Role of oxygen in $TiN(111)/Si_xN_y/TiN(111)$ interfaces: Implications for superhard nanocrystalline nc-TiN/a-Si₃N₄ nanocomposites

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We report first-principles density-functional theory calculations to investigate the role oxygen impurites play in determining the strength of TiN(111)/Si_xN_y/TiN(111) interfaces, as may occur in the superhard and highly thermally stable "nc-TiN/*a*-Si₃N₄" nanocomposite. For nitrogen-rich conditions, our investigations predict that the interfacial region consists of a thin " β -like Si₂N₃" 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 $\langle 111 \rangle$ direction is found to be notably higher than in the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions (90 GPa, similar to the weakest $\langle 111 \rangle$ 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 segregation,¹¹ leading to nanocomposites with strong and sharp interfaces between nanocrystalline regions and thin amorphous layers.¹² The nanocomposite, so-called "nc-TiN/a-Si₃N₄," 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, $\sim 18-22$ 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-Si₃N₄/a- and nc-TiSi₂," which exhibit reported hardnesses of 80-105 GPa.7 Other members of this family of superhard nanocomposites include, e.g., nc-MN/a-Si₃N₄ (M=W, V, Al_{1-x}Ti_x). The nc-TiN/a-Si₃N₄ 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-Si₃N₄ nanocomposite. In particular, there has been some difficulty in repro-

ducing 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 impurites.¹⁷ Clearly, it is of significant importance to know whether all the ceramic nano-composites 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-Si₃N₄ system. Quantitative experiments provided some guidance: High-resolution transmission electron microscopy (HRTEM) studies ¹⁹ reported that the main crystallographic orientational relationship is [0001] Si₃N₄ \parallel [110] TiN with $(10\overline{1}0)$ Si₃N₄ \parallel $(1\overline{1}1)$ TiN. Thus, the interfaces we considered involved Si_vN_v 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 $\{10\overline{1}0\}$ lattice planes of Si₃N₄ are polar planes, formed by either nitrogen or silicon atoms.¹⁸ In the orientation $\{10\overline{1}0\}$ Si₃N₄ $\|\{111\}$ 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 β -Si₃N₄, 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 DMol³ program with the generalized gradient-approximation (GGA) for the exchange-correlation functional (PBE).^{22,23} In DMol³, 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 allelectron pseudopotentials which include scalar relativistic corrections (VPSR).^{20,21} We use an atomic cutoff radius of 9 bohr for all calculations.¹⁸ For supercells with (1×1), (1×3), and (2×2) 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

$$E^{f}(\mu_{\mathrm{Si}},\mu_{\mathrm{N}},\mu_{\mathrm{Ti}}) = (E_{\mathrm{tot}}^{\mathrm{int}} - E_{\mathrm{slab}}^{\mathrm{TiN}} - n\mu_{\mathrm{N}} - m\mu_{\mathrm{Si}} - l\mu_{\mathrm{Ti}})/S,$$
(1)

where E_{tot}^{int} and E_{slab}^{TiN} are the total energies of the interfacial system under consideration and the 20-layer reference TiN(111) slab with interface area S. $\mu_{\rm N} \mu_{\rm Si}$, and $\mu_{\rm Ti}$ 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 $\mu_{\rm N} = \frac{1}{2} E_{\rm N_2}$ (half the total energy of N₂) and for the latter, $\mu_{\rm Ti} = E_{\rm Ti}^{\rm bulk}$, which is the total energy of a bulk hcp Ti atom. We assume that in equilibrium, $\mu_{TiN} = \mu_{Ti} + \mu_N$, where μ_{TiN} is the chemical potential of bulk rocksalt structure TiN. For N-rich conditions we then have $\mu_{\text{Ti}} = E_{\text{TiN}} - \frac{1}{2}E_{\text{N}_2}$ and for N-poor conditions we have $\mu_{\rm N} = E_{\rm TiN} - E_{\rm Ti}^{\rm bulk}$. For the Si atom chemical potential, $\mu_{\rm Si}$, under nitrogen-rich conditions we assume an upper limit determined by $\mu_{\text{Si}_2\text{N}_4}=3\mu_{\text{Si}}+4\mu_{\text{N}}$, where $\mu_{\text{Si}_3\text{N}_4}$ is the chemical potential of bulk β -Si₃N₄. This gives $\mu_{\text{Si}} = \frac{1}{3} (E_{\text{tot}}^{\text{Si}_3\text{N}_4} - 2E_{\text{tot}}^{\text{N}_2})$, where $E_{\text{tot}}^{\text{Si}_3\text{N}_4}$ is the total energy of a bulk unit of β -Si₃N₄. For N-poor conditions, we take an upper limit of the Si chemical potential determined by bulk TiSi₂, so $\mu_{\text{TiSi}_2} = \mu_{\text{Ti}} + 2\mu_{\text{Si}}$, where μ_{TiSi_2} is the chemical potential of bulk TiSi₂. Then $\mu_{\text{Si}} = \frac{1}{2} (E_{\text{tot}}^{\text{TiSi}_2} - E_{\text{Ti}}^{\text{bulk}})$ where $E_{\text{tot}}^{\text{TiSi}_2}$ is the total energy of a bulk unit of TiSi2. These choices for the Si atom potential arise because in order to have a realistic estimate of the formation energy, we must determine μ_{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 TiSi₂ while for N-rich conditions, this phase was bulk Si₃N₄. This "crossover" of reference phases is responsible for the kink in Fig. 2 at around μ_{N} =-1.9 eV.

