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Metastability of fcc-related Si-N phases

B. Alling,[1,2] E. I. Isaev,[1,3] A. Flink,[1] L. Hultman,[1] and I. A. Abrikosov[1]
[1]*Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden*
[2]*Institute of Physics of Complex Matter, Swiss Federal Institute of Technology Lausanne (EPFL), 1015 Lausanne, Switzerland*
[3]*Department of Theoretical Physics, Moscow State Institute of Steels and Alloys (Technological University), 4 Leninskii Prospect, Moscow 117049, Russia*

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The phenomenon of superhardening in TiN/SiN$_x$ nanocomposites and the prediction of extreme hardness in bulk γ-Si$_3$N$_4$ have attracted a large interest to this material system. Attempts to explain the experimental findings by means of first-principles calculations have so far been limited to static calculations. The dynamical stability of suggested structures of the SiN$_x$ tissue phase critical for the understanding of the nanocomposites is thus unknown. Here, we present a theoretical study of the phonon-dispersion relations of B1 and B3 SiN. We show that both phases previously considered as metastable are dynamically unstable. Instead, two pseudo-B3 Si$_3$N$_4$ phases derived from a L1$_2$- or D0$_{22}$-type distribution of Si vacancies are dynamically stable and might explain recent experimental findings of epitaxial SiN$_x$ in TiN/SiN$_x$ multilayers.

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In the continuous search for ever harder materials, the Ti-Si-N system has recently attracted strong attention. The nanocomposite (NC) system nc-TiN/SiN$_x$ has shown superhardening[1,2] and the high-pressure spinel γ phase of Si$_3$N$_4$ has been predicted to have hardness similar to that of SiO$_2$ stishovite, the third hardest known bulk material.[3] The high hardness of the nanocomposites, about 35–50 GPa,[2] has phenomenologically been attributed to the small crystallite size in conjunction with strong intergrain bonds via an alleged SiN$_x$-based tissue phase.[1] However, the possible structure of this tissue phase is not completely understood. It was first considered as amorphous[4] or effectively x-ray amorphous[5] but the possibility of crystalline structures was also shown.[6–10] Hao *et al.*[11,12] considered the TiN/SiN$_x$/TiN [111] interfaces theoretically and found different specific interfacial structures to be energetically favorable, depending on the nitrogen chemical potential, all having just a few atomic layers of the SiN$_x$ phase. Moreover, Söderberg *et al.*[6–8] studied the [001] interfaces using transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) and concluded that a SiN$_x$ phase with cubic B1 (NaCl) appearances could be epitaxially stabilized. Later Hultman *et al.*[9] showed that such epitaxial SiN$_x$ could be stabilized up to approximately six monolayers in between TiN [001] surfaces. Si-N phases have also attracted substantial interest in bulk forms. Besides the cubic spinel Si$_3$N$_4$ phase that is formed at pressures above 15 GPa and is metastable at ambient conditions,[3] B1 SiN as well as B3 (zinc blende) SiN have been considered in works discussing the solubility of Si in TiN.[13,14] Although the mechanical strength of B1 SiN has been shown to be rather weak,[15] it has up to now been considered as metastable.[9,13,15]

In this Brief Report we test the *dynamical* stabilities of fcc-related Si-N phases. This is a procedure not previously applied to this class of materials. A necessary condition for the term metastable to be meaningful when discussing a certain phase under given conditions is that it could persist if it is actually created. This means that the phase should be stable with respect to lattice vibrations. We examine the vibrational, electronic, and energetic properties of B1 and B3 SiN as well as for pseudo-B1 and pseudo-B3 Si$_3$N$_4$ phases derived from the B1 and B3 SiN phases, but allowing 1/4 of the Si sites to be vacant with vacancies forming L1$_2$—and D0$_{22}$-type ordered structures, respectively. For simplicity, these phases are labeled "L1$_2$-B1," "D0$_{22}$-B1," "L1$_2$-B3," and "D0$_{22}$-B3." We compare the results with two known phases of Si$_3$N$_4$: the β and the γ phases.

