Ab Initio Structural Energetics of $\beta$-$\text{Si}_3\text{N}_4$ Surfaces

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Motivated by recent electron microscopy studies on the $\text{Si}_3\text{N}_4$/rare-earth oxide interfaces, the atomic and electronic structures of bare $\beta$-$\text{Si}_3\text{N}_4$ surfaces are investigated from first principles. The equilibrium shape of a $\text{Si}_3\text{N}_4$ crystal is found to have a hexagonal cross section and a faceted dome-like base in agreement with experimental observations. The large atomic relaxations on the prismatic planes are driven by the tendency of Si to saturate its dangling bonds, which gives rise to resonant-bond configurations or planar $sp^2$-type bonding. We predict three bare surfaces with lower energies than the open-ring (1010) surface observed at the interface, which indicate that non-stoichiometry and the presence of the rare-earth oxide play crucial roles in determining the termination of the $\text{Si}_3\text{N}_4$ matrix grains.

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The desirable mechanical and physical properties of silicon nitride ceramics [1] in many high temperature applications are hindered by their intrinsic brittleness which limits their wide-spread use and reliability as structural components. It has been empirically known for some time that this problem can be overcome by microstructural and compositional design with sintering additives, in particular rare-earth oxides [2]. The resulting ceramic microstructure consists of elongated $\text{Si}_3\text{N}_4$ matrix-grains embedded in an intergranular, typically amorphous, rare-earth oxide phase. However, precise information about the structure and chemistry of the interface has been lacking for many years. Recently, there have been three experimental studies using scanning transmission electron microscopy (STEM), which revealed for the first time, results from first principles calculations on low-index $\beta$-$\text{Si}_3\text{N}_4$ surfaces focusing in particular on (i) the equilibrium shape of the crystal, and (ii) the atomic structure and stoichiometry at the prismatic plane (1010) surface, which is the relevant surface studied in recent STEM experiments [Fig. 1(a)].

Our calculations were performed within density functional theory using the projector augmented wave method [5]. For exchange-correlation, we used the Perdew-Wang parametrization of the generalized gradient approximation (GGA), and repeated some of the calculations using the Ceperley-Alder functional within the local density approximation (LDA) for comparison. An energy cutoff of 270 eV was used in all calculations. For structural optimization of the bulk, a $\Gamma$-centered $3\times3\times8$ $k$-point grid was employed. Doubling the $k$-point grid and increasing the cutoff to 400 eV had no appreciable effect on the calculated structural parameters. The hexagonal unit cell of $\beta$-$\text{Si}_3\text{N}_4$ contains 14 atoms with 6 structural parameters ($a$, $c$, and 4 internal parameters). Half of the atoms are in the plane $z = \frac{1}{4}c$, and the other half are in the $z = \frac{3}{4}c$ plane, as shown in Figure 1(b). Si atoms are four-fold coordinated with N atoms in a slightly distorted tetrahedral configuration, and N atoms are threefold coordinated with Si atoms. The
six structural parameters \((a, c, x_{Si}, y_{Si}, x_{N}, y_{N})\) optimized with GGA (7.667 Å, 2.928 Å, 0.1752, 0.7692, 0.3299, 0.031) and LDA (7.585 Å, 2.895 Å, 0.1738, 0.7675, 0.3301, 0.0295) are in good agreement with previous calculations \( \mathbf{R} \) and experimental values \( \mathbf{H} \) of (7.608 Å, 2.911 Å, 0.1733, 0.7694, 0.3233, 0.0314). The surface calculations were performed with the relaxed structural parameters using a slab geometry. Depending on the surface, we used hexagonal and simple or base-centered monoclinic supercells (Table I). For each surface, we considered up to 4 different stoichiometric terminations to find the lowest-energy atomic configuration. We performed several tests to assess the convergence of the surface energy with respect to number of layers (up to 7) and the size of the vacuum region (up to 10 Å). Although the convergence was observed to be rapid [with the exception of the \((1\overline{1}0)\) surface], we used 5-layer slabs (10-layer for \((1\overline{1}0)\)) with \(8 - 10\) Å vacuum.