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

$$E_i^f = (E_{\text{tot}}^{\text{int-O}} - E_{\text{tot}}^{\text{int}} - \mu_{\text{O}}),$$
$$E_s^f = (E_{\text{tot}}^{\text{int-O}} - E_{\text{tot}}^{\text{int}} - \mu_{\text{O}} + \mu_{\text{X}}),$$

respectively. $E_{\text{tot}}^{\text{int-O}}$ is the total energy of the interface with oxygen (or of a supercell of bulk TiN with oxygen, which we also consider), and $\mu_{\rm X}$ is the chemical potential of the Ti or N atom which is substituted by oxygen. For the chemical potential of oxygen $\mu_{\rm O}$, we assume an upper limit determined by $\mu_{\rm TiO_2} = \mu_{\rm Ti} + 2\mu_{\rm O}$, where $\mu_{\rm TiO_2}$ is the total energy of bulk titanium dioxide. Using the relationships described above for $\mu_{\rm N}$ and $\mu_{\rm Ti}$, this gives for nitrogen-rich conditions $\mu_{\rm O} = 1/2(E_{\rm TiO_2} - E_{\rm TiN} + \frac{1}{2}E_{\rm N_2})$ and for titanium-rich (nitrogenpoor) conditions, $\mu_{\rm O} = 1/2(E_{\rm TiO_2} - E_{\rm TiN}^{\rm bulk})$.

We also consider the tensile stress of the low energy interfaces, σ_{ii} , which is calculated by²⁴

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

where U is the internal (or total) energy, V is the volume of the region under strain, and η_{ij} is the infinitesimal strain. In this work, we only consider σ_{zz} , 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 $W_{\text{sep}} = (E_1^{\text{tot}} + E_2^{\text{tot}} - E_{12}^{\text{tot}})/S$, where E_i^{tot} is the total energy of the separated slab *i* and E_{12}^{tot} is the total energy of whole system.

III. LOW ENERGY INTERFACE STRUCTURES

In our previous publication,¹⁸ we predicted various low energy $TiN(111)/Si_xN_v/TiN(111)$ 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 socalled (1×3) " β -like Si₂N₃(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 (1×1) "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 μ_N =-1.3 to -1.2 eV, see Fig. 2), the "top-



FIG. 1. (Color online) Atomic structure of various TiN(111)/Si_xN_y/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-poor conditions). Lower left: the (2×2) " γ -like Si₃N₄" interface (involving N-Si-N bonding), and right, the (1×3) " β -like Si₂N₃(1010)" interface (involving N-Si-N bonding, most favorable for nitrogen-rich conditions).

hcp-Si" structure is most favorable (Fig. 1, upper left). In this configuration the Si atoms are threefold bonded to Ti atoms (of the upper slab), and singly bonded to N atoms (of the lower slab). For N-rich conditions, the next most favorable structures involve a thin " γ -like Si₃N₄" layer (Fig. 1, lower left) and a "top-top-SiN" structure¹⁸ (Fig. 1, upper center). Interestingly, from Fig. 2 it can be seen that for $\mu_N \sim -1.25$ eV, all these interface structures have a very similar formation energy.

