

**Single-monolayer SiN<sub>x</sub> embedded in TiN: A first-principles study**Tobias Marten,<sup>1,\*</sup> Eyvaz I. Isaev,<sup>1,2</sup> Björn Alling,<sup>1</sup> Lars Hultman,<sup>1</sup> and Igor A. Abrikosov<sup>1</sup><sup>1</sup>*Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden*<sup>2</sup>*Theoretical Physics Department, Moscow State Institute of Steels and Alloys, 4 Leninskii Prospect, Moscow 119049, Russia*

(Received 20 February 2010; revised manuscript received 15 May 2010; published 30 June 2010)

The dynamical and thermodynamic stability of a single monolayer of SiN<sub>x</sub> sandwiched isostructurally between B1-TiN(001) and (111) oriented slabs are investigated by means of density functional theory. Possible dynamical stabilization of the (001) interface, by distortion of the Si-N bonds, is considered and found to almost, but not completely, remove the phonon instabilities. The (111) interface on the other hand is found to be dynamically stable. We furthermore relax the stoichiometry degree of freedom by allowing for Si vacancies in the lattice and show that the ideal 1:1 SiN stoichiometry in both interfaces are thermodynamically unstable with respect to Si vacancy formation regardless if the system is grown under nitrogen-rich or nitrogen-poor conditions, and therefore ruling out its relevance for performance of real materials.

DOI: [10.1103/PhysRevB.81.212102](https://doi.org/10.1103/PhysRevB.81.212102)

PACS number(s): 63.22.-m

Superhard nanocomposites attract large scientific and industrial interest for their intriguing physical properties, and possible usage in protective coatings on cutting tools and mechanical components. The TiN-SiN<sub>x</sub> nanocomposites have become a model system for this class of materials that exhibit superhardness ( $H \geq 40$  GPa) (Refs. 1 and 2) combined with high thermal stability and oxidation resistance.<sup>1</sup> The increased hardness with respect to pure TiN coatings has qualitatively been attributed to the nanometer dimensions of the TiN grains, preventing dislocation nucleation and motion. Moreover, the so-called tissue phase of SiN<sub>x</sub> prevents grain boundary sliding by providing strong intergranular bonds. However, even though this qualitative picture of the hardening mechanism seems to be established in the field, a quantitative understanding, built on the most fundamental principles of physics, are still not present.

The structure of the SiN<sub>x</sub> tissue phase is an important issue under debate. It was first considered to be amorphous,<sup>3</sup> later modified to “x-ray amorphous.”<sup>4</sup> It was then shown experimentally that the tissue phase could be crystalline in up to six monolayers (ML) stabilized between TiN(001) slabs.<sup>5–8</sup> A transition to highly disordered SiN<sub>x</sub> followed in thicker layers. The structure of the crystalline SiN<sub>x</sub> layers first appeared to be isostructural with TiN that is the B1 structure. This suggestion was reconsidered in the work by Alling *et al.*<sup>9</sup> who showed theoretically that both B1 (rock-salt) and B3 (zinc blende) SiN are utterly unstable with respect to lattice vibrations in bulk and also as an ideal 1 ML interface between TiN(001) surfaces. Instead Si<sub>3</sub>N<sub>4</sub> structures created through formation of Si vacancies in the cubic B3 lattice was shown to be dynamically stable, reasonably low in formation energies and well lattice matched with TiN(001), thus possibly explaining the structure in the experiments.<sup>9</sup>

A series of different SiN<sub>x</sub> structures in the (111) interface was theoretically studied by Hao *et al.*<sup>10,11</sup> concluding that the relative chemical potentials of nitrogen and silicon could alter the thermodynamically favored interfacial structure, including its stoichiometry. Zhang *et al.*<sup>12,13</sup> argued that the B1 SiN was still relevant as a metastable 1 ML interface due to epitaxial stabilization and charge transfer effects and that a small distortion of the Si-N bond could stabilize the (001) B1

monolayer. Based on their study of the (111) isostructural B1 interface the same authors suggested that Friedel oscillations were the fundamental limiting factor of the hardness for this material system.<sup>12</sup> However, based on the issue of stability with respect to lattice vibrations, so called dynamical stability, raised in Ref. 9 and the concern of the stoichiometry of the tissue phase ventilated in Refs. 9–11 one could question if the admittedly fascinating suggestion connecting the hardness of the material and Friedel oscillations are real or just artifacts of a particular interface type not relevant for materials that can exist.

