Role of oxygen in TiN(111)/Si$_x$N$_y$/TiN(111) interfaces: Implications for superhard nanocrystalline nc-TiN/a-Si$_3$N$_4$ nanocomposites

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We report first-principles density-functional theory calculations to investigate the role oxygen impurities play in determining the strength of TiN(111)/Si$_x$N$_y$/TiN(111) interfaces, as may occur in the superhard and highly thermally stable “nc-TiN/a-Si$_3$N$_4” nanocomposite. For nitrogen-rich conditions, our investigations predict that the interfacial region consists of a thin “β-like Si$_x$N$_y” layer with the silicon atoms tetrahedrally coordinated to nitrogen atoms, while under nitrogen-poor conditions, an octahedrally bonded Ti-Si-Ti arrangement is preferred. The tensile strength of TiN in the ⟨111⟩ direction is found to be notably higher than in the ⟨100⟩ and ⟨110⟩ directions (90 GPa, similar to the weakest ⟨111⟩ bonding direction in diamond), and is likely connected to the observed enhanced hardness of these nanocomposites. For the structure favored under the technically relevant nitrogen-rich conditions, oxygen atoms are predicted to diffuse to the interface region and occupy nitrogen sites. This gives rise to a notable reduction in the calculated interface tensile strength, which could lead to a decreased hardness, in accord with recent experimental indications. For the structure favored under nitrogen-poor conditions, oxygen impurities are predicted to have little effect on the tensile strength.

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I. INTRODUCTION

In recent years there has been considerable effort aimed at identifying and developing new and improved superhard and ultrahard materials.1–10 Such structures clearly have current and potential technological and industrial applications, but are also of fundamental interest with regard to understanding the mechanisms responsible for the enhanced hardness. One strategy, that has led to reported hardnesses equal to, and exceeding, that of diamond (≥100 GPa),6,7 is based upon a generic design concept involving self-organized spinodal phase segregation11 leading to nanocomposites with strong and sharp interfaces between nanocrystalline regions and thin amorphous layers.12 The nanocomposite, so-called “nc-TiN/a-Si$_3$N$_4”, may be regarded as the prototype for these systems. Although it does not possess the highest reported hardness [but values of 50–60 GPa,7,12–14 which are still significantly higher than that of crystalline rocksalt structure TiN, ~18–22 GPa (Refs. 15 and 16)], it is the most studied and is comparatively “simple” compared to the more complex ternary nanocomposites as such “nc-TiN/a-Si$_3$N$_4/a-$ and “nc-TiSi$_2”,12 which exhibit reported hardnesses of 80–105 GPa.7 Other members of this family of superhard nanocomposites include, e.g., nc-MN/a-Si$_3$N$_4$ (M=W, V, Al$_{1-x}$Ti$_x$). The nc-TiN/a-Si$_3$N$_4$ nanocomposite, similar to the others, apparently exhibits the maximum hardness when prepared with only a very thin layer of silicon nitride (0.3–0.5 nm) between the TiN nanocrystallites.12 It is thought that in addition to a strong interface, the amorphous phase plays an important role in determining the hardness since a dislocation which might form in the crystalline component cannot propagate into the amorphous phase.

Recently, there have been conflicting reports regarding the reported hardness of the “model” nc-TiN/a-Si$_3$N$_4$ nanocomposite. In particular, there has been some difficulty in reproducing the hardness values of 50–60 GPa by some authors, e.g., Ref. 15 obtained <32 GPa. Subsequently, it has been suggested that this difficulty could be due to either a too low nitrogen pressure, or a too low deposition temperature (which may prevent the realization of the stable structure), or to contamination by oxygen impurities.17 Clearly, it is of significant importance to know whether all the ceramic nanocomposites exhibit such a superstrengthening, and critical experimental and theoretical evidence is needed to verify these findings which should include detailed structural and mechanical characterization.

In our previous study,18 we performed extensive density-functional theory (DFT) calculations in order to predict the atomic structure of the interfaces which may occur in the nc-TiN/a-Si$_3$N$_4$ system. Quantitative experiments provided some guidance: High-resolution transmission electron microscopy (HRTEM) studies19 reported that the main crystallographic orientational relationship is [0001] Si$_3$N$_4∥[110] TiN with (1010) Si$_3$N$_4∥(111) TiN. Thus, the interfaces we considered involved Si$_3$N$_4$ configurations sandwiched between TiN(111) planes. This is a somewhat special orientational relationship since it allows polar-plane matching: The {111} lattice planes of TiN are polar, formed by either nitrogen or titanium atoms; similarly, the {1010} lattice planes of Si$_3$N$_4$ are polar planes, formed by either nitrogen or silicon atoms.18 In the orientation {1010} Si$_3$N$_4∥{111} TiN, the polar planes are parallel, which may afford a minimization of the electrostatic potential. Our calculations18 found that for nitrogen-rich conditions, the most favorable configurations involve very thin layers of Si, which are purely nitrogen-coordinated and tetrahedrally bonded. For increasingly nitrogen-poor conditions, interfaces involving Ti-Si-N, and predominantly octahedral Ti-Si-Ti, bonding are preferred. In the present work we investigate the strength of the identified low energy interfaces and the effect of oxygen impurities thereon, and the
implications this has for the practical creation of superhard coatings. The manuscript is organized as follows: In Sec. II we describe the calculation method, in Sec. III we briefly explain the identified low energy interface structures, and in Sec. IV the results of the tensile strength of these interfaces, as well as of bulk TiN and $\beta$-Si$_3$N$_4$, are described. In Sec. V the effect of oxygen impurities on the strength of the low energy interfaces are reported, and Sec. VI contains the conclusion.