In Ref. 18 we correlated the N-chemical potential, as it appears in Fig. 2, to its dependence on the N_2 gas pressure and temperature via the ideal gas equations [see, e.g., Ref. 25]. From this it could be predicted that under the typically employed experimental nitrogen pressures and growth tem-



FIG. 2. (Color online) Interface formation energies [see Eq. (1)] as a function of the nitrogen chemical potential μ_N for the low energy interface configurations.¹⁸ The chemical potential is given with respect to half the total energy of the N₂ molecule.

peratures (corresponding to values of $\mu_N \ge -1.4 \text{ eV}$), the lowest energy interface was predominantly the β -like Si₂N₃ structure.

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,²⁶ 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.²⁷ Recently, Jhi et al.²⁸ have investigated the correlation between valence electron concentration and hardness, and related the hardness to the band structure, while Gao *et al.*⁴ 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.^{29,30} 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 clathrates¹ and carbonboron-nitride based materials.^{2,3}

In this section we calculate the tensile strength of the four interfaces: (1×1) hcp-fcc-TiSi, (1×1) top-top-SiN, (1×3) β -like Si₂N₃, and (2×2) γ -like Si₃N₄, as well as of various crystallographic directions of bulk TiN and bulk β -Si₃N₄. For TiN, we consider strain in the $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 110 \rangle$ directions, and for β -Si₃N₄, in the $\langle 10\overline{10} \rangle$ direction. For these calculations we model the bulk systems similarly to the in-



FIG. 3. (Color online) The tensile stress for various low energy interface and bulk systems: (a) For a uniform strain with no atomic relaxation and (b) for the bulk systems, applying strain only between two atomic planes and thereby deliberately breaking the bonds. Full relaxation of all the other atoms in response to the applied strain is included.

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 $\langle 111 \rangle$ 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 ($\varepsilon = 0.12$ vs 0.45) indicating a more brittle character. For diamond, the tensile strength in the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions (225 and 130 GPa, respectively¹) are notably larger than in the $\langle 111 \rangle$ direction, and so the latter limits the critical stresses that diamond can withstand. For TiN, the tensile strength in the $\langle 100 \rangle$ direction is the smallest, being around 35 GPa, in the $\langle 110 \rangle$ 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.¹⁸ The strength of β -Si₃N₄ in the $\langle 10\overline{10} \rangle$ 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 (\sim 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, $(1 \times 3) \beta$ -like Si₂N₃, (1×1) hcp-fcc-TiSi, and $(2 \times 2) \gamma$ -like Si_3N_4 , where the values are ~20, ~35, ~27, and 25 GPa, respectively; the interface tensile strength being greatest for the lowest energy β -like Si₂N₃ 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 strain. The results are shown in Fig. 3(b),



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.

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 $\langle 111 \rangle$ direction is 37 GPa, where in this case the strain at maximum strength is ε_{zz} =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. 5. (Color online) The electron density distribution of the β -like Si₂N₃ interface region for different strains without oxygen at (a) ε_{zz} =0, (b) ε_{zz} =0.09 (maximum strength), (c) ε_{zz} =0.12, and different strains with oxygen $(\frac{1}{65} \approx 1.54\%)$ at (d) ε_{zz} =0, (e) ε_{zz} =0.06 (maximum strength), and (f) ε_{zz} =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) $\varepsilon_{zz}=0$, (b) $\varepsilon_{zz}=0.08$ (maximum strength), (c) $\varepsilon_{zz}=0.12$, and different strains with oxygen ("high" concentration, $\frac{1}{23} \approx 4.35\%$) at (d) $\varepsilon_{zz}=0$, (e) $\varepsilon_{zz}=0.8$ (maximum strength), and (f) $\varepsilon_{zz}=0.12$.



FIG. 7. (Color online) Favorable oxygen sites (small gray circles) in (a) the (2×2) top-top-SiN interface with "low" oxygen concentration $(\frac{1}{89} \approx 1.12\%)$, (b) the β -like Si₂N₃ interface (concentration $\frac{1}{66} \approx 1.52\%$), and (c) the (2×2) hcp-fcc-TiSi interface with low oxygen concentration $(\frac{1}{89} \approx 1.12\%)$. The solid lines indicate the bonds that break on applying strain perpendicular to the plane of the interface in the systems without oxygen. The dashed lines indicate the bonds that break in the systems containing oxygen. Large gray, small black, and white circles represent Ti, N, and Si atoms, respectively.

strength of bonding between TiN(100) planes is still the lowest (~16 GPa), and the top-top-SiN interface is next lowest (~20 GPa). The strength of bonds between TiN(110) planes is slightly higher than the latter two at ~23 GPa.

