN/ $Al_{0.72}Sc_{0.28}N$ superlattice with 7.5 nm/7.5 nm period thicknesses are deposited on MgO (001) substrates using the dc-magnetron sputtering system (PVD Products, Inc.) with a base pressure of  $2.5 \times 10^{-8}$  Torr in a bottom-up confocal arrangement. All substrates were cleaned in acetone and methanol prior to the film deposition. A substrate temperature of 750 °C was used during the deposition. A deposition pressure of 10 mTorr arising from the Ar/N2 mixture with 4 sccm of Ar and 6 sccm  $\mathrm{N}_2$  was maintained throughout the growth. With a base pressure of  $2.5 \times 10^{-8}$  Torr in the deposition chamber, an oxygen partial pressure is estimated to be of the order of  $10^{-9}$ Torr. Scandium (99.998% purity), titanium (99.99%), and aluminum (99.99%) targets (2 in. diameter × 0.25 in. thick) were used as the source materials. The targets were sputtered in the constant power mode, and power was varied in the Al and Sc targets to achieve the desired Al<sub>0.72</sub>Sc<sub>0.28</sub>N stoichiometry.

### Material characterization

Thin film superlattices were characterized by high-resolution x-ray diffraction (HR-XRD), high-resolution STEM and EDS mapping, Hall measurements, and x-ray photoelectron spectroscopy (XPS), as previously reported.  $^{48,49,57}$ 

For the present work, XANES measurements were performed in total electronic yield (TEY) mode using the SXAS beamline (BL-01) of the Indus-2 synchrotron source at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. BL-01 of the Indus-2 synchrotron source beamline contains a toroidal mirror to focus the beam on to the sample surface. The slit width before the monochromator was 1 mm, while that before the sample was set at 0.1 mm. A minimum energy resolution of 0.2 eV was noted. The details of the experimental setup for XANES measurements are discussed elsewhere.<sup>58</sup> Background subtraction and normalization of the recorded XANES spectra were performed using the Athena software package.<sup>59</sup>

HR-STEM imaging and EDS analysis were performed using the Sydney Microscopy and Microanalysis image and probecorrected and monochromated FEI Themis-Z TEM equipped with a high-brightness XFEG source and operated at 300 kV. For EDS mapping, the large solid-angle SuperX EDS detector system for ultra-high-count rates was used. By using the probe corrector, a spatial resolution of 0.7 Å for STEM imaging and EDS mapping was achieved. EDS quantification was done on maps with count statistics higher than 1M counts, using the k-factor method and absorption correction for background modeling.

TEM sample preparation was done with a Helios Hydra Dual Beam Plasma FIB. Samples were coated with 20 nm of Au to prevent charging prior to SEM and FIB. For TEM sample preparation, a 100 nm Pt + C protective cap was deposited with a 5 kV electron beam followed by a  $1 \mu$ m Pt + C protective cap with a 12 kV Xe beam. A 30 kV Xe beam at 60, 15, and 4 nA was used for trenching and lift out. The TEM specimens were welded to Mo grids using Xe beam Pt welding. Thinning was achieved with a tilt angle of ±1.5° with currents of 300 and 100 pA. Final thinning was done with 30 kV at 30 pA, checking for electron transparency using a 5 kV electron beam with an SE detector. When the ROI was thin enough, it was finally polished with 5 kV at 30 and 10 pA, checking for electron transparency using a 2 kV electron beam with an SE detector.