II. CALCULATION METHOD

All the DFT calculations are performed using the DMol$^3$ program with the generalized gradient-approximation (GGA) for the exchange-correlation functional (PBE). In DMol$^3$, the wave functions are expanded in terms of accurate numerical basis sets. We use the double-numeric quality basis-set with polarization functions (DNPs) and local all-electron pseudopotentials which include scalar relativistic corrections (VPSR). We use an atomic cutoff radius of 9 bohr for all calculations. For supercells with (1 $\times$ 1), (1 $\times$ 3), and (2 $\times$ 2) lateral periodicity, we use Monkhorst-Pack meshes of 6 $\times$ 6 $\times$ 1, 2 $\times$ 6 $\times$ 1, and 4 $\times$ 4 $\times$ 1, respectively, yielding 20, 8, and 10 k points in the irreducible part of Brillouin zone. Convergence tests which justify these parameter choices are reported in Ref. 18.

The formation energy of an interface is calculated as

$$E^f(\mu_{\text{Si}}, \mu_{\text{N}}, \mu_{\text{T}}) = (E^\text{int}_{\text{tot}} - E^\text{TN}_{\text{slab}} - n\mu_{\text{N}} - m\mu_{\text{Si}} - l\mu_{\text{T}})/S,$$

where $E^\text{int}_{\text{tot}}$ and $E^\text{TN}_{\text{slab}}$ are the total energies of the interfacial system under consideration and the 20-layer reference TiN(111) slab with interface area $S$. $\mu_{\text{N}}$, $\mu_{\text{Si}}$, and $\mu_{\text{T}}$ are the nitrogen, silicon, and titanium atom chemical potentials, and $n$, $m$, and $l$ are the number of N, Si, or Ti atoms that are added to the TiN slab in order to create the interface of interest. The interface is located in the center of the 20-layer TiN(111) slab (containing 20 atoms), which is surrounded by a vacuum region of 20 Å. We consider so-called nitrogen-rich and nitrogen-poor (or Ti-rich) conditions. For the former, corresponding to excessive nitrogen molecules in the system, we take $\mu_{\text{N}} = \frac{1}{2}E_{\text{N}_2}$ (half the total energy of $N_2$) and for the latter, $\mu_{\text{T}} = E^\text{bulk}_{\text{Ti}}$, which is the total energy of a bulkhcp Ti atom. We assume that in equilibrium, $\mu_{\text{TN}} = \mu_{\text{Si}} + \mu_{\text{N}}$, where $\mu_{\text{TN}}$ is the chemical potential of bulk rocksalt structure TiN. For N-rich conditions we then have $\mu_{\text{T}} = E^\text{TN} - \frac{1}{2}E_{\text{N}_2}$, and for N-poor conditions we have $\mu_{\text{N}} = E^\text{TN} - E^\text{bulk}_{\text{Ti}}$. For the Si atom chemical potential, $\mu_{\text{Si}}$, under nitrogen-rich conditions we assume an upper limit determined by $\mu_{\text{Si}} = 2\mu_{\text{N}} = 4\mu_{\text{N}}$, where $\mu_{\text{Si}}$, $\mu_{\text{N}}$, and $\mu_{\text{N}}$ are the chemical potential of bulk $\beta$-Si$_3$N$_4$, which gives $\mu_{\text{Si}} = \frac{1}{2}(E^\text{bulk}_{\text{Si}_3\text{N}_4} - 2E_{\text{N}_2})$, where $E^\text{bulk}_{\text{Si}_3\text{N}_4}$ is the total energy of a bulk unit of $\beta$-Si$_3$N$_4$. For N-poor conditions, we take an upper limit of the Si chemical potential determined by bulk TiSi$_2$, so $\mu_{\text{TiSi}_2} = \mu_{\text{Ti}} + 2\mu_{\text{Si}}$, where $\mu_{\text{TiSi}_2}$ is the chemical potential of bulk TiSi$_2$. Then $\mu_{\text{Si}} = \frac{1}{2}(E^\text{TiSi}_2 - E^\text{bulk})$, where $E^\text{TiSi}_2$ is the total energy of a bulk unit of TiSi$_2$. These choices for the Si atom potential arise because in order to have a realistic estimate of the formation energy, we must determine $\mu_{\text{Si}}$ from the most stable phase for a given value of the nitrogen chemical potential. In Ref. 18, we showed that for N-poor conditions this phase was bulk TiSi$_2$ while for N-rich conditions, this phase was bulk Si$_3$N$_4$. This “crossover” of reference phases is responsible for the kink in Fig. 2 at around $\mu_{\text{N}} = -1.9$ eV.