The study is performed within a density-functional theory framework using two complementing methods. To calculate phonon spectra we have used the ultrasoft pseudopotentials method as introduced by Vanderbilt[16] together with the harmonic approximation to the force constants and the linear-response method[17] as implemented in the QUANTUM-ESPRESSO code.[18] To calculate formation energies as well as the electronic density of states (DOS), we used the projector augmented wave (PAW) method implemented in the Vienna *ab initio* simulation package (VASP).[19–21] In both cases the generalized gradient approximation (GGA) was used for the exchange-correlation functional.[22] The formation energies at 0 K were calculated with respect to diamond-structure Si and N$_2$ molecules as $E_f = E(\mathrm{Si}_x\mathrm{N}_y) - xE(\mathrm{Si}) - yE(\mathrm{N}_2)/2$. In all calculations, the studied property was converged with respect to the number of k points as well as the energy cutoff of the plane-wave basis set so that only negligible changes of our results would be the effect of a further increase. Pseudopotentials and PAW methods agree with each other within less than one percent for calculated lattice parameters for B1 and B3 phases. Furthermore, Isaev *et al.*[23] showed that the used pseudopotentials gave results in excellent agreement with both experiments and all-electron methods considering both bulk parameters and vibrational properties of B1 transition-metal nitrides and carbides.

We first investigate the suggestion that B1 SiN can be metastable. Figure 1 [panel (a)] shows the calculated phonon spectrum of B1 SiN. The spectrums show imaginary phonon frequencies. This means that the B1 structure is unstable to arbitrary small vibrations of the atoms since the motion of the atoms away from their lattice points actually lowers the energy of the system. In this case the dynamical instability is due to imaginary *optical* phonon branches. The instability of

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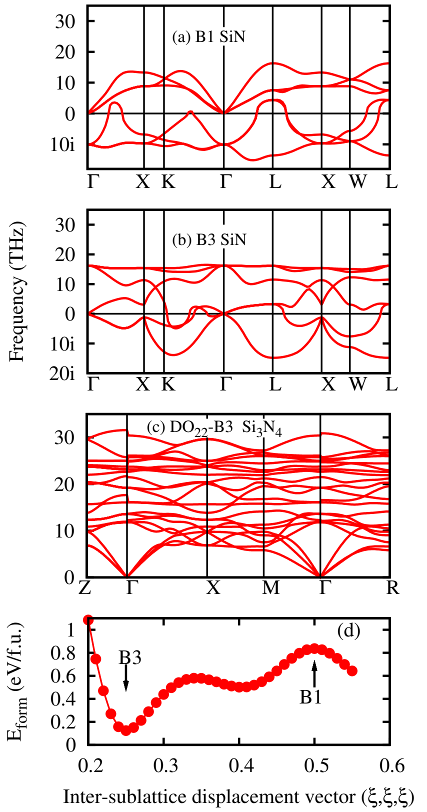

FIG. 1. (Color online) Calculated phonon spectra for (a) B1 SiN, (b) B3 SiN, and (c) "D0$_{22}$-B3" Si$_3$N$_4$. Note that B1 SiN and B3 SiN are dynamically unstable due to imaginary phonon frequencies while "D0$_{22}$-B3" Si$_3$N$_4$ is dynamically stable. Panel (d) shows calculated formation energies for 1:1 stoichiometric fcc-related SiN phases as a function of the intersublattice displacement (ξ,ξ,ξ). It shows that octahedral (B1) coordination of N with respect to Si is most unfavorable.

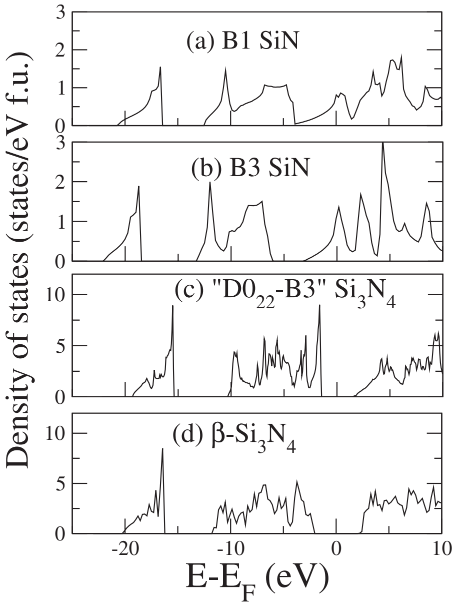

FIG. 2. Electronic density of states as a function of energy relative to the Fermi energy, for (a) B1-SiN, (b) B3-SiN, (c) a B3-based Si$_3$N$_4$ structure with Si vacancies forming a D0$_{22}$-type ordering, and (d) the ground-state structure β-Si$_3$N$_4$. Note that both structures with 1:1 Si to N ratio show peaks at E_F while both Si$_3$N$_4$ structures are semiconductors.