#### **Computational details**

The formation energies of various oxygen and native defects are determined with total energy calculations using ab initio Density Functional Theory (DFT) as implemented in SIESTA code.<sup>60</sup> Generalized Gradient Approximation (GGA) proposed by Perdew *et al.*<sup>61</sup> is used to approximate the exchange and correlation energy functional. A double zeta with a polarization function is used as the basis set for the construction of atomic orbitals. Norm-conserving pseudopotentials of Troullier and Martins<sup>62</sup> are used with the valence electron configurations of scandium, titanium, aluminum, nitrogen, and oxygen as 3d<sup>1</sup> 4s<sup>2</sup>, 3d<sup>2</sup> 4s<sup>2</sup>, 3s<sup>2</sup> 3p<sup>1</sup>,  $2s^2 2p^3$ , and  $2s^2 2p^4$ , respectively. A  $\Gamma$ -centered k-point mesh of  $12 \times 12 \times 12$  and  $16 \times 16 \times 16$  is used in sampling the Brillouin zone of the conventional 8-atoms unit cell in the reciprocal spaces of TiN and Al<sub>0.75</sub>Sc<sub>0.25</sub>N, respectively. A uniform grid of points with the maximum kinetic energy of 200 Ry in real space is used in the estimation of the Hartree and exchange-correlation energies. The structure is optimized by allowing all the atoms to relax until the forces on each atom become less than 0.02 eV/Å. In the construction of the unit cell of (Al,Sc)N alloys, an eight atom supercell containing three Al, one Sc, and four N atoms is used, which

results in mole fractions of 75% of AlN and 25% of ScN in the  $Al_{0.75}Sc_{0.25}N$  configuration which is close to the experimental stoichiometry ( $Al_{0.72}Sc_{0.28}N$ ).

Furthermore, a  $3 \times 3 \times 3$  supercell with 216 atoms is used to calculate the formation energy  $E_F(def)$  of oxygen defects in TiN and Al<sub>0.75</sub>Sc<sub>0.25</sub>N using the Zhang–Northrup scheme,<sup>63</sup> which is given by

$$E_F(def) = E_{tot}(def) - E_{tot}(pristine) + \sum_i x_i \mu_i, \qquad (1)$$

where  $E_{tot}(def)$  is the total energy of the supercell with defects and  $E_{tot}(pristine)$  is the total energy of the pristine supercell.  $\mu_i$  is the chemical potential of the element added or removed from/to the pristine supercell to form a defect supercell.  $x_i$  is the number of atoms added (or removed) in the pristine supercell to form the defect supercell. The chemical potential of nitrogen in nitrogen-rich conditions is obtained with Eq. (2), while the chemical potential of oxygen is calculated in both oxygen-rich and poor conditions as Eqs. (3a)–(3c), respectively,

$$\mu_N = E_{tot}(N) - D_0(N).$$
 (2)

In oxygen-rich conditions,

$$\mu_{O} = E_{tot}(O) - D_{0}(O).$$
(3a)

In oxygen-poor conditions,

$$u_{O} = E_{tot}(Ti_{6}O) - 6 \times \mu_{Ti} \text{ for TiN}$$
(3b)

and

$$\mu_O = \frac{1}{3} (E_{tot}(Sc_2O_3) - 2 \times \mu_{Sc}) \text{ for AlScN}, \qquad (3c)$$

where  $E_{tot}(N)$  and  $E_{tot}(O)$  are the atomic energies of N and O atoms, respectively, calculated by considering one atom in a supercell with a vacuum of at least 25 Å in all three directions.  $D_0(N)$ and  $D_0(O)$  are the experimental dissociation energy of nitrogen  $(9.80 \text{ eV})^{64}$  and oxygen (5.16 eV),<sup>64</sup> respectively.  $E_{tot}(Ti_6O)$  is the total energy of Ti<sub>6</sub>O in the trigonal crystal system.  $E_{tot}(Sc_2O_3)$  is the total energy of Sc<sub>2</sub>O<sub>3</sub> in the cubic crystal system.  $\mu_{Ti}$  and  $\mu_{Sc}$  are the chemical potentials of Ti and Sc, respectively, calculated in their metallic form. The abovementioned method to calculate the O and N chemical potential is more accurate than the conventional method, where  $\mu_{\rm O}$  or  $\mu_{\rm N}$  is obtained by calculating the total energy of the  $O_2$  or  $N_2$  molecule in a supercell. The use of a  $3\times 3\times 3$ supercell with 216 atoms ensures that the maximum defect concentration within the supercell is ~2.3% that is close to the experimental oxygen concentration. In addition, with the use of the  $3 \times 3 \times 3$ supercell, the interactions between defects from different supercells are also reduced.