For the consideration of interstitial and substitutional oxygen in the interface systems, the relative stability is evaluated by the quantities

$$E^f = (E^\text{int}_{\text{tot}} - E^\text{int}_{\text{tot}} - \mu_{\text{O}}),$$

$$E^f = (E^\text{int}_{\text{tot}} - E^\text{int}_{\text{tot}} - \mu_{\text{O}} + \mu_{\chi}),$$

respectively. $E^\text{int}_{\text{tot}}$ is the total energy of the interface with oxygen (or of a supercell of bulk TiN with oxygen, which we also consider), and $\mu_{\text{O}}$ is the chemical potential of the Ti or N atom which is substituted by oxygen. For the chemical potential of oxygen $\mu_{\text{O}}$, we assume an upper limit determined by $\mu_{\text{TiO}_2} = \mu_{\text{Ti}} + 2\mu_{\text{O}}$, where $\mu_{\text{TiO}_2}$ is the total energy of bulk titanium dioxide. Using the relationships described above $\mu_{\text{N}}$ and $\mu_{\text{Ti}}$, this gives for nitrogen-rich conditions $\mu_{\text{O}} = 1/2(E_{\text{TiO}_2} - E^\text{Si}_2 - 2E_{\text{N}_2})$ and for titanium-rich (nitrogen-poor) conditions, $\mu_{\text{O}} = 1/2(E_{\text{TiO}_2} - E^\text{bulk})$.

We also consider the tensile stress of the low energy interfaces, $\sigma_{ij}$, which is calculated by

$$\sigma_{ij} = \frac{1}{V} \left( \frac{\partial U}{\partial \eta_{ij}} \right),$$

where $U$ is the internal (or total) energy, $V$ is the volume of the region under strain, and $\eta_{ij}$ is the infinitesimal strain. In this work, we only consider $\sigma_{yy}$, that is, tensile strain perpendicular to the plane of the interface (or of the crystallographic plane of interest for the bulk systems).

We also calculate the work of separation of certain interfaces by the standard definition $W_{\text{sep}} = (E^\text{tot}_{1} + E^\text{tot}_{2} - E^\text{tot}_{12})/S$, where $E^\text{tot}_{1}$ is the total energy of the separated slab $i$ and $E^\text{tot}_{12}$ is the total energy of whole system.

III. LOW ENERGY INTERFACE STRUCTURES

In our previous publication, we predicted various low energy TiN(111)/Si$_3$N$_4$/TiN(111) interface structures from the consideration of a possible 55. The atomic geometries and formation energies of the determined lowest energy structures are shown in Figs. 1 and 2, respectively. The most favorable configuration for nitrogen-rich conditions is a so-called (1 $\times$ 3) “$\beta$-like Si$_3$N$_4$(1010)” interface (Fig. 1, lower right). In this geometry there is a thin layer of Si atoms which are tetrahedrally coordinated to nitrogen atoms. The preferred configuration for nitrogen-poor conditions is a (1 $\times$ 1) “hcp-fcc-TiSi” interface (Fig. 1, upper right), in which the Si atoms are octahedrally bonded to Ti atoms. The label “hcp-fcc” reflects the atomic position of the TiSi-layer with respect to the lower and upper surrounding ten-layer TiN slabs. For a very small range of the nitrogen chemical potential (around $\mu_{\text{N}} = -1.3$ to $-1.2$ eV, see Fig. 2), the “top-
The role of oxygen in boron-nitride based materials. The hardness of a material is defined as the resistance it offers to an external mechanical action. In static indentation tests, a pyramid is forced into a surface and the load per unit area of impression is taken as the measure of hardness. The Vickers scale, for example, is frequently used.

In this section we calculate the tensile strength of the four interfaces: (1×1) hcp-fcc-TiN, (1×1) top-top-SiN, (1×3) β-like Si3N3, and (2×2) γ-like Si3N4. For TiN, we consider strain in the various inequivalent crystallographic directions, the weakest link that sets the limit on the material strength can be identified. First-principles calculations of the ideal strength have recently been performed, for example, to understand and predict the behavior the hard carbon clathrates and carbon-boron-nitride based materials.

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FIG. 1. (Color online) Atomic structure of various TiN(111)/Si3N4/TiN(111) interfaces: Upper, from left to right: the (1×1) “top-hcp-Si” interface (involving tetrahedral N-Si-Ti bonding), the (1×1) “top-top-SiN” interface (involving N-Si-N bonding), and the (1×1) “hcp-fcc-TiSi” interface (involving Ti-Si-Ti bonding, most favorable for nitrogen-rich conditions). Lower left: the (2×2) “γ-like Si3N4” interface (involving N-Si-N bonding), and right, the (1×3) “β-like Si3N3(1010)” interface (involving N-Si-N bonding, most favorable for nitrogen-rich conditions).

