

Chapter 2

Models of the Interfaces in Superhard TiN-Based Heterostructures and Nanocomposites from First-Principles

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Abstract This chapter reviews structures and properties of various TiN-based heterostructures. The study of such systems is of vital importance in development of new materials with desired optimum properties. After discussion of the current literature, the recently published results of first-principles quantum molecular dynamics (QMD) calculations of heterostructures consisting of one monolayer of interfacial SiNx, SiC, BN and AlN inserted between several monolayers thick slabs of B1(NaCl)-TiN (001) and (111) in the temperature range of 0–1,400 K are reviewed in some detail. The results revealed that SiN(001) exists as pseudo-morphic B1-SiN interfacial layer only at 0 K. At finite temperature, this heterostructure transforms into distorted octahedral SiN₆ and tetrahedral SiN₄ units aligned along the {110} directions. At 300 K, the aggregates of the SiN_x units are close to a disordered, essentially amorphous SiN. After heating to 1,400 K and subsequent relaxation at 300 K, the interfacial layer corresponds to a strongly distorted Si₃N₄-like structure. The B1-SiN, Si₃N₄-like SiN and Si₃N₄-like Si₂N₃ interfaces between the TiN(111) slabs are stable in the whole temperature range considered here. The B1-Si₃N₄-like interfaces derived from SiN by the formation of Si-vacancies are unstable at finite temperatures. An estimate of interfacial

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formation energies showed that the most favorable configurations of the (111) interfaces are silicon atoms tetrahedrally coordinated to nitrogen. The most stable (001) B1-derived heterostructure with $\text{Si}_{0.75}\text{N}$ interface consist of both tetrahedrally and octahedrally coordinated silicon atoms. The $\text{TiN}(001)/\text{B1-SiC}/\text{TiN}(001)$ interface exists as pseudo-morphic B1-SiC layer between 0 K and 600 K. After heating to 900–1,400 K and subsequent static relaxations, the interfacial layer corresponds to a strongly distorted 3C-SiC-like structure oriented in the (111) direction in which the Si and C atoms are located in the same interfacial plane. The Si atoms form fourfold coordinated $\text{N-Si} \equiv \text{C}_3$ configurations, whereas the C atoms are located in the $\text{Ti}_2 = \text{C} \equiv \text{Si}_3$ surrounding. All the (111) interfaces simulated at 0, 300, and 1,400 K have the same atomic configurations. For these interfaces, the Si and C layers correspond to the Si-C network in the (111) direction of 3C-SiC. The Si and C atoms are located in $\text{N-Si} \equiv \text{C}_3$ and $\text{Ti}_3 \equiv \text{C} \equiv \text{Si}_3$ configurations, respectively. The $\text{BN}(001)$ interfacial layer forms a disordered h-BN-like structure consisting of BN_3 units in the whole temperature range considered here. Finally, the $\text{B1-AlN}(001)$ interface is found to be stable within the whole temperature range.

Phonon calculations show that the observed modifications of the interfaces are due to dynamical instability of the B1-type (001) and (111) interfacial layers of BN, SiC and SiN driven by soft modes within the given planes. The calculated electronic densities of states (EDOS) of the (001) interfaces suggest that the reconstructed interfaces should be semiconducting.

A comparison with the results obtained by earlier “static” *ab initio* DFT calculations at 0 K shows the great advantage of the QMD calculations that account for the effects of thermal activation of structural reconstructions. The results, which can be understood also without the knowledge of theoretical methods, were used to interpret the available experimental results on TiN-based heterostructures and nanocomposite coatings in order to provide guidance to the experimentalists for the preparation of better coatings.

2.1 Introduction

In this chapter we review our recent results of the first-principles quantum molecular dynamics (QMD) calculations of the TiN/XY heterostructures ($\text{XY} = \text{one mono-layer, 1 ML of SiN}_x, \text{SiC, BN, AlN}$) that model the corresponding nanocomposites. Results of the electronic and phonon spectra of the heterostructures are described. First we present a short review of the experimental and theoretical investigations of these nanocomposites and heterostructures to illustrate the need to perform theoretical studies of the interfaces. In Sect. 2.2 we describe the computational details. In the follow-up three sections, the results of QMD simulations performed on the $\text{TiN}(001)/\text{XY}$ ($\text{XY} = \text{SiN}_x, \text{SiC, BN, AlN}$), $\text{TiN}(111)/\text{SiN}_x$ and $\text{TiN}(111)/\text{SiC}$ heterostructures are presented and discussed. The emphasis is on the analysis of the SiN_x -based heterostructures since for these nanostructures extensive experimental and theoretical results are available. The conclusions are drawn in the last Section.