The binding energy of the defect complex is calculated using the following equation:

$$E_b(nO_N + O_i) = nE_F(O_N) + E_F(O_i) - E_F(nO_N + O_i),$$

where  $E_b(nO_N + O_i)$  and  $E_F(nO_N + O_i)$  are the binding energy and formation energy, respectively, of the defect complex  $nO_N + O_i$ .  $E_F(O_N)$  and  $E_F(O_i)$  are the formation energies of the isolated  $O_N$  and  $O_i$  defects, respectively.

XANES spectra of O K-edge were simulated using the *ab initio* multiple scattering code FEFF9.05,<sup>65</sup> where self-consistent spherical muffin-tin scattering potentials with the Hedin–Lundqvist exchange and an imaginary part of 0.02 eV are used. Relaxed atomic coordinates obtained from DFT calculations are used to construct the cluster in calculating XANES spectra. A cluster with a radius of 8 Å was used to construct the atomic potential, while it was increased to 12 Å in computing the scattering cross section.

#### **RESULTS AND DISCUSSION**

Density functional theory (DFT) calculations resulted in optimized lattice parameters of 4.26 Å and 4.25 Å for TiN and Al<sub>0.75</sub>Sc<sub>0.25</sub>N, respectively, that are very similar to the experimentally observed lattice constant of 4.24 Å for TiN and 4.26 Å for Al<sub>0.75</sub>Sc<sub>0.25</sub>N. The bandgap of Al<sub>0.75</sub>Sc<sub>0.25</sub>N was calculated to be 1.82 eV, which is underestimated compared with the experimentally observed bandgap of 3.5 eV for Al<sub>0.72</sub>Sc<sub>0.28</sub>N. Such an underestimation of the bandgap, however, is well known for the DFT calculations.<sup>66</sup> For the calculation of O defects, a  $3 \times 3 \times 3$  supercell is formed by repeating the unit cells of TiN and Al<sub>0.75</sub>Sc<sub>0.25</sub>N. In this formation, Sc always occupies the same lattice rather than being randomly distributed in the supercell. However, a recent study by Harris et al.<sup>67</sup> revealed that the formation energy of the neutral O defect in Al<sub>0.65</sub>Ga<sub>0.35</sub>N alloys is relatively independent of the local chemistry (i.e., the configuration of Al and Ga atoms surrounding the defect) within an error of 0.1 eV. Thus, our results with an ordered Al<sub>0.75</sub>Sc<sub>0.25</sub>N are also expected to be similar to the quasi-random alloy configurations. The substitutional oxygen defect (O<sub>N</sub>) in TiN (TiN:O<sub>N</sub>), where one oxygen atom replaces a nitrogen site, has a low formation energy (-3.05 eV) in an O-rich condition [see Fig. 1(a)]. The interstitial oxygen ( $O_i$ ) defect in TiN at the tetrahedral interstitial site has a formation energy of 1.47 eV [see Fig. 1(a)], which is lower than that at other possible interstitial sites, which is in agreement with the previous reports.<sup>68</sup> Since the formation energy of the TiN:O<sub>i</sub> defect is positive, the presence of these defects will be scarce in the TiN films. Furthermore, a defect complex O<sub>N</sub> + O<sub>i</sub> in TiN, where both O<sub>N</sub> and O<sub>i</sub> are in proximity  $(O_N-O_i \text{ distance was 2.16 Å.})$ , i.e., one of the four nearest-neighbor nitrogen atoms of TiN:Oi is replaced by an oxygen atom, is considered. The results showed that such a defect complex has a formation energy of -2.49 eV. When the O<sub>N</sub>-O<sub>i</sub> separation was increased to 9.24 Å, the formation energy of the TiN: $O_N + O_i$  defect complex became higher at -1.59 eV. The reduction in the formation energy when O<sub>i</sub> comes in the close vicinity of O<sub>N</sub> suggests that even though isolated Oi defects are not favorable, they can be present in TiN in the  $O_N + O_i$  complex form. The substitutional oxygen atom numbers in the vicinity of O<sub>i</sub> in the crystal were increased, and various other defect configurations, such as  $2O_N + O_i$ ,  $3O_N + O_i$ , and 4O<sub>N</sub> + O<sub>i</sub> (see Fig. S2 in the supplementary material), were constructed. We find that with an increase in the number of O<sub>N</sub> near the O<sub>i</sub> site, the formation energy of these defect complexes reduces even further and becomes -13.42 eV in O-rich growth conditions, when all four nitrogen atoms surrounding O<sub>i</sub> are replaced with oxygen atoms (4O<sub>N</sub> + O<sub>i</sub>). Furthermore, the formation energies of all oxygen defects in a wide range of the chemical potential of O were calculated, and these are presented in Fig. 1(a).