FIG. 2. (Color online) Interface formation energies [see Eq. (1)] as a function of the nitrogen chemical potential \( \mu_N \) for the low energy interface configurations. The chemical potential is given with respect to half the total energy of the N₂ molecule.

IV. TENSILE STRENGTH

The hardness of a material is defined as the resistance it offers to an external mechanical action. In static indentation tests, a pyramid is forced into a surface and the load per unit area of impression is taken as the measure of hardness. The Vickers scale, for example, is frequently used. In the search for new super- and ultrahard materials, research has been directed at finding structures with high values of the bulk modulus and shear modulus. While there is some correlation of the former with hardness values, it has little direct connection. A better correlation has been observed between hardness and shear modulus, although the dependence is not unequivocal and monotonic. Recently, Jhi et al. have investigated the correlation between valence electron concentration and hardness, and related the hardness to the band structure, while Gao et al. have attempted to relate the hardness to the bond length, ionicity, and band gap of a material in equilibrium. A more stringent test may be provided by the ideal strength, i.e., the stress at which a crystal becomes mechanically unstable. By determining the stresses along various inequivalent crystallographic directions, the weakest link that sets the limit on the material strength can be identified. First-principles calculations of the ideal strength have recently been performed, for example, to understand and predict the behavior the hard carbon clathrates and carbon-boron-nitride based materials.

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terfaces, namely, for TiN we use 20-atom supercells surrounded by 20 Å of vacuum, where the lateral (1 × 1) unit cell contains the crystallographic plane of interest. For TiN(111), TiN(110), and TiN(100) there will be one, two, and two atoms per lateral unit cell, respectively, resulting in 20, 10, and 10 atomic layers. For the β-Si3N4 system, we use a 28-atom slab, corresponding to two bulk unit cells, which we also surround by 20 Å of vacuum space. The (1010) crystallographic orientation lies in the plane of the lateral (1 × 1) unit cell, similarly to that of the β-like Si2N3 interface.

We calculate the strength in two ways: (i) by applying a uniform strain throughout the system perpendicular to the plane of the interface (or crystallographic plane of interest for the bulk systems) and (ii) allowing atomic relaxations, as will be explained below. The results for the first approach are shown in Fig. 3(a) in terms of stress-strain curves.

It can be clearly seen that TiN(111) has the highest tensile strength, where it is greater than 90 GPa. This value is very similar to the tensile strength of diamond in the ⟨111⟩ direction, which we calculate to be 86 GPa [determined analogously by using a slab surrounded by vacuum (and H-terminated)]. Compared to TiN(111), however, the strain at maximum strength is considerably smaller (ε = 0.12 vs 0.45) indicating a more brittle character. For diamond, the tensile strength in the ⟨100⟩ and ⟨110⟩ directions (225 and 130 GPa, respectively) are notably larger than in the ⟨111⟩ direction, and so the latter limits the critical stresses that diamond can withstand. For TiN, the tensile strength in the ⟨100⟩ direction is the smallest, being around 35 GPa, in the ⟨110⟩ direction it is around 50 GPa. This trend is reasonable since it reflects the ordering of the surface energies of the TiN(111), ⟨110⟩, and ⟨100⟩ surfaces. The strength of β-Si3N4 in the ⟨1010⟩ direction is slightly larger than that of TiN(110), being close to 60 GPa. Interestingly, three of the interface systems exhibit a rather similar tensile strength (~70 GPa), which lies in between the values for TiN(111) and β-Si3N4 ⟨1010⟩, while that of the more atomically dense γ-like Si3N4 interface is considerably higher, 85 GPa.

In the second approach for investigating the interface tensile strength, we do as follows. As for approach (i) we uniformly strain the system, then we fix the positions of the atoms in the upper and lower layers of the slab, and relax all other atoms. We do this in two ways. First, we start with small applied strain and obtain the relaxed atomic configuration. Then, in the next incremental strain step, we apply the strain to this atomically relaxed system, fix the positions of the atoms in the upper and lower layers of the slab, and relax all other atoms; and so on for subsequent strains. For the second way, we simply apply the strain, always starting with the atomic positions of the interface system in the equilibrium (zero strain) geometry. The results obtained from both approaches are actually found to be identical. When allowing for atomic relaxation, we find that bonds break at the interface and the strength is reduced compared to that of approach (i) [shown in Fig. 3(a)]. This can be seen from the full curves in Fig. 4 for the four interfaces: (1 × 1) top-top-SiN, (1 × 3) β-like Si3N4, (1 × 1) hcp-fcc-TiSi, and (2 × 2) γ-like Si3N4, where the values are ~20, ~35, ~27, and 25 GPa, respectively; the interface tensile strength being greatest for the lowest energy β-like Si3N4 structure (for N-rich conditions).