the optical branches can be contrasted to other known cases of dynamical instability in B1 compounds, where unstable branches most often are of acoustic character.[23] Optical phonons correspond to vibrations where the two sublattices are out of phase with each other. Optical instabilities thus indicate the presence of a driving force to move N atoms off the octahedral positions within the Si fcc framework. Panel (d) explains this result. It shows the formation energy of fcc-related SiN compounds as a function of the vector separating the Si and N atoms in the unit cell. The energies are calculated for positions on a line across the body center of the structure. The octahedral position of the N sublattice in the B1 structure is actually a local energy maximum. Any small fluctuation of the N atoms will shift them away from this position toward the less unfavorable tetrahedral coordination. In the figure all values of E_{form} are calculated at their own equilibrium volumes, but if the volume is fixed at the B1 value, the results are qualitatively the same. Thus, it is natural to study also the tetrahedrally coordinated B3 SiN. The phonon spectrum for this structure is presented in Fig. 1 [panel (b)] and it shows that also B3 SiN is dynamically unstable. In this case the acoustic branches dominate among the imaginary frequencies. It is worth noting that regardless of the N coordination, the 1:1 stoichiometric fcc-related SiN phase shows a positive formation energy with respect to pure Si and N$_2$ gas as indicated in panel (d) of Fig. 1. This is a strong indication that the search for candidates of metastable phases in this system should be directed toward other stoichiometries or off stoichiometry.

The physical origin of the instability of B1 and B3 SiN as well as their positive formation energies can be understood from studies of the electronic DOS shown in Fig. 2. Panels (a) and (b) show the DOS of the B1 and B3 phases of SiN, respectively. The results for the B1 phase are similar as in Refs. 14 and 15. Both structures exhibit peaks positioned right at the Fermi level. The origin of these peaks can be understood from simple electron counting arguments. Hybridization between nearest neighbors gives rise to bonding and antibonding states where six electrons can be accommodated in each of the bands. However, neglecting the N 2s electrons that do not participate in the hybridization, there are seven valence electrons per unit cell in stoichiometric SiN. That is one more than can be accommodated in the bonding states. This gives rise to the very unfavorable electronic structure with a sharp peak at the Fermi level. For comparison, in the related AlN system, which has one less valence electron, the number of bonding states is sufficient to accommodate all valence electrons and the system forms a stoichiometric semiconductor where both the B1 and B3 phases are metastable. All known stable Si-N phases show instead the Si$_3$N$_4$ stoichiometry which fulfills the electron counting argument. Motivated by this fact, but keeping in mind the experimental evidence of epitaxial growth of what appears to be cubic SiN$_x$ between B1 TiN layers, we have studied fcc-related Si$_3$N$_4$ structures realized with Si vacancies. We have considered Si vacancies ordered in a L1$_2$ and

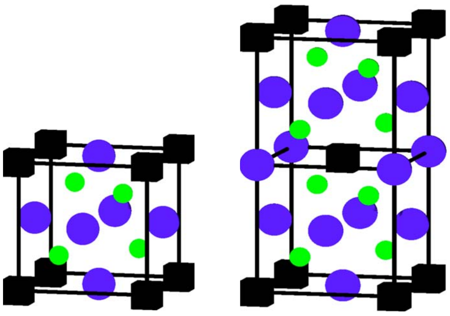

FIG. 3. (Color online) The two dynamically stable B3-derived Si_3N_4 structures. The cubic "$L1_2$-B3" (left) and the tetragonal "$D0_{22}$-B3" (right). Si: blue large spheres, N: green small spheres, and Si vacancies: black boxes.

$D0_{22}$ manner, both with octahedral (B1-related) and tetrahedral (B3-related) nitrogen.

The B1-related Si_3N_4 structures are found to be dynamically unstable and have high formation energy. However, both the tetrahedrally coordinated B3-related Si_3N_4 structures considered here and shown in Fig. 3 are dynamically stable. The $D0_{22}$-type ordering of Si vacancies is energetically preferred compared to the $L1_2$ structure as can be seen in Fig. 4. It is possible that yet another but very similar vacancy ordering could show a slightly lower energy still, but a complete ground-state search for the vacancy ordering is not directly relevant for this work and will be considered elsewhere. The phonon-dispersion relations of the "$D0_{22}$-B3" phase can be seen in panel (c) of Fig. 1. They show no imaginary frequencies or peculiarities of any of the modes. In both the B3-related cases all N atoms are coordinated by three Si atoms and exhibit only a small shift away from their ideal fcc sublattice of the B3 structure. The electronic DOS of the "$D0_{22}$-B3" structure is present in panel (c) of Fig. 2 and can be compared to the electronic DOS of the hexagonal ground state β-Si_3N_4 shown in panel (d). They show that the electron counting argument holds as both these 3:4-stoichiometric structures are semiconductors.