Figure 1(a) also shows that at a very low  $O_2$  partial pressure (below  $10^{-12}$  Torr), the formation energies of all kinds of oxygenrelated defects are positive, indicating their inability to form spontaneously.  $O_N$  was found to be the most stable defect when the oxygen partial pressure was less than  $\sim 10^{-12}$  Torr, albeit with positive formation energies. As the partial pressure of O increases, the  $4O_N$  defect complex becomes most favorable for partial pressure between  $10^{-12}$  Torr and  $10^{-5}$  Torr [see Fig. 1(c)]. Above  $10^{-5}$  Torr



**FIG. 1.** Defect formation energy as a function of oxygen chemical potential (partial pressure of  $O_2$ ) for various defect configurations in TiN (a) and  $AI_{0.75}Sc_{0.25}N$  (b) calculated with density functional theory simulations. (c) The most stable defect configuration at a given oxygen chemical potential for TiN and  $AI_{0.75}Sc_{0.25}N$ . The red shaded region corresponds to the background partial pressure of O.

partial pressure of O, 4O<sub>N</sub> + O<sub>i</sub> becomes the most favorable defect in TiN. The shaded region in Fig. 1 represents the background O partial pressure that originated from the base pressure  $(2.5 \times 10^{-8})$ Torr) in our sputtering system. In this partial pressure region, 40<sub>N</sub> is the most stable defect complex in TiN. Other defect complexes such as  $nO_N$  and  $nO_N$  +  $O_i$  also have negative formation energies in this partial pressure region; thus, these defect complexes will also be present in the samples and their relative concentrations will depend on their formation energy values.<sup>69</sup> However, note that O can be incorporated into films not only from the background O but also from the O contamination in process gases (Ar and N<sub>2</sub>), impurities in metal targets, and possible diffusion from the MgO substrate, which will result in an increased O partial pressure. All these factors will lead to a higher O concentration than the expected O concentration at the background O partial pressure (~10<sup>-9</sup> Torr). This increased O concentration will result in a stabilization of the defect complex 4O<sub>N</sub>+O<sub>i</sub>, which, though, is not the most stable defect complex at a given experimental background partial pressure but will become the most stable defect at a comparatively high O partial pressure. During the growth process, O will be incorporated as an isolate O<sub>N</sub> or as defect complexes as they all have negative formation energies, but in equilibrium, it forms a defect complex of nO<sub>N</sub> + O<sub>i</sub>, as its formation energy is low and has a high BE (see Table I). Nevertheless, modeling data suggest a clustering of oxygen impurities in epitaxial TiN thin films.

In Al<sub>0.75</sub>Sc<sub>0.25</sub>N, both O<sub>N</sub> and O<sub>i</sub> were found to exhibit negative formation energies in oxygen-rich growth conditions [see Fig. 1(b)]. Unlike in TiN, O<sub>i</sub> at the tetrahedral site of Al<sub>0.75</sub>Sc<sub>0.25</sub>N is not stable, and O<sub>i</sub> moves from the tetrahedral site to the split interstitial site along the [111] direction [see Fig. S2(f) in the supplementary material], where it forms bonds with three Al atoms and one N atom. It also displaces the nearest-neighbor N along the [111] direction to the split interstitial site. But in the case of the  $nO_N + O_i$  defect complex, O<sub>i</sub> moves toward the tetrahedral site with increasing *n* from its initial split interstitial site and finally occupies the tetrahedral site for the  $4O_N + O_i$  defect complex. At a very low O<sub>2</sub> partial pressure (below ~10<sup>-16</sup> Torr), O<sub>N</sub> is the most favorable defect in Al<sub>0.75</sub>Sc<sub>0.25</sub>N as well. But as the partial pressure increases, the  $2O_N + O_i$  (~10<sup>-16</sup>-10<sup>-14</sup> Torr) and  $3O_N + O_i$  (~10<sup>-14</sup>-10<sup>-13</sup> Torr) defects become favorable for some region, and finally above a  $10^{-13}$  Torr O<sub>2</sub> partial pressure,  $4O_N + O_i$ 