For the β-like Si2N3 interface, we plotted the electron density for several strain values as shown in Figs. 5(a)–5(c). It can be seen that the bonds that break involve Si atoms which form the “upright,” single bonds to nitrogen atoms in the upper and lower planes, as opposed to the Si-N bonds where Si is threefold coordinated to the N atoms. For the (1 × 1)-SiN interface, the bonds that break are the “upright,” single bonds between nitrogen and titanium atoms (see Fig. 1). For the (1 × 1) hcp-fcc-TiSi structure, from the electron density for several strain values as shown in Figs. 6(a)–6(c), it can be seen that the bonds that break are between the lower Si and Ti atoms of the Si-Ti-Si interface region. The bonds which break under application of tensile strain for these interfaces are indicated by the (full) lines in Fig. 7. The behavior for the γ-like Si3N4 interface is rather different to the other interface systems, such as the β-like Si2N3 interface in that it is difficult to determine exactly which bonds are broken. These atomic movements with applied strain are quite complex, giving rise to a rather “sticky” or plastic behavior.

For the strength of the bulk TiN systems in the three low index crystallographic directions considered, clearly allowing atomic relaxation would not result in any preferential bonds breaking due to symmetry, i.e., the bonding between all atomic planes is identical. To compare more closely with the strength of the relaxed interface systems (described above), we deliberately break the bonds between two planes by applying strain only between the two atomic planes involved. The positions of all other atoms are fully relaxed in response to the applied strain. The results are shown in Fig. 3(b),
where the same trend to that in Fig. 3(a) is found. Comparing these values to those of the interface systems (Fig. 4, full curves) we can notice that the strength of bonding between TiN(111) planes is still the highest (~48 GPa) and that of the interface system β-like Si₂N₃ has the next highest strength (~35 GPa). For comparison, the interplanar strength of bonding between the C-C bonds of diamond in the (111) direction is 37 GPa, where in this case the strain at maximum strength is εzz = 0.14, versus 0.09 for the β-like Si₂N₃ interface. The strength of bulk β-Si₃N₄(1010) interplanar bonding is next highest (~27 GPa) (breaking the same bonds as found occurs for the β-like Si₂N₃ interface), followed closely by the hcp-fcc-TiSi interface (~25 GPa). The

FIG. 4. (Color online) Interface tensile stress with no oxygen (full curve) and with different oxygen concentrations as indicated (see text) for the (a) top -top-SiN, (b) β-like Si₂N₃, (c) hcp-fcc-TiSi, and (d) γ-like Si₃N₄ interfaces.

FIG. 5. (Color online) The electron density distribution of the β-like Si₂N₃ interface region for different strains without oxygen at (a) εzz = 0, (b) εzz = 0.09 (maximum strength), (c) εzz = 0.12, and different strains with oxygen (εzz = 1.54%) at (d) εzz = 0, (e) εzz = 0.06 (maximum strength), and (f) εzz = 0.1. The small dots indicate the position of atoms projected in the plane of the plot.

FIG. 6. (Color online) The electron density distribution of the (1 × 1) hcp-fcc-TiSi interface region for the different strains without oxygen at (a) εzz = 0, (b) εzz = 0.08 (maximum strength), (c) εzz = 0.12, and different strains with oxygen (“high” concentration, εzz = 4.35%) at (d) εzz = 0, (e) εzz = 0.8 (maximum strength), and (f) εzz = 0.12.
TABLE I. Formation energies of atomic oxygen in various sites (see Fig. 8) in bulk TiN, as calculated in a 54-atom supercell. The unit is eV. The lowest formation energies are given in bold type.

<table>
<thead>
<tr>
<th>Oxygen site</th>
<th>N-poor</th>
<th>N-rich</th>
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</thead>
<tbody>
<tr>
<td>O_i</td>
<td>6.39</td>
<td>4.65</td>
</tr>
<tr>
<td>O_j</td>
<td>8.86</td>
<td>7.12</td>
</tr>
<tr>
<td>O_N</td>
<td>-0.98</td>
<td><strong>0.76</strong></td>
</tr>
<tr>
<td>O_Ti</td>
<td>12.76</td>
<td>7.54</td>
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</table>

V. EFFECT OF OXYGEN IMPURITIES

A. Preferred oxygen site

We first consider the behavior of oxygen in bulk rocksalt structure TiN. In particular, we calculate the preferred site using a 54-atom supercell. We investigate two interstitial sites O_i, O_j and two substitutional sites O_N and O_Ti for oxygen on a nitrogen and on a titanium site, respectively. These sites are sketched in Fig. 8, and the formation energies are listed in Table I. It can be seen from Table I that the O_N site is significantly most favorable under both N-rich and N-poor conditions, which is not surprising given the good atomic size match of N and O (and hence low deformation energy cost).