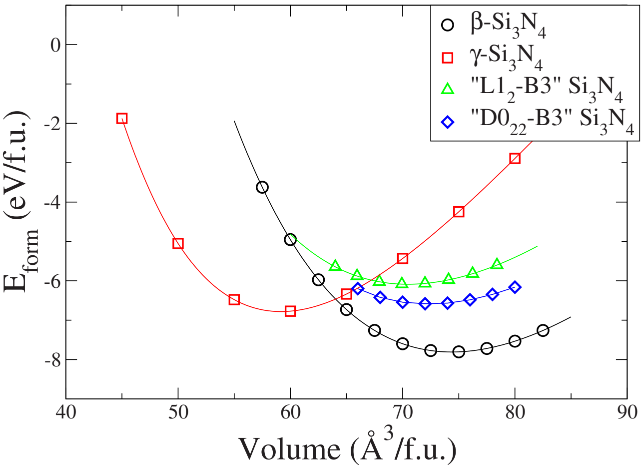

FIG. 4. (Color online) Formation energy as a function of volume per formula unit for four different prototypes of Si_3N_4: the ground-state structure β-Si_3N_4 (circles), the high-pressure cubic spinel phase γ-Si_3N_4 (squares), the "$L1_2$-B3" (triangles) and the "$D0_{22}$-B3" structures (diamonds).

The formation energies of four prototypes of Si_3N_4 are shown in Fig. 4 as a function of volume. It is obvious that the B3-related phases can only be metastable since they have roughly the same volume behavior as the ground-state structure. This is opposite to the γ phase which is stable under high pressure. However, the formation energy of the "$D0_{22}$-B3" phase is not substantially higher compared to the spinel γ phase which is experimentally found to be metastable under ambient conditions.[3] Also interesting is that the lattice parameter of both B3-related structures is very close to that of B1 TiN. "$L1_2$-B3" has $a=4.13$ Å while "$D0_{22}$-B3" has $a=4.18$ Å, as calculated by the PAW method to be compared to that of TiN; $a=4.24$ Å (experimental) and 4.26 Å (calculated PAW). These facts make it plausible that epitaxial pseudo-B3 Si_3N_4 phases can actually be stabilized in multilayers or sandwiches with TiN. The calculated zero-point vibrational energies derived in our phonon calculations of the two B3-related Si_3N_4 structures are very similar and do not change their relative energetics. It is noteworthy that the formation energy of Si vacancies in B3 SiN is negative: $E_{V_{Si}} = E(D0_{22}\text{-B3-}Si_3N_4) + E(Si) - 4E(\text{B3-SiN}) = -7.09$ eV per Si atom.

Since the pseudo-B3 phases treated here have atomic coordinates close to ideal fcc-lattice positions and allowing for the difficulty to resolve individual atoms in TEM and STEM measurements, we propose that the epitaxial growth of SiN_x on TiN as reported in Refs. 6–9 can be related to the formation of the phases discussed in this Brief Report.

In the cases of just one or two monolayers interfacing with a substrate, the entire system is obviously heavily influenced by the epitaxial forces. In order to see if such forces could stabilize thin layers of B1-SiN we have calculated phonon frequencies for a system where one [001] layer of B1-SiN is surrounded by five TiN B1 [001] layers. The structure was of course statically relaxed before the phonon calculation. It turns out that also this system, which should experience a maximum of epitaxial stabilization of the SiN layer, is dynamically unstable due to imaginary phonon frequencies both at the gamma point (magnitude 8.99 THz) and at the in-plane x point of the SiN layer (magnitude 3.12 THz). This calculation finally establishes that the B1 structure of SiN should be discarded. Yet epitaxy of SiN_x is observed also up to 13 Å corresponding to approximately six monolayers.[9] In order for structures with so many monolayers to be stable, they are likely to be related to systems which are at least metastable in bulk.

In conclusion, we have shown that the 1:1 stoichiometric B1 and B3 phases of SiN are dynamically unstable and should not exist in bulk or thick layers. B1 SiN is unstable also as a single [001] monolayer in between TiN [001] slabs. However, fcc-related pseudo-B3 Si_3N_4 where 1/4 of the fcc Si sites are vacant and vacancies ordered in line with a $D0_{22}$ or $L1_2$ structure are dynamically stable and have a lattice spacing very close to TiN. The results support the suggestion that the SiN_x tissue phase in nanocomposite TiN/SiN_x materials can be crystalline and have coherent interfaces with TiN. Our study also underlines the importance of testing the dynamical stability when new materials, structures, and phases are discussed.

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