**TABLE I.** Binding energies of the  $nO_N$  and  $nO_N + O_i$  defect complexes. The high positive energy corresponds to a strongly bound complex.

Configuration	Binding energy (eV)	
	TiN	Al <sub>0.75</sub> Sc <sub>0.25</sub> N
20 <sub>N</sub>	-0.06	-0.15
30 <sub>N</sub>	-0.15	-0.79
$4O_N$	-0.27	-1.09
$O_N + O_i$	0.92	0.73
$2O_N + O_i$	1.64	3.28
$3O_N + O_i$	2.21	4.43
$4O_{N} + O_{i}$	2.68	4.78

becomes the most energetically favored configuration. Similar to TiN, in  $Al_{0.75}Sc_{0.25}N$  too, oxygen defects will be in cluster form  $(nO_N + O_i)$  in a high  $O_2$  partial pressure regime [see Fig. 1(c)].

For bringing about clarity on the stability of defect clusters, the binding energies of such defect complexes are calculated with respect to their isolated defect configurations and presented in Table I. The results show that with an increase in n, the binding energy of the  $nO_N + O_i$  defect complex increases in both TiN and  $Al_{0.75}Sc_{0.25}N$ . The highest binding energy of the  $4O_N + O_i$  defect complex suggests that it preferably forms at high oxygen concentrations. The binding energy of the  $nO_N + O_i$  defects in Al<sub>0.75</sub>Sc<sub>0.25</sub>N is also higher than that in TiN, except for the  $O_N + O_i$  defect. On the other hand, the binding energies of the  $nO_N$  defects are negative and decrease with increasing n. The negative binding energy suggests that these defect complexes will be unstable and will prefer forming n isolated  $O_N$  defects instead of forming the defect complex nO<sub>N</sub>. For example, the 4O<sub>N</sub> defect complex in Al<sub>0.75</sub>Sc<sub>0.25</sub>N will have a formation energy of -7.51 eV, which is higher by 1.09 eV (the binding energy of  $4O_N$ ) than the combined formation energy of four isolated  $O_N$  defects  $[4 \times (-2.15) = -8.60 \text{ eV}]$ . Thus, the higher negative binding energy of the  $nO_N$  defects in Al<sub>0.75</sub>Sc<sub>0.25</sub>N will make these defects thermodynamically unstable. Similarly in TiN, the binding energy of the  $nO_N$  defects is negative, but the values are smaller than those in Al<sub>0.75</sub>Sc<sub>0.25</sub>N. There will always be a possibility of the formation of nO<sub>N</sub> defects in nonequilibrium conditions, especially for TiN, as it has very small negative binding energy. Previous first-principles modeling results show that nitrogen vacancies (V<sub>N</sub>) in InN prefer to stay clustered with each other<sup>70</sup> with binding energies that are comparable to calculated values in TiN and Al<sub>0.75</sub>Sc<sub>0.25</sub>N. Similarly, a recent positron annihilation spectroscopy measurement and analysis indicated the presence of V<sub>N</sub> clusters in ScN deposited with N-poor conditions.