We now consider the preferred adsorption site of oxygen in the interface systems, (1×1) top-top-SiN (containing 22 atoms), (1×3) β-like Si_2N_3 (containing 65 atoms), (1×1) hcp-fcc-TiSi (containing 22 atoms), and (2×2) γ-like Si_3N_4 (containing 87 atoms). For the (1×1) interfaces, we investigate both “low” and “high” oxygen concentrations, where for the former case, we use larger (2×2) cells (containing 88 atoms) and for the latter, the (1×1) cells. We consider interstitial O_i and substitutional sites O_N and O_Ti at various locations as sketched in Fig. 9. The formation energies are listed in Table II and the preferred sites are depicted in Fig. 10.

For the (1×1) top-top-SiN interface, for nitrogen-rich conditions, oxygen prefers to occupy the interstitial site (O_i) at the interface, while under nitrogen-poor conditions (where...
TABLE II. Formation energy (in eV) of oxygen in various sites for the four interfaces. The values in brackets are for the high oxygen concentration as calculated in lateral (1 × 1) cells, while the other values are for the low oxygen concentration calculated in lateral (2 × 2) cells (see text). The lowest formation energies are given in bold type.

<table>
<thead>
<tr>
<th></th>
<th>(1 × 3)β-like Si₂N₃</th>
<th>hcp-fcc-TiSi</th>
<th>(2 × 2)γ-like Si₁N₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N-poor</td>
<td>N-rich</td>
<td>N-poor</td>
</tr>
<tr>
<td>O₁₁</td>
<td>0.70 (0.84)</td>
<td>−1.04 (−0.90)</td>
<td>O₁₁</td>
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<tr>
<td>O₁₂</td>
<td>2.19 (0.89)</td>
<td>0.46 (−0.85)</td>
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<tr>
<td>O₁₃</td>
<td>4.02 (3.17)</td>
<td>2.28 (1.43)</td>
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<tr>
<td>O₁₄</td>
<td>6.71 (4.49)</td>
<td>4.97 (2.75)</td>
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<td>7.63 (2.71)</td>
<td>5.89 (0.97)</td>
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<tr>
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<td>0.50 (0.36)</td>
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<td>−0.29 (−0.42)</td>
<td>1.45 (1.32)</td>
<td>O₁₈</td>
</tr>
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</table>

this is not an energetically favorable interface), oxygen prefers to occupy substitutional sites (O₁₁) at the interface. This trend is the same for both low and high oxygen concentrations. From comparison with the formation energies of O in bulk TiN (Table I), it is clear that oxygen atoms in these sites at the interface are considerably more favorable.

For the (1 × 3) β-like Si₂N₃ interface (the preferred structure for N-rich conditions), it can be seen that there are two N-substitutional sites for oxygen which have the lowest energy under both N-rich and N-poor conditions. These sites are also located at the interface and are significantly more favorable than for oxygen in bulk TiN in any site (see Table I). Thus, again we have the preference for oxygen to be located in the interface region. This picture is consistent with experimental measurements which indicate that impurities would have enough time to diffuse into the interface region at the deposition temperatures.³¹

For the hcp-fcc-TiSi interface under nitrogen-poor conditions (where this is the preferred structure), for both low and high oxygen concentrations, oxygen prefers to occupy a substitutional N site (O₁₁) just under the Ti-Si-Ti interface. On comparing this value to that of O in bulk TiN, however, we see that it is not as favorable as for O in bulk TiN. Thus, for this structure, under the N-poor conditions where it is the most stable interface considered, oxygen does not prefer to be located at the interface. For nitrogen-rich conditions (where this structure is not favorable), for the low oxygen concentration, oxygen atoms prefer to substitute Ti atoms at the interface (O₁₁), becoming bonded with Si and N atoms, while for high oxygen concentration, they prefer to be located at the interface in interstitial sites (O₁₂, O₁₃).

For the γ-like Si₁N₄ interface, the preferred O site (O₁₅) for both N-rich and N-poor conditions lies in the upper interface region and is bonded to a Si atom. The formation energies show that this site is practically degenerate with several other similar N sites.

B. Affect of oxygen on the tensile strength

Having established the preferred site for oxygen impurities in the low energy interfaces, we now investigate the effect they have on the tensile strength. We perform these calculations following approach (ii) as discussed above in Sec. IV, where strain is applied and the atoms relaxed. The results are presented in Fig. 4 (dashed and dot-dashed lines). For the top-top-SiN and β-like Si₂N₃ interface systems involving N-Si-N bonding, the O atoms are placed in the energetically favorable sites under nitrogen-rich conditions, namely, of O₁₁ and O₁, respectively (see Figs. 9 and 10). It can be seen that oxygen induces a significant reduction in the strength, the effect of which becomes greater for higher oxygen concentrations, and also bond breaking occurs for smaller strain values. For the top-top-SiN interface, the bond breaking occurs between the same atoms as for the case with no oxygen as described above, namely, between the “up-right,” single N, and Ti bonds. For the β-like Si₂N₃ interface,
Figs. 5(d)–5(f) show the electron density for selected values of strain. It can be seen that the presence of oxygen causes different bonds to break as compared to without oxygen. In particular, in the local vicinity of the oxygen impurity, the Si-O and the two lower Ti-N bonds break, in contrast to the upright single Si-N bonds for no oxygen. We attribute this to the strong Ti-O bond that forms as discussed below.