Experimentally, it is observed that the Si\(_3\)N\(_4\) microstructure consists of elongated structures with hexagonal cross sections. The preferential growth along the \(c\)-axis is rather rapid, while the growth of the \((10\overline{1}0)\) and \((1\overline{1}00)\) prismatic planes is reaction limited and very sensitive to the type of additives \(\mathbf{S}\). In order to understand the growth process of bare Si\(_3\)N\(_4\) grains, we calculated the surface energies of five low-index Si\(_3\)N\(_4\) surfaces (Table I). The equilibrium shape of \(\beta\)-Si\(_3\)N\(_4\) calculated from these energies by the Wulff construction \(\mathbf{W}\) is shown in Figure 2. The exposed faces consist of the \(\{1\overline{1}2\overline{0}\}\), \(\{10\overline{1}1\}\), \(\{1\overline{1}1\}\), and \(\{0001\}\) families of planes making up \(\sim 53\%\), 25\%, 19\%, and 3\% of the total surface area, respectively. The calculated aspect ratio for bare surfaces between the crystal length and its width is 1.4, which is in agreement with the measured aspect ratios near 2 for Si\(_3\)N\(_4\) samples sintered without or only the minimum amount of the additive. We expect that in the presence of the rare-earth oxide additive, the energies of \((1\overline{1}2\overline{0})\) or \((10\overline{1}0)\) will be lower, thereby increasing the calculated aspect ratio. We also note that our calculations predict an equilibrium shape, in which the base is not flat, but like a faceted dome even when only two tilted families of planes, \(\{1\overline{1}2\overline{1}\}\) and \(\{10\overline{1}1\}\), are included. This is in agreement with the experimental observation on macroscopic Si\(_3\)N\(_4\) matrix-grains embedded in the intergranular phase, where the basal planes look atomically rough \(\mathbf{II}\).

It is particularly interesting to notice that of the two lowest-index prismatic planes rotated by 30\° with respect to each other, it is the \((1\overline{1}2\overline{1})\) surface which is exposed in the Wulff construction and not the \((10\overline{1}0)\) surface with open hexagonal rings, which has been shown to exhibit an abrupt interface with the rare-earth oxide additive in recent STEM experiments. The reason for the significantly lower surface energy of \((1\overline{1}2\overline{1})\) (1.95 J/m\(^2\)) compared to the other surface candidates is in agreement with the measured aspect ratios near 2 for Si\(_3\)N\(_4\) samples sintered without or only the minimum amount of the additive. We expect that in the presence of the rare-earth oxide additive, the energies of \((1\overline{1}2\overline{0})\) or \((10\overline{1}0)\) will be lower, thereby increasing the calculated aspect ratio. We also note that our calculations predict an equilibrium shape, in which the base is not flat, but like a faceted dome even when only two tilted families of planes, \(\{1\overline{1}2\overline{1}\}\) and \(\{10\overline{1}1\}\), are included. This is in agreement with the experimental observation on macroscopic Si\(_3\)N\(_4\) matrix-grains embedded in the intergranular phase, where the basal planes look atomically rough \(\mathbf{II}\).

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pared to (10\(\overline{1}0\)) (2.57 \(\text{J/m}^2\)) can be understood from the nature of the atomic relaxations and the way the dangling bonds of Si are saturated. On the ideal (unrelaxed) (10\(\overline{1}0\)) surface, there are one Si and one N atom, which have one dangling bond each. These are shown by Si2 and N1 in Fig 3(a). When the surface is relaxed, while N1 still remains with a dangling bond, Si2 undergoes a considerable displacement (\(\sim 0.8 \text{Å}\)) forming a new Si-Si bond with Si4 at 2.58 Å, only 10% larger than the bulk Si-Si distance [Fig. 3(b)]. As such, the dangling bond of Si2 is saturated, and the 5-fold coordinated Si4 atom has two resonant bonds, reminiscent of overcoordination of Si in negatively charged \(E\)–center defect [11]. The surface is still somewhat rough due to the presence of the Si1-N1 unit, which does not relax significantly. On the ideal (11\(\overline{2}0\)) surface, on the other hand, there are 2 Si and 2 N atoms with one dangling bond each, labeled by Si6, Si4, N5, and N3 in Fig. 3(c). When this surface is relaxed, the resulting atomic displacements for most of the atoms are very large. For example, the displacements of N7, Si5, and Si6 are 1.51 Å, 1.49 Å, and 1.33 Å, respectively. Such large relaxations saturate all the dangling bonds except for N3, resulting in a rather smooth surface with 7-fold, 3-fold, and 4-fold Si-N rings [Fig. 3(d)]. The only undercoordinated Si atom on the relaxed surface (Si5 with no dangling bonds on the ideal surface) exhibits an \(sp^2\)–type bonding in an almost planar coordination with 3 N atoms.