The formation of isolated nitrogen vacancies (V<sub>N</sub>) and interstitial nitrogen (N<sub>i</sub>) in N-rich conditions are not favorable in both TiN and Al<sub>0.75</sub>Sc<sub>0.25</sub>N as their formation energies are very high (see the supplementary material). If both V<sub>N</sub> and O<sub>i</sub> are present in the material, interstitial oxygen may diffuse to the nitrogen vacancy site and become O<sub>N</sub> as it will release 6.73 eV and 5.55 eV of energy in TiN and Al<sub>0.75</sub>Sc<sub>0.25</sub>N, respectively. Similarly, if O<sub>N</sub> and N<sub>i</sub> are present simultaneously in TiN, N<sub>i</sub> will swap its position with O<sub>N</sub> by displacing it to the interstitial (O<sub>i</sub>) site as it will result in an energy gain of 0.59 eV, which can result in an increase in O<sub>i</sub> defect concentrations in TiN. In Al<sub>0.75</sub>Sc<sub>0.25</sub>N, O<sub>N</sub> + N<sub>i</sub> configuration is like O<sub>i</sub> one, as in both cases, one O and one N occupy the split interstitial site along the [111] direction [Fig. S2(f) in the supplementary material].

To validate the computational results, XANES measurements are performed on TiN and  $Al_{0.72}Sc_{0.28}N$  films with a focus on the oxygen K-edges. The spectrum in TiN [see Fig. 2(a)] reveals two peaks, highlighted as TI and TII, that are centered around 532 eV and 543 eV, respectively. Though the peak at ~532 eV (TI) usually exhibits splitting into two sub-peaks due to the hybridization of O-2*p* orbitals with the *d* orbitals of transition metals in several oxides, where metals have an octahedral coordination, in the present case, no such splitting is observed for reasons described later. The other broad peak at ~543 eV (TII) in Fig. 2(a) arises due to the hybridization of O-2*p* states with Ti-4*p* states and was also



FIG. 2. Experimental (red line) and simulated (green and blue lines) XANES spectra of the O K-edge in TiN (a) and AIScN (b). In the simulated graph, the green line represents the K-edge of O<sub>N</sub>, and the blue line represents the K-edge of O<sub>i</sub>.

previously observed in other oxides.<sup>72–74</sup> Similarly, the O K-edge XANES spectrum of  $Al_{0.72}Sc_{0.28}N$  exhibits three localized bands named BI, BII, and BIII [see Fig. 2(b)]. To understand the origin and shape of the peaks, the XANES spectrum of the O K-edge is simulated in TiN and (Al,Sc)N for isolated  $O_N$  and  $O_i$  defects and the most stable defect configuration  $4O_N + O_i$  obtained from DFT by the full potential multi-scattering method [see Figs. 2(a) and 2(b)].

The theoretically obtained XANES spectrum for O<sub>N</sub> in TiN shows two peaks near the absorption threshold named A1 and A2 in Fig. 2(a). The Ti-3d orbitals split into  $t_{2g}$  and  $e_g$  states as a result of ligand field splitting in octahedral geometry. These t<sub>2g</sub> and e<sub>g</sub> states hybridize with O-2p states resulting in the two peaks  $(A_1 \text{ and } A_2)$  in the O K-edge. Similar splitting of the peak in the O K-edge is also observed in other transition metal oxides where the transition metals have octahedral geometry,75-77 such as the O K-edge splitting in anatase and rutile TiO2. On the contrary, the calculated XANES spectrum for interstitial oxygen reveals only one peak near the absorption edge (~530 eV) and no splitting of the peak which is due to a tetrahedral coordination occupation of O<sub>i</sub> consistent with other transitional metal oxides having tetrahedral coordination.<sup>78</sup> The O K-edge in the most stable defect complex  $(4O_N + O_i)$ also shows a splitting of the peak for O<sub>N</sub> with small shoulder features. Also, the relative intensities of A1 and A2 in isolated ON and O<sub>N</sub> in the 4O<sub>N</sub> + O<sub>i</sub> defect complex are different. A distorted octahedral geometry caused by Oi can give rise to these extra features. The O K-edge of O<sub>i</sub> in this defect complex also shows a single broad peak similar to that of the isolated O<sub>i</sub>. The presence of both  $O_N$  and  $O_i$  in the  $4O_N + O_i$  defect complex will give rise to a single broad peak observed experimentally. The broad TII peak observed experimentally is slightly shifted toward higher energy compared with the peak present in the simulated spectra of  $4O_N + O_i$ . The presence of other types of O defects in small amounts along with the most stable defect  $4O_N + O_i$  might result in such little shifts of the TII peak. Also, multiple overlapped peaks in the simulated spectra near 543 eV can result in a single broad peak.