For the hcp-fcc-TiSi interface, predicted to be most favorable under nitrogen-poor conditions, oxygen is placed in the preferred ON site (see Fig. 9). In this case oxygen does not cause any reduction in the strength and bond breaking also occurs between Ti and Si bonds at the interface as for the system without oxygen; however, in this case the breaking is between the alternate Ti-Si bonds. This can be seen from Figs. 6(d)–6(f) which show the electron density distribution for several strains. Figure 7 summarizes the bonds that break under application of tensile strain for these interface systems with oxygen impurities (dashed lines) as compared to without oxygen present (continuous lines).

For the γ-like Si3N4 interface, the presence of oxygen does not induce a reduction in the strength, and in fact it is slightly larger for strain $e_{zz} > 0.09$. When oxygen is incorporated into this interface, the most stable position is in a substitutional site at the bottom of the upper TiN slab. During each applied strain, this oxygen atom almost does not change its environment with the Ti atoms in the upper slab. The other Si and N atoms of the interface region undergo a similar behavior as the case without oxygen. This results in a rather similar form of the strength-strain curve as that with no oxygen. The atomic geometries for increasing strain values are depicted in Fig. 11, which exhibit an “unfolding” or “consetinalike” behavior. This explains why the strength exhibits a rather “flat” behavior for strain values $e_{zz} > 0.12$.

C. Affect of oxygen on the nature of the bonding

It is interesting to consider the nature of the bonding of oxygen in the interface systems in order to understand the observed effect on the tensile strength. As an example, we performed an analysis of the electron density of the ground state of the top-top-SiN interface with tetrahedral N-Si-N bonding with different oxygen concentrations as shown in Fig. 12. The addition of a “low” oxygen concentration [Fig. 12(b)] is seen to reduce the electron density between the closest Si-N bond to oxygen, as well as between this same N atom and the Ti atom above it. The oxygen impurity primarily forms a bond with the neighboring Ti atoms. For the “high” concentration case [Fig. 12(c)], this O-Ti bond formation is very apparent and there is now practically no electron density between the O atom and the N and Si atoms below it. This change in bonding is reflected in, and responsible for, the extremely small value of the tensile strength [see Fig. 4(a), diamond symbols]. We attribute this behavior to be related to the greater bond strength of O to Ti as compared to Si: the heat of formation of TiO2 is $-9.73$ eV (Ref. 32) per formula unit while that of SiO2 is $-9.43$ eV per formula unit.

We also calculate the work of separation for this interface with no oxygen and with a low oxygen concentration ($\frac{1}{25} = 1.12\%$). The values are $0.127$ and $0.064$ eV/Å$^2$, respectively. This notable reduction is consistent with the found lower interface strength and with the described change in the electron density distributions.

In Table III we compare the various bond lengths of the four interface systems with the oxygen impurities present, to those of the equilibrium geometry without oxygen. In particular, we show the average bond lengths and the corresponding percentage deviation. To see the effect of oxygen most clearly, we list the values corresponding to high oxygen concentration for the top-top-SiN and hcp-fcc TiSi interfaces. For the former, where oxygen atoms are located in the interstitial site ($O_{11}$), the single, upright Ti-N bonds expand significantly to incorporate the O atoms, by up to 72.1%. The oxygen atoms bond preferably with the Ti atoms. In the “right side” of the β-like Si$_2$N$_3$ interface, which has no oxygen in the immediate neighborhood [see Fig. 7(b)],...
TABLE III. Calculated average bond lengths for the four interfaces of interest (in Å). For top-top-SiN and hcp-fcc-TiSi, the oxygen concentration is 4.35% (i.e., the high concentration). Values in parentheses give the percentage deviation to the equilibrium geometry without oxygen. For reference, the average bond length in SiO$_2$ is 1.617 Å, and in TiO$_2$, 1.956 Å.

<table>
<thead>
<tr>
<th>Interface</th>
<th>With oxygen</th>
<th>β-like Si$_3$N$_4$</th>
<th>With oxygen</th>
<th>hcp-fcc-TiSi</th>
<th>With oxygen</th>
<th>γ-like Si$_3$N$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d_{N,Si}$</td>
<td>$d_{N,Ti}$</td>
<td>$d_{Si,N}$</td>
<td>$d_{Ti,N}$</td>
<td>$d_{Si,O}$</td>
<td>$d_{O,Si}$</td>
</tr>
<tr>
<td>top-top-SiN</td>
<td>2.169</td>
<td>3.733 (72.1%)</td>
<td>2.128</td>
<td>2.143 (0.75%)</td>
<td>2.658</td>
<td>2.657 (−0.03%)</td>
</tr>
<tr>
<td></td>
<td>1.818</td>
<td>1.797 (−1.15%)</td>
<td>1.709</td>
<td>1.678 (−1.81%)</td>
<td>2.697</td>
<td>2.651 (−1.72%)</td>
</tr>
<tr>
<td></td>
<td>1.703</td>
<td>1.753 (2.96%)</td>
<td>1.808</td>
<td>1.815 (0.39%)</td>
<td>2.106</td>
<td>2.175</td>
</tr>
<tr>
<td></td>
<td>1.737</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.763</td>
</tr>
<tr>
<td></td>
<td>2.077</td>
<td>2.060 (−0.82%)</td>
<td>2.092</td>
<td>2.346 (12.14%)</td>
<td>2.125</td>
<td>2.199</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.695</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.684 (−0.65%)</td>
</tr>
</tbody>
</table>