In this Brief Report we investigate theoretically the stability of the (001) and (111) interfaces of TiN with 1 ML of B1 SiN<sub>x</sub> with respect to individual atomic relaxations, collective lattice vibrations, and with respect to change in the stoichiometry. Phonon spectra calculations are performed within the framework of density-functional theory as implemented in the QUANTUM-ESPRESSO package<sup>14</sup> utilizing *ab initio* pseudopotentials by Vanderbilt,<sup>15</sup> harmonic approximation to the force constants and linear response method.<sup>16</sup> The used pseudopotentials have previously been shown to give excellent agreement with experiments considering phonon and bulk parameters, see Refs. 17 and 18. Two complementary methods were used to optimize the structures and calculate total energies, the above-mentioned QUANTUM-ESPRESSO approach and the projector augmented wave method<sup>19,20</sup> implemented in the Vienna *ab initio* simulation package (VASP).<sup>21,22</sup> The generalized gradient approximation was used for the exchange-correlational functional throughout all calculations.<sup>23</sup>

The ideal B1 TiN/SiN/TiN(001) interface shown in Fig. 1(a) is modeled by a slab including five TiN layers and one SiN layer. Energies and lattice spacings were converged with respect to slabs with more TiN layers. We also define the in-plane coordinates as shown in Fig. 1(b).

For the phonon calculations we used in-plane  $1 \times 1$  supercells with fully relaxed internal positions of Si, N, and Ti atoms. This means that distortions of the SiN bonds were allowed. Moreover, larger  $2 \times 2$  in-plane supercells were used for calculations of the Si-vacancy formation energy in both the (001) and (111) interfaces.

Our first objective is to systematically investigate the ef-

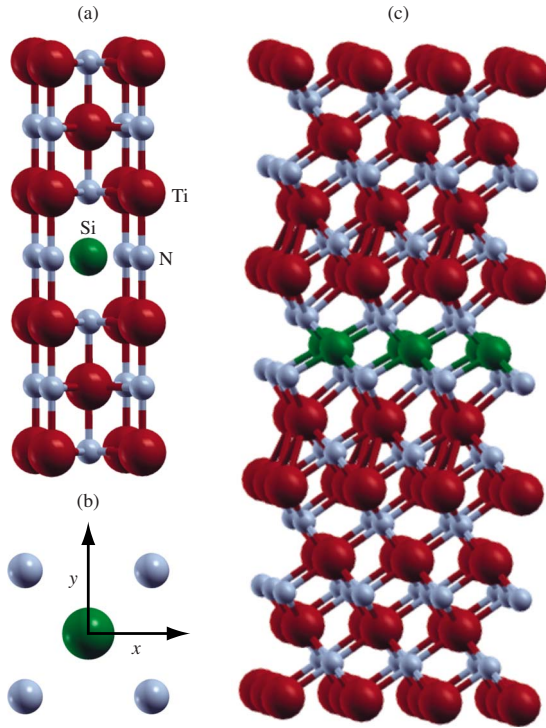


FIG. 1. (Color online) (a) The ideal TiN/SiN/TiN(001) interface. Top view of the SiN(001) plane is presented in (b) defining our  $x$ - and  $y$ -coordinate axes. The (111) interface is shown in (c).

fect of distorting the Si-N bond in the (001) ML as suggested in Refs. 12 and 13 to induce stabilization of this interfacial structure. Figure 2 shows the energy landscape describing the position of the Si atom relative the undisturbed ideal (001) interface. The landscape is built up from total energy calculations of a slab consisting of one Ti and one N atom in each TiN layer and one Si and one N atom in the SiN layer in the same way as in Ref. 13. The grid is given in distortions of the Si position in steps of 1% of the Si-Si nearest-neighbor distance. It is obvious that the ideal B1 lattice point, corresponding to the origin in Fig. 2, is a local energy maximum.

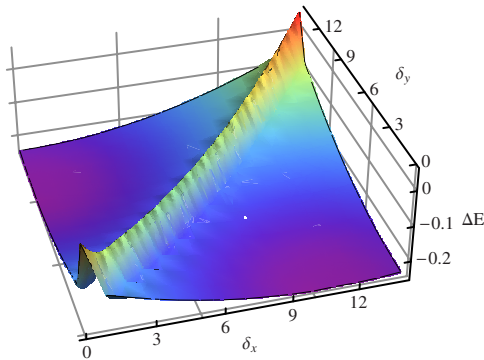


FIG. 2. (Color online) Energy landscape calculated for 001 TiN/1ML SiN/TiN interface as a function of the positions of the Si atom relative to N atom. The zero corresponds to the energy when both atoms occupy the ideal B1 lattice positions.  $\Delta E$  is measured in electron volt per Si and N pair. The distortions in  $x$  and  $y$  directions are shown in percentage of the Si-Si nearest-neighbor spacing and are denoted  $\delta_x$  and  $\delta_y$ , respectively.