Similar to TiN, theoretical XANES spectra of the O K-edge in Al<sub>0.75</sub>Sc<sub>0.25</sub>N:O with both O<sub>N</sub> and O<sub>i</sub> configurations and their defect complex [see Fig. 2(b)] are computed. Note that the isolated O<sub>N</sub> also splits into two features, while when located at an interstitial site, the behavior of oxygen atoms is similar to what is found in glassy materials<sup>79,80</sup> probably due to a high structural distortion near O<sub>i</sub> in Al<sub>0.75</sub>Sc<sub>0.25</sub>N as it occupies the split interstitial site instead of the tetrahedral site [see Fig. 2(f) in the supplementary material]. In energetically favorable defect complexes such as  $nO_N + O_i$  (here shown only for  $4O_N + O_i$ ), the K-edge of both  $O_N$  and  $O_i$  shows multiple overlapped peaks. Thus, the broad XANES spectra observed experimentally is due to the presence of  $nO_N + O_i$  kind of defects.

The XANES spectra reflect the empty density of states above the Fermi level in the conduction band, implying that XANES absorption spectra can be directly correlated with the partial density of states in the conduction band if the absorption edge is aligned with the Fermi level. Thus, to validate the role of the  $4O_N + O_i$  defect complex in the observed XANES spectra, we have calculated the partial density of states (p-DOS) of O-2*p*, Ti-3*d*, and Sc-3*d* states in these defect complexes, and they are shown in Fig. 3. Ti and Sc-3*d* states show a clear splitting in  $t_{2g}$  and  $e_g$  orbitals due to ligand field splitting. The 3*d* states of Ti bonded with O



FIG. 3. Partial density of electronic states (p-DOS) of Ti (a) and O (c) in TiN:40<sub>N</sub> + O<sub>i</sub> and Sc (b) and O (d) in AlScN:40<sub>N</sub> + O<sub>i</sub> is presented.

are shifted toward a lower energy side compared to Ti bonded with N [see Fig. 3(a)]. A similar shifting of the 3d states is also observed for Sc in  $Al_{0.72}Sc_{0.28}N:4O_N + O_i$  [Fig. 3(b)]. The p-DOS of the O-2p states in TiN:O<sub>N</sub> clearly shows splitting due to its hybridization with the Ti-3d states as described earlier. On the other hand, O<sub>i</sub>-2p shows a single intense peak similar to the simulated XANES spectra. The difference in the coordination geometry between O<sub>N</sub> and O<sub>i</sub> is the reason behind the non-splitting of the 2p states in O<sub>i</sub>. The intense peak from O<sub>i</sub> will significantly dominate the DOS of oxygen in the  $4O_N + O_i$  defect complex, and the splitting of the  $O_N$ states will broaden the peak, which will result in a single broad peak observed in the experimental XANES spectra. In contrast to TiN, the O-2p states in  $Al_{0.72}Sc_{0.28}N:4O_N + O_i$  consist of multiple overlapped peaks due to their hybridization with both Sc and Al states. The experimental XANES of the O K-edge in Al<sub>0.72</sub>Sc<sub>0.28</sub>N has an overall effect of these multiple peaks present in the  $nO_{N} + O_{i}$  (here shown only for  $4O_{N} + O_{i}$ ) defect complex.