There are almost no changes in the average bond lengths as compared to the system without oxygen (and thus the values are not listed). However, in the “left side” of the interface, which has oxygen in the N-site in the immediate neighborhood [see Fig. 7(b)], the presence of oxygen induces a contraction of the upright single bond between Si and the N atom above it (by 1.81%), and significantly lengthens (by 12.14%) and weakens the bonds between the lower N atoms and the Ti atoms (which are also bonded to O) in the surrounding bulk TiN. This explains why the interface breaks at these N-Ti bonds, as well as at the O-Si bonds.

For the hcp-fcc-TiSi interface, from comparison of the electron density distributions at the equilibrium geometries with and without oxygen [Figs. 6(a) and 6(d)], it can be seen that the Si atom and the lower Ti atom are slightly closer for the case of oxygen present, suggesting a small O-induced strengthening of the Si-Ti bonds. This change in bond length, as seen from Table I, amounts to a contraction of 1.72%. This is consistent with the fact that the interface breaks between the upper Ti-Si bonds when oxygen is present and not between the lower Ti-Si bonds as occurs when it is absent. The works of separation for this interface system, with and without oxygen, are rather similar. For no oxygen the value is 0.32 eV/Å$^2$, while for a low oxygen concentration it is 0.33 eV/Å$^2$ and for a high oxygen concentration it is 0.30 eV/Å$^2$, as is consistent with the similar values of the tensile strength.

For the γ-like Si$_3$N$_4$ interface, in contrast to the β-like Si$_2$N$_3$ interface, the presence of O does not induce any significant lengthening (weakening) of neighboring Ti-N bonds (but actually a slight contraction of −2.10%), and the O-Si bond, which breaks in the β-like Si$_2$N$_3$ interface, is slightly shorter in the γ-like interface. These slight changes are consistent with the small variation of the strength with oxygen incorporations, which is connected to the different and more dense γ-like Si$_3$N$_4$ interface.

VI. CONCLUSION

We report first-principles DFT investigations into the strength of TiN(111)/Si$_3$N$_4$/TiN(111) interfaces as may occur in the novel superhard and highly thermally stable nc-TiN/a-Si$_3$N$_4$ nanocomposites, and the effect of oxygen impurities thereon. The favorable interface formed under the technically relevant more nitrogen-rich conditions involves a single Si layer tetrahedrally coordinated to N atoms (i.e., the so-called “β-like Si$_3$N$_3$ interface”). Oxygen impurities are predicted to diffuse to the interface region and occupy nitrogen sites, forming strong bonds with Ti atoms and inducing a striking reduction in the tensile strength of the interface. In contrast, no significant decrease in the tensile strength is observed in the preferred phase under N-poor conditions (the so-called “hcp-fcc-TiSi” interface) and the tensile strength is limited by the Ti-Si bonds at the interface. The tensile strength of bulk TiN in the (111) direction is found to be notably greater than in the (100) and (110) directions (90 GPa vs 35 and 50 GPa, respectively). This suggests that the enhanced hardness of the nc-TiN/a-Si$_3$N$_4$ nanocomposites compared to that of its constituent materials is primarily due to their affording and enhancing predominant interface formation involving the polar TiN(111) planes. Given the found deteriorating effect of oxygen on the tensile strength of the interfaces favorable under nitrogen-rich conditions, this indicates that oxygen contamination should be avoided in the creation of the nanocomposites if superhard coatings are desired.

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For systems in which the free energy of mixing has regions of negative curvature, the mechanism by which the system decomposes into its equilibrium phases is different from the mechanism when the curvature is positive, and is called the spinodal decomposition mechanism. When the curvature is positive, it is called the nucleation and growth mechanism.

The Vickers hardness test consists of indenting a material with a diamond indenter, in the form of a right pyramid with a square base and an angle of 136° between opposite faces subjected to a load of 1 to 100 kgf. The full load is normally applied for 10 to 15 s. The two diagonals of the indentation left in the surface of the material after removal of the load are measured using a microscope and their average calculated. The area of the sloping surface of the indentation is calculated. The Vickers hardness is the quotient obtained by dividing the kgf load by the square mm area of indentation.