Given that the strength of bonding between TiN(111) planes is the greatest, it indicates therefore that the Sicontaining interface structures reduce and limit the strength. This suggests that the enhanced hardness of the nc-TiN/a-Si₃N₄ nanocomposites is primarily due to their affording and enhancing predominant interface formation involving the polar TiN(111) planes.



FIG. 8. (Color online) Various oxygen sites in bulk rocksalt structure TiN: Interstitial sites (O_i), and Ti (O_{Ti}), and N (O_N) substitutional sites. Large gray, small black, and small gray circles represent Ti, N, and O atoms, respectively.

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.

Oxygen site	N-poor	N-rich		
O _{i1}	6.39	4.65		
O _{<i>i</i>2}	8.86	7.12		
O _N	-0.98	0.76		
O _{Ti}	12.76	7.54		

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_{i1} , O_{i2} 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), $(1 \times 3) \beta$ -like Si₂N₃ (containing 65 atoms), (1×1) hcp-fcc-TiSi (containing 22 atoms), and $(2 \times 2) \gamma$ -like Si₃N₄ (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_{i1}) at the interface, while under nitrogen-poor conditions (where



FIG. 9. (Color online) Various oxygen sites considered in the (a) top-top-SiN, (b) β -like Si₂N₃, (c) hcp-fcc-TiSi, and (d) γ -like Si₃N₄ interface systems. Interstitial sites are labeled as O_i and substitution on a N and Ti site by O_N and O_{Ti}, respectively. White and small gray circles represent Si and O atoms, and large gray and small black circles represent Ti and N atoms, respectively.

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.

	top-top-SiN		$(1 \times 3)\beta$ -like Si ₂ N ₃				hcp-fcc-TiSi			$(2 \times 2)\gamma$ -like Si ₃ N ₄		
	N-poor	N-rich		N-poor	N-rich		N-poor	N-rich		N-poor	N-rich	
O _{<i>i</i>1}	0.70 (0.84)	-1.04 (-0.90)	O _{<i>i</i>1}	5.18	3.44	O _{<i>i</i>1}	3.37 (1.88)	1.63 (0.14)	O _{<i>i</i>1}	3.55	1.81	
O_{i2}	2.19 (0.89)	0.46 (-0.85)	O_{i2}	4.24	2.49	O_{i2}	2.63 (1.13)	0.89 (-0.61)	O_{i2}	6.06	4.32	
O _{i3}	4.02 (3.17)	2.28 (1.43)	O _{N1}	-1.68	0.06	O _{i3}	2.50 (1.13)	0.76 (-0.61)	O _{<i>i</i>3}	5.27	3.53	
O_{i4}	6.71 (4.49)	4.97 (2.75)	O_{N2}	-0.74	1.00	O_{i4}	3.15 (4.52)	1.41 (2.78)	O_{i4}	3.54	1.79	
O_{i5}	7.63 (2.71)	5.89 (0.97)	O _{N3}	-1.63	0.11	O_{i5}	2.91 (2.01)	1.17 (0.27)	O_{i5}	4.73	2.99	
O _{N1}	-1.24 (-1.38)	0.50 (0.36)				O _{Ti1}	4.72 (5.43)	- 0.50 (0.21)	O_{N1}	-1.38	0.35	
O _{N2}	0.66 (0.37)	2.40 (2.11)				O_{N1}	-0.07 (-0.33)	1.67 (1.41)	O_{N2}	-1.40	0.33	
O _{N3}	-0.29 (-0.42)	1.45 (1.32)							O_{N4}	-1.41	0.32	
									O_{N4}	-1.40	0.33	
									O_{N5}	-1.44	0.30	
									O _{N6}	-0.72	1.02	

this is not an energetically favorable interface), oxygen prefers to occupy substitutional sites (O_{N1}) 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 $(1 \times 3) \beta$ -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



FIG. 10. Oxygen formation energies for the lowest energy sites in the top-top-SiN, β -like Si₂N₃, hcp-fcc-TiSi, and γ -like Si₃N₄ interfaces. The nitrogen chemical potential, μ_N , is given with respect to half the total energy of the N₂ molecule.

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 (O_{N1}) 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 (O_{Ti1}), becoming bonded with Si and N atoms, while for high oxygen concentration, they prefer to be located at the interface in interstitial sites (O_{i2} , O_{i3}).