While the first-principles density functional theory modeling and x-ray absorption spectroscopy analysis were used to understand the structure of the oxygen defects in TiN and Al<sub>0.72</sub>Sc<sub>0.28</sub>N, HRTEM-STEM imaging and oxygen EDS mapping and quantitative estimations are performed to understand their spatial distribution. EDS quantitative mapping (across several sample regions and several superlattices) indicates that close to the MgO substrate (up to 350 nm), TiN layers exhibit ~1.5 at. % higher oxygen than in the  $Al_{0.72}Sc_{0.28}N$  layers [see Figs. 4(a)-4(d)]. However, higher up in the superlattice [from 350 nm to the top surface of the films (~1.8  $\mu$ m) away from the substrate], no significant difference in the oxygen content between the TiN and Al<sub>0.72</sub>Sc<sub>0.28</sub>N layers was observed [see Figs. 4(e)-4(h)]. The concentration of oxygen, however, was similar in both the TiN and the Al<sub>0.72</sub>Sc<sub>0.28</sub>N layers higher up in the superlattice compared with regions that are close to the MgO (substrate). These results, therefore, indicate the possibility of oxygen diffusion during the growth process most likely from the MgO substrate. As mentioned earlier, there are other sources from which oxygen can be incorporated into the samples. Therefore, as the modeling results represent the oxygen incorporation during the growth process primarily, caution should be exercised before directly comparing the quantitative estimates from STEM-EDS analysis and the modeling results. However, the present study clearly establishes that O in transition metal nitrides stays in the form of a defect complex  $(nO_N + O_i)$ , i.e., a complex of substitutional (O<sub>N</sub>) and interstitial (O<sub>i</sub>) defects. A significant intensity of the  $Ti-O_x$  peak in Ti-2p core levels spectra obtained with x-ray photoelectron spectroscopy also supports our conclusions here.<sup>31</sup> The clustering of O is also observed in EDS mapping of O near the defective region in the superlattice [see Fig. S3(c) in the supplementary material]. Possibly, the difference in the oxygen



FIG. 4. (a) HAADF-STEM micrograph of the TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattice having a 15 nm period thickness with regions that are close to the MgO substrate. (b) and (c) STEM-EDS mapping of titanium and oxygen elements, respectively, that shows well-defined and sharp interfaces. (d) EDS line profile of oxygen concentration across the interfaces is presented, which shows a higher oxygen content in TiN layers in comparison with that in Al<sub>0.72</sub>Sc<sub>0.28</sub>N. (e) HAADF-STEM micrograph of the same superlattice with regions that are further away from the interface. Titanium (f) and oxygen (g) elemental STEM-EDS maps are shown. (h) EDS line profile of oxygen concentration across the interface is presented, which shows similar oxygen content in both layers.

concentration in TiN and Al-rich  $Al_{0.72}Sc_{0.28}N$  could be a leading factor in the small difference in the estimation of the Schottky barrier height of the TiN/(Al,Sc)N heterostructure determined by x-ray spectroscopy and from the theoretical calculations.<sup>31</sup>

### CONCLUSION

In conclusion, by employing a combination of experimental x-ray absorption measurement and first-principles theoretical modeling, the oxygen impurity defect configurations in transition metal nitrides such as TiN and  $Al_{0.72}Sc_{0.28}N$  and in their epitaxial TiN/ $Al_{0.72}Sc_{0.28}N$  metal/semiconductor superlattice structures are analyzed. The results show the site preference of oxygen in TiN in the form of a defect complex consisting of substitutional and tetrahedrally occupied interstitial oxygen atoms  $(4O_N + O_i)$ . In contrast to TiN, in  $Al_{0.75}Sc_{0.25}N$ , the interstitial defect site in the  $nO_N + O_i$  strongly depends on the number of  $O_N$  and migrates from a split interstitial site to a tetrahedral site with an increasing number of  $O_N$ . The number of substitutional oxygen atoms that are attached to cations in  $Al_{0.75}Sc_{0.25}N$  in the  $nO_N + O_i$  defect complex is sensitive to the oxygen partial pressure. The electronic DOS shows the shifting of Ti-3*d* and Sc-3*d* states in the presence of oxygen.

Partial-DOS of  $O_N$  and  $O_i$  in the  $4O_N + O_i$  defect complex shows similar behavior as simulated and experimental XANES and very well support the presence of such defect complexes in these transitional metal nitrides as predicted by DFT. Overall, our work sheds light on the energetics and electronic structures of oxygen impurity defects in TiN,  $Al_{0.72}Sc_{0.28}N$ , and their lattice-matched TiN/ $Al_{0.72}Sc_{0.28}N$  metal/semiconductor superlattices for a range of solid-state energy conversion applications.

#### SUPPLEMENTARY MATERIAL

The supplementary material contains information related to the superlattice structure, the representation of various defect configurations, and evidence of oxygen clustering inside the superlattices.

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#### DATA AVAILABILITY

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

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