2.1.1 *nc-TiN/SiN_x Nanocomposites*

During the last 20 years, significant progress in the design and understanding of superhard nanocomposites and nanolaminates nc-MN/XY, where MN is a stable and hard transition metal nitride and XY is a covalent nitride such as Si₃N₄ or BN, has been achieved [1–11]. (Note that “nc-” stands for nanocrystalline). Among superhard nanocomposite materials, nc-TiN/SiN_x nanocomposites and heterostructures represent the most studied systems. The nc-TiN/Si₃N₄ nanocomposites exhibit superhardness higher than 65 GPa combined with high-thermal stability and oxidation resistance [1–5, 11]. The large increase of the hardness of the nanocomposites as compared with pure TiN coatings (20–21 GPa) has been explained by the existence of a nanostructure made of 3–4 nm in size TiN nanocrystals, which deform only elastically, connected by about 1 monolayer (1 ML) thick SiN_x interfacial layer around which the plastic flow occurs [12–15]. The interfacial SiN_x layer, that is percolating through the nanocomposite [3], is strengthened by valence charge transfer from the neighbor TiN [14–17], thus reducing grain boundary shear (“sliding”), which is otherwise limiting the achievable hardness enhancement in nano-sized materials to about a factor of ≤ 2 (see Refs. [11, 18] and references therein). Due to the random orientation of the TiN nanocrystals in the fully segregated nanocomposites, the interfacial SiN_x monolayer appears amorphous in XRD [3] as well as in electron diffraction [19]. The thickness of the interfaces strongly influences the strength of the nanocomposite: the highest hardness is achieved with about 1 ML thick SiN_x. When the thickness reaches about 2 ML, the hardness enhancement is almost lost [3] due to a weakening of the neighbor Ti-N bonds [20]. A dense, fully segregated 1 ML Si₃N₄-like interfacial layer provides the nanocomposites also with high oxidation and corrosion resistance because it hinders diffusion of oxygen and other corrosive elements along the grain boundaries [5, 18].

Iwamoto and Tanaka investigated crystalline TiN/Si₃N₄ interfaces in nanocomposites deposited by thermal CVD and found that the TiN crystals were aligned to the Si₃N₄ crystals with the [110] direction of B1(NaCl)-TiN (in the following simply referred to as TiN) being parallel to the [0001] direction of the hexagonal h-Si₃N₄ thus forming a semi-coherent $(10\bar{1}0)\text{Si}_3\text{N}_4 \parallel (1\bar{1}1)\text{TiN}$ interface [21]. Several papers recently reported the formation of pseudomorphic B1-related interfaces in TiN/SiN/TiN heterostructures [6, 8–10]. All the papers on heterostructures agree that the 1–2 ML thick interfacial SiN_x layer in the heterostructures is pseudomorphic, albeit in some cases distorted, and that it becomes amorphous when its thickness exceeds several monolayers.

Both the coherent and incoherent TiN/SiN_x interfaces were widely investigated in the framework of different first-principles methods [13–17, 20, 22–25]. The stability of a variety of TiN(111)/Si_xN_y heterostructures, including the above mentioned semicoherent $(10\bar{1}0)\text{Si}_3\text{N}_4 \parallel (1\bar{1}1)\text{TiN}$ interface studied by Iwamoto and Tanaka, was theoretically investigated by Hao et al. [16, 17] who also considered the effect of oxygen impurities [22] that strongly degrade the mechanical properties