For the γ -like Si₃N₄ interface, the preferred O site (O_{N5}) 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 O_{i1} and O_{N1} , 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 "upright," single N, and Ti bonds. For the β -like Si₂N₃ interface,



FIG. 11. (Color online) The atomic positions of the (2×2) γ -like Si₃N₄ interface structure for different strains with oxygen at the O_{N5} site: (a) ε_{zz} =0, (b) ε_{zz} =0.08, (c) ε_{zz} =0.12, (d) ε_{zz} =0.14, and (e) ε_{zz} =0.24.

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 O_N 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 Si₂N₃ interface, the presence of oxygen does not induce a reduction in the strength, and in fact it is slightly larger for strain $\varepsilon_{zz} > 0.09$. 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 $> \varepsilon_{zz} = 0.12$.

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 TiO_2 is -9.73 eV (Ref. 32) per formula unit while that of SiO_2 is -9.43 eV per formula unit.32

We also calculate the work of separation for this interface with no oxygen and with a low oxygen concentration $(\frac{1}{89} \approx 1.12\%)$. The values are 0.127 and 0.064 eV/Å², 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_{i1}), the single, upright Ti-N bonds expand significantly to incorporate the O atoms, by up to 72.1%. The oxygen atoms bonds preferably with the Ti atoms.

In the "right side" of the β -like Si₂N₃ interface, which has no oxygen in the immediate neighborhood [see Fig. 7(b)],



FIG. 12. (Color online) The electron density distribution of the top-top-SiN interface region for the fully relaxed structure for different oxygen concentrations: (a) no oxygen, (b) low oxygen concentration, $\frac{1}{89} \approx 1.12\%$ as calculated in a lateral (2×2) cell, and (c) high oxygen concentration $\frac{1}{23} \approx 4.35\%$ as calculated in a lateral (1×1) cell.

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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 SiO₂ is 1.617 Å, and in TiO₂, 1.956 Å.

top-top-SiN		β -like Si ₂ N ₃			hcp-fcc-TiSi						
With oxygen			With oxygen			With oxygen			γ-like Si ₃ N ₄		
d _{Ti-N}	2.169	3.733 (72.1%)	$d_{\rm Ti-N}$	2.128	2.143 (0.75%)	d _{Ti-Si}	2.658	2.657 (-0.03%)	d _{N-Ti}	2.132	2.089 (-2.10%)
$d_{\text{N-Si}}$	1.818	1.797 (-1.15%)	$d_{\text{N-Si}}$	1.709	1.678 (-1.81%)	$d_{\text{Si-Ti}}$	2.697	2.651 (-1.72%)	$d_{\rm Ti-N}$	2.114	2.124 (0.47%)
$d_{\rm Si-N}$	1.703	1.753 (2.96%)	$d_{\rm Si-N}$	1.808	1.815 (0.39%)	$d_{\rm Ti-N}$	2.106		$d_{\text{Ti-O}}$		2.270
$d_{\rm Si-O}$		1.737				$d_{\text{Ti-O}}$		2.175	$d_{\text{N-Si}}$	1.763	
$d_{\text{N-Ti}}$	2.077	2.060 (-0.82%)	$d_{\text{N-Ti}}$	2.092	2.346 (12.14%)	$d_{\text{N-Ti}}$	2.125		$d_{\text{O-Si}}$		1.725
			$d_{\text{O-Ti}}$		2.143	$d_{\text{O-Ti}}$		2.199	$d_{\rm Si-N}$	1.695	1.684 (-0.65%)

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 see 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 $0.32 \text{ eV}/\text{Å}^2$, 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 Si₃N₄ interface, in contrast to the β -like Si₂N₃ 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 Si₂N₃ 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 Si₃N₄ interface.

VI. CONCLUSION

We report first-principles DFT investigations into the strength of $TiN(111)/Si_xN_y/TiN(111)$ interfaces as may oc-

cur in the novel superhard and highly thermally stable nc-TiN/a-Si₃N₄ 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 Si₂N₃ 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 $\langle 111 \rangle$ direction is found to be notably greater than in the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions (90 GPa vs 35 and 50 GPa, respectively). This suggests that the enhanced hardness of the nc-TiN/a-Si₃N₄ 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 nitrogenrich conditions, this indicates that oxygen contamination should be avoided in the creation of the nanocomposites if superhard coatings are desired.

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