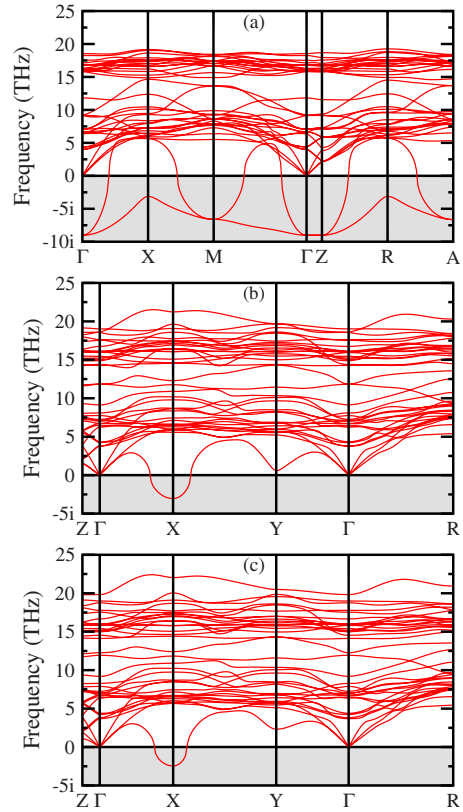


FIG. 3. (Color online) Phonon spectra of the (001) interface when (a) both Si and N occupy ideal positions, (b) when the Si atoms are distorted 5% along  $x$  direction, and (c) when the Si positions are optimized so they correspond to the energy minima shown in Fig. 2.

The dynamical instability of the ideal B1 TiN/1ML SiN/TiN interface is also clearly seen in its phonon spectrum presented in Fig. 3(a). Indeed, our calculations give large number of phonon modes with imaginary frequencies. This means that arbitrary small distortions with the corresponding wave vectors will lead to a collapse of the structure. Correspondingly, the energy of the system is lowered if the atoms move away from their lattice points. Distorting the Si atom along the  $x=y$  line an energy ridge is followed and a saddle point is reached at  $\sim 5\%$  distortions. As soon as the Si atom is slightly distorted from this line, i.e.,  $x=y+\delta$  it will relax into the energy minima at  $\sim 10\%$  distortion along one of the axis, corresponding to the deepest energy minima in Fig. 2. The latter result is in agreement with Ref. 13.

However, the question is if this relaxed interface is dynamically stable with respect to lattice vibrations. To investigate this issue we calculate the phonon dispersion relations for the distorted geometry. For instance, starting from the ideal structure and distorting the Si atom along one of the axis, we still see imaginary frequencies at 5% distortion, corresponding to a partially relaxed structure shown in Fig. 3(b). At fully optimized geometry the phonon spectrum, Fig. 3(c), is slightly changed as compared to the partially relaxed structure. Still, imaginary phonon frequencies appear around the X point in the orthorhombic Brillouin zone. The presence of a phonon instability at this point shows that this particular geometry is unstable at very low temperatures, but the insta-

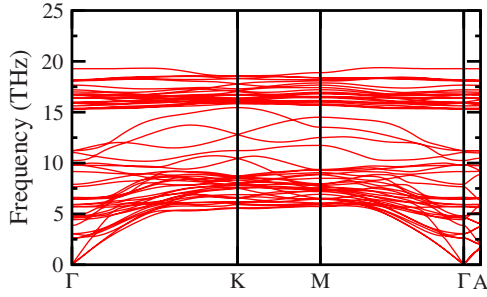


FIG. 4. (Color online) Phonon spectra for the optimized TiN-SiN-TiN(111) interface.

bility is rather small, and thermal effects due to anharmonic lattice vibrations<sup>24,25</sup> can, in principle, stabilize the interface dynamically. Moreover, an in-plane superstructure along the direction corresponding to the point with the imaginary phonon frequencies, the (100) direction in the case of (001) interface, can also be dynamically stable.

Turning to the (111) interface, the structure is given in Fig. 1(c), showing the slab including eight Ti layers, nine N layers, and one Si layer. When similar static relaxations as above, breaking the symmetry, are applied to this interface the ideal lattice points are retained, with only a small relaxation in the  $z$  direction.<sup>12</sup> In Fig. 4 the phonon spectrum of the (111) interface is shown. Interestingly, all phonon branches are real indicating that the (111) oriented interface is dynamically stable.

Comparing our study of the dynamical stability for SiN monolayer sandwiched between TiN layers with those for bulk stoichiometric B1 SiN,<sup>9</sup> one can clearly see a strong stabilization effect of the interface geometry in the former case. Still, this does not mean that a stoichiometric TiN/1ML SiN/TiN system exists. In particular, the work by Hao *et al.*<sup>10</sup> underlined the importance of relaxing also the stoichiometry degree of freedom for this system. Moreover, the work by Alling *et al.*<sup>9</sup> showed that the formation of Si vacancies in the lattice was preferable in bulk SiN so we are led to consider the formation of Si vacancies also in these 1-ML interfacial structures. We calculate the formation energy of a single Si vacancy in both (001)- and (111)-interface supercells containing four Si atoms. The formation energy is calculated as

$$E_v^f = E_{\text{vac}} - E_{\text{ideal}} + E_{\text{Si}}, \quad (1)$$

where  $E_{\text{vac}}$  and  $E_{\text{ideal}}$  denote the total energies of supercells with relaxed coordinates with and without one Si vacancy, respectively.  $E_{\text{Si}}$  is the total energy per atom of bulk Si in its diamond structure ground state.

Our results are compiled in Table I. The obtained large negative vacancy formation energies mean that the systems should *spontaneously* form Si vacancies, at least until the favorable Si<sub>3</sub>N<sub>4</sub> stoichiometry (represented by our in-plane 2×2 supercell with a single Si vacancy) is reached. Correspondingly, in the process of growth: a second SiN<sub>x</sub> layer will start to form instead of completing a 1:1 SiN stoichiometry in the first layer due to the combined energetic and entropic favoring of Si vacancies. This is the case for both

TABLE I. Vacancy formation energy,  $E_v^f$ , according to Eq. (1), for the relaxed (001) and (111) interfaces. The size of the in-plane supercells are indicated as superscript.

	(001) <sup>2×2</sup>	(111) <sup>2×2</sup>
$E_v^f$ (eV)	-1.59	-0.65

interface orientations. At this point we note that our choice of Si chemical potential, if anything, *underestimates* the driving force for vacancy formation. It was proven in Refs. 10 and 11 that Si<sub>3</sub>N<sub>4</sub> is the most relevant Si chemical reservoir under nitrogen rich conditions, while for nitrogen poor conditions, TiSi<sub>2</sub> is the relevant reservoir. In both cases the vacancy formation is more favorable as compared to our choice of bulk Si made for simplicity and transparency. Our results together with the conclusions of Ref. 9 thus imply that the real structure of TiN/SiN<sub>x</sub> interfaces should have another stoichiometry and another coordination than the ideal B1 interfaces. Because in general one deals with systems, which may not be in thermodynamic equilibrium, a precise theoretical determination of the exact interface structures is beyond the scope of the present communication. However, metastable fcc-related phases of silicon nitride, pseudo-B3 Si<sub>3</sub>N<sub>4</sub> phases derived from a  $L1_2$ - or  $DO_{22}$ -like distribution of Si vacancies, have been recently suggested in Ref. 9 as an explanation of the experimental findings of epitaxial SiN<sub>x</sub> in TiN/SiN<sub>x</sub> multilayers. They are dynamically stable even in the bulk and their lattice parameters are close to that of TiN. A consideration of these SiN structures at the interface with TiN should be clearly included in the discussion of this problem.

In summary, we have carried out static relaxations, phonon calculations and vacancy formation energy calculations for 1 ML of B1 SiN interfaced with TiN. These calculations test, not only the mechanical stability but also the dynamical and thermodynamic stability which one must consider discussing the existence of real materials. We were able to show that the distortion of the Si-N bond almost, but not completely, stabilizes the (001) interface dynamically while the (111) interface is dynamically stable. However, both interfaces are unstable with respect to formation of Si vacancies. This means that unlike the conclusions in some previous studies, the interesting physical properties of real existing TiN-SiN<sub>x</sub> nanocomposites cannot be understood from the calculated properties of isostructural SiN/TiN interfaces with a Si<sub>1</sub>N<sub>1</sub> stoichiometry. In order to understand the materials properties of this system, theoretical investigations of more complicated interfacial geometries with an open mind for different stoichiometries need to be carried out.

The Swedish Research Council (VR), the Swedish Foundation for Strategic Research (SSF) MS<sup>2</sup>E Strategic Research Center, and the Göran Gustafsson Foundation for Research in Natural Sciences and Medicine are acknowledged for financial support. E.I.I. thanks also RFBR. Calculations were performed at the Swedish National Infrastructure for Computing (SNIC).

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