We also investigated the relative structural stability of the (10\(\overline{1}0\)) bare surface as a function of stoichiometry. The formation energy of a surface, \(E_{\text{form}}\), can be written as [12]

\[
E_{\text{form}} = E_{\text{slab}}^{\text{tot}} - n_i \mu_i - n_N \mu_N,
\]

where \(E_{\text{slab}}^{\text{tot}}\) is the total energy of the slab, \(n_i\) is the number of atoms of type \(i\) in the slab, and \(\mu_i\)'s are the corresponding chemical potentials, which satisfy \(3\mu_{\text{Si}} + 4\mu_{\text{N}} = \mu_{\text{Si}_3\text{N}_4, \text{bulk}}\). Figure 4 shows the calculated energies as a function of the stoichiometry of the surface. All energies are relative to the stoichiometric surface with open hexagonal rings, which we will refer to as the “open-ring surface”. This reference configuration is quite stable in the full allowed region of \(\mu_N\) with the exception of two other terminations. The first one, which we will refer to as the “half-surface”, is obtained by removing half the atoms from the open-ring surface as shown by the dotted line in Fig. 3(a). This surface, while stoichiometrically terminated and quite smooth even in its ideal structure, does not have the open hexagonal rings, which are present at the \(\text{Si}_3\text{N}_4\) rare-earth oxide interfaces studied in recent STEM experiments. When relaxed, the half-surface becomes 0.17 eV (GGA) and 0.1 eV (LDA) lower in energy compared to the open-ring surface. The only significant relaxation occurs for the Si atom (Si4) with the dangling bond which moves inward by \(\sim 0.64 \text{Å}\). As a result, the Si atom exhibits a \(sp^2\)–type bonding in a nearly planar coordination with 3 N atoms [Fig. 3(e)].

One possibility for the discrepancy between the theoretical prediction of the half-surface having a lower energy than the experimentally observed open-ring surface at the rare-earth oxide interface is that theory incorrectly predicts the lowest energy termination of the bare (10\(\overline{1}0\)) \(\text{Si}_3\text{N}_4\) surface. This could be verified by studying the bare surface with low-energy electron diffraction experiments. More likely reason for the discrepancy, which would also explain the prediction of the (11\(\overline{2}0\)) surface as the lower-energy prismatic plane contrary to experimental observations, is that the rare-earth oxide additive changes the relative stability of different \(\text{Si}_3\text{N}_4\) surfaces and different terminations of the same-index surfaces.

The second termination, which results in a lower energy surface under N-poor conditions, is obtained by re-
moving a SiN$_2$ unit (N1, N4, Si1) from the open-ring surface, as shown by the dashed ellipse in Fig. 3(a). In its ideal structure, this surface has 2 Si atoms, Si4 and Si2, with 1 and 2 dangling bonds, respectively, along with a N atom (N3) with one dangling bond. In spite of a large number of broken bonds, when the surface is relaxed, large atomic displacements of Si2 (1.29 Å) and Si4 (1.27 Å) saturate all Si dangling bonds (via the formation of a new Si-Si bond at 2.5 Å), which reduces the surface energy considerably. The relaxed surface is smooth and has 7-fold and 3-fold rings, similar to those observed on the (1120) surface [Fig. 3(f)]. It is interesting to note that under extreme N-poor conditions, the energy of this surface is 1.85 J/m$^2$, which is lower than that of (1120), providing a possible explanation for the dominant observation of (10$ar{1}$0) surfaces in the STEM experiments.

In summary, we have presented results from ab initio calculations on the atomic and electronic structures of bare β-Si$_3$N$_4$ surfaces with emphasis on the prismatic plane (10$ar{1}$0) surface observed in recent STEM experiments. The equilibrium shape of a macroscopic Si$_3$N$_4$ crystal is found to have a hexagonal cross section, a faceted dome-like base, and an aspect ratio of 1.4, in agreement with experimental observations. We find large distortions on the prismatic planes driven primarily by the tendency of Si atoms to saturate their dangling bonds and achieve either resonant-bond, $sp^3$–, or $sp^2$–bonded configurations. The stoichiometric (1120) surface, the (10$ar{1}$0) “half-surface”, and a non-stoichiometric (10$ar{1}$0) surface obtained by removing a SiN$_2$ unit are predicted to have lower energies than the open-ring (10$ar{1}$0) surface. In light of the consistent experimental observations of the open-ring (10$ar{1}$0) surface at the interface, the present results obtained with state-of-the-art ab initio techniques strongly indicate that (i) the rare-earth oxide additive changes the relative stability of β–Si$_3$N$_4$ surfaces, and (ii) non-stoichiometry (especially resulting from N-poor conditions) should play an important role in determining the termination of the Si$_3$N$_4$ matrix grains. We expect that future ab initio studies of the interface will not only focus on the bonding nature of the additives to the open-ring (10$ar{1}$0) surface, but also address why the proposed mechanisms do not favor promotion of the (1120) termination, which has a lower bare surface energy. This work was supported by DOE under grants No. DE-FG02-03ER15488 (JCI and SÖ), DE-AC05-03ER46057 (AZ and NDB), and DE-AC02-05CH11231 (ROR), and by the ACS Petroleum Research Fund under grant No. 40028-AC5M (HI).

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