of the nanocomposites [3, 18] and apparently stabilizes the Ti-Si-N solid solution [9, 18]. Density functional theory (DFT) calculations at 0 K of almost 50 different Si_xN_y interfacial configurations sandwiched between two and ten monolayers thick slabs of TiN(111) showed that, under conditions of high nitrogen activity (pressure during the deposition or annealing), the β -like $(1 \times 3)\text{-Si}_2\text{N}_3$ structure involving tetrahedral N-Si-N bonding was most favorable, while for nitrogen-poor conditions the $(1 \times 1)\text{-TiSi}$ structure was preferred which involved octahedral Ti-Si-Ti bonding [16, 17]. This is in agreement with the experimental finding that only signals from Si tetrahedrally bonded to nitrogen have been found by XPS in nanocomposites deposited in intense plasmas under a sufficiently high nitrogen pressure, whereas Ti-Si bonds have been found in coatings deposited either in a weak plasma or under low pressure of nitrogen (see Ref. [3] and references therein). The results of Hao et al. are also in agreement with thermodynamic calculations of Zhang et al. [26–28]. Hao et al. have also found that the Si-N bonds in the 1 ML thick β -like Si_2N_3 interface are stronger than in the $[10\bar{1}0]$ oriented bulk $\beta\text{-Si}_3\text{N}_4$, because the decohesion strength of that interfacial layer was larger than that of bulk ideal Si_3N_4 crystal.

Zhang et al. conducted extensive *ab initio* DFT studies on tensile and shear strength, and on the mechanism of the tensile decohesion (that is relevant for crack initiation and growth) and shear deformation (that is relevant for plastic flow) for a variety of TiN/1 ML SiN/TiN heterostructures [13–15]. They have shown that the SiN interfacial layer is strengthened by valence charge transfer from the metallic TiN, and that the weakest links are Ti-N bonds near that layer. Thus decohesion and shear occur within the Ti-N bonds weakened by Friedel-like oscillations of the valence charge density, and not in the interfacial SiN layer [14, 15]. These authors have also shown that the experimentally found loss of the hardness enhancement when the thickness of the interfacial SiN layer increased to ≥ 2 ML [29], resulted from a further weakening of the adjacent Ti-N bonds [20].

Zhang et al. have also studied the stability of different interfaces by displacing the Si atoms within the interfacial layer and following the changes of the total energy calculated at 0 K. They found that the pseudomorphic TiN(111)/B1-SiN and TiN(110)/B1-SiN interfacial SiN structures were, after a structural relaxation to the minimum of total energy under periodic boundary conditions, stable against finite displacements, whereas the TiN(001)/B1-SiN was unstable, showing a local maximum of the total energy [15]. However, this interface could be stabilized by displacement of 12 % in the $[110]$ direction, whereas a displacement along $[100]$ or $[010]$ direction resulted in a saddle point [15]. The semicoherent TiN(111)/ $\beta\text{-Si}_3\text{N}_4$ -like interface, which has been derived from the SiN-like interface by introducing Si-vacancies, was unstable upon the relaxation to the minimum of the total energy at 0 K, and it underwent structural transformation with the formation of Si-Si bonds [13]. Because no Si-Si bonds were found in well segregated, stable and superhard nanocomposites by means of XPS [3, 5], such a TiN(111)/ Si_3N_4 -like interface derived from B1-SiN by Si-vacancies is unlikely to occur in the nanocomposites deposited at $\geq 550^\circ\text{C}$, which have high thermal stability and oxidation resistance.

Alling et al. have shown that bulk B1-SiN is, within the harmonic approximation at 0 K, inherently dynamically unstable, and also the 1 ML B1-SiN(001) interface is dynamically unstable in its fully symmetric configuration [23]. More recently, Marten et al. [24] showed that this interface is dynamically more stable when distorted in the x and y direction in agreement with the earlier results of Zhang et al. [15]. The small indication of phonon instability around the X point in the Brillouin zone (BZ) indicates that this configuration is slightly unstable in the harmonic approximation at 0 K, but at finite temperature this instability disappears due to anharmonicity of the lattice vibrations [24]. The (111) interface has been found to be dynamically stable [24], also in agreement with the results of the “static” calculations of Zhang et al. [15].

Marten et al. have suggested atomic arrangements of the interfacial phase to explain the apparent epitaxial TiN(001)/SiN_x interfaces [25]. It is shown that the 1 ML B3-derived and 3 ML B3-D00₂₂-derived SiN_x interfaces are both dynamically and thermodynamically stable with respect to vacancy formation.

Although these studies provided much in-depth understanding of the heterostructures, their results are limited to DFT calculations at 0 K. Therefore, thermally activated structural reconstruction of these structures, which are likely to occur during deposition and application of nanocomposite coatings on tools at elevated temperatures, were not accessible by these calculations. As mentioned above, Zhang et al. [15] and Marten et al. [24] were forced to artificially shift the silicon atoms at the TiN(001)/1 ML B1-SiN interface to reach a saddle point or a minimum of the total energy. As result of the periodic boundary conditions and symmetry of the system during the “static” DFT calculations, the interfacial SiN layer was distorted in a regular manner keeping periodicity of that distortion. Therefore the question arises about the possible effect of thermal activation on the existence of a more distorted configuration with higher stability. Furthermore one has to ask if it be possible for the B1-SiN(111) interface, that was found to be dynamically stable at 0 K [24], to reconstruct at elevated temperatures, and for the Si₃N₄-like interfaces derived from SiN by the formation of Si vacancies [23, 24] to be stable at elevated temperatures? Finally, it is important to clarify whether the Si₃N₄-, SiN- and Si₂N₃-like interfaces, which are stable at 0 K [17], will be preserved between TiN(111) slabs at finite temperatures.

These questions have been partially resolved by first-principles quantum molecular dynamic calculations (QMD) [30]. The first-principles QMD calculations account for the effect of finite temperature by including the thermal motion of the atoms in the lattice (or a molecule or a liquid). This method automatically accounts for any thermally activated changes of the structure that lead to a lowering of the energy of the system (notice that the entropy is zero in the “static” DFT calculations at 0 K). Ivashchenko et al. [30] carried out QMD calculations of TiN/SiN_x heterostructures at finite temperatures, and relaxed them afterwards to reduce the statistic errors. In such a way, the relaxed atomic configurations were obtained. The study [30] focused on the following selected heterostructures: the dynamically unstable TiN(001)/1 ML B1-SiN that could be stabilized by artificial distortion in the [110] direction as mentioned above, and the TiN(111)/SiN_x heterostructures with one monolayer of interfacial B1-SiN, Si₃N₄-like SiN and Si₃N₄-like Si₂N₃.

2.1.2 TiN/SiC Nanolayered Coatings

In contrast to the TiN/SiN_x nanostructures, the TiN/SiC heterostructures have been studied to a lesser extent. We carried out an extensive literature search on this system, and found only one paper that was devoted to the study of the structural and mechanical properties of TiN/SiC nanolayered coatings [31]. Kong, Dai, Lao *et al.* prepared thin TiN/SiC nanolayered coatings at a relatively low temperature under different conditions of magnetron sputtering [31]. They showed that coherent 3C-SiC interfacial layers have been formed between TiN slabs with the (111) orientation when the thickness of the SiC layers was less than 0.8 nm. When the thickness of the SiC layer was about 0.6 nm, the hardness of the coatings reached a maximum value of about 60 GPa (a relatively small load of 10 mN has been used by the authors).

There are some important differences in the chemistry of the Ti-Si-N and Ti-C-N systems: Whereas pure and stoichiometric TiN and Si₃N₄ are immiscible [32] the Ti-C-N system forms a substitutional solid solution [33] with hardness increasing from that of TiN (21–22 GPa) to that of TiC (40–41 GPa) following the rules of mixtures (see Fig. 2.8 in Ref. [34]). It is therefore of great interest to study the TiN/SiC heterostructure where the carbon is bonded to silicon because the Gibbs free energies of formation at a typical deposition temperature of 800 K are –66.9 kJ/mol for SiC, –174.8 kJ/mol for TiC and –261.2 kJ/mol for TiN (see Ref. [35], pages 634, 640 and 1,542, respectively). It is therefore an open question if the SiC interfacial layer is stable at a final temperature.

To the best of our knowledge, the TiN/SiC interfaces have been theoretically investigated only in Ref. [36]. Given the limited experimental results achieved on the TiN/SiC nanolayered coatings [31], first-principles QMD calculations of the TiN/SiC heterostructures were carried out to understand the role of interfaces on strength enhancement of TiN/SiC nanolayered coatings [36].

2.1.3 TiN/BN Nanocomposites

BN has been used as interfacial material in nc-TiN/BN nanocomposites [37, 38], and in heterostructures [39, 40]. A variety of methods, such as plasma chemical vapor deposition (P CVD e.g. [3, 5, 38, 40]), physical vapor deposition (PVD, e.g. reactive sputtering [41–48], and laser ablation (e.g. [39]) has been used for the deposition of these coatings. It was shown that the B3-BN did not grow hetero-epitaxially on TiN, but that the h-BN tended to “wrap” the TiN nanocrystalline grains [39]. In contrast, the analysis of the P CVD TiN/BN heterostructures revealed that B3-BN had formed on the template TiN layer when the BN layer thickness was sufficiently thin (< 1 nm) [40]. Unlike Si₃N₄, BN cannot form any semicoherent interface with TiN because of the large difference in the atomic radii [3, 38]. Nevertheless, a hardness enhancement by a factor of about 2 has been found

in the nc-TiN/BN nanocomposites when the thickness of the interfacial BN was about 1 ML [38]. The thermal stability of these nanocomposites was limited to about 900–1,000 °C [37] and the oxidation resistance was relatively low, similar to that of pure TiN coatings [38]. In contrast, the nc-TiN/Si₃N₄ nanocomposites are thermally stable up to 1,100 °C and oxidation resistant up to ≥ 800 °C [3].

Atomic configuration, electronic density of states (EDOS) and stress-strain relation for the TiN(001)/BN and TiN(111)/BN interfaces were investigated in Refs. [49]. The results revealed that, by analogy with the TiN/SiN heterostructures [14, 15], Friedel oscillations of bond distances weakened the Ti-N interplanar bonds next to the interface. Large-scale QMD simulations of the TiN(001)/BN heterostructures showed that the BN interface transformed to an amorphous-like h-BN layer consisting of BN₃ units at any temperatures [50].

2.1.4 TiN/AlN Nanolayered Systems

Several publications reported on the epitaxial stabilization of the cubic B1-AlN in TiN/AlN [51, 52] and VN/AlN [53] heterostructures. B1-AlN layers were formed when the layer thickness (d_{AlN}) was below 2 nm, whereas for $d_{\text{AlN}} > 2$ nm, the thermodynamically stable hexagonal h-AlN was found [52]. The critical thickness below which the cubic B1-AlN was pseudomorphically stabilized increased up to 6 nm for the VN/AlN heterostructures, where the lattice mismatch of 1.46 % was smaller than in the TiN/AlN one (mismatch of 3.84 %) [53]. The formation of cubic B1-AlN was also found during spinodal decomposition of the metastable Ti_{1-x}Al_xN solid solution at about 900–1,000 °C. This phase however transformed into a thermodynamically stable hexagonal structure accompanied by a decrease of the hardness upon further annealing [54].

QMD calculations of the TiN(001)/AlN heterostructures were carried out in Ref. [50]. It was shown that, the epitaxially stabilized B1-AlN interfacial layer was preserved over all the whole temperature range in agreement with the experiments [51, 52].

2.1.5 Concluding Remarks to Sect. 2.1

It should be emphasized that any calculations of heterostructures with specific interfaces have certain limitations as regards to their implications to superhard nanocomposites with randomly oriented 3–4 nm size TiN nanocrystals, because in the nanocomposites a variety of (hkl) interfaces of small areas of a few nm², attached to different neighbor (h'k'l') planes and terminated by triple junctions have to coexist, which will surely influence the energy of the interfaces in a manner that is difficult to quantify. Therefore, it would be more appropriate to simulate the deposition of the Ti, X and Y atoms forming a solid solution, followed by its

segregation with the formation of nanocomposites, before studying the mechanical behavior of such self-organized, stable nanostructures. However in this case, extremely large scale QMD simulations would have to be used, which is impossible within the framework of the present first-principles methods. Such large-scale simulations could only be carried out by using classical MD with empirical potentials. However, reliable potentials for the Ti-X-Y system are not available yet. Therefore, a first-principles QMD study of the stability of the TiN/1 ML XY heterostructures, and their behavior as a function of temperature and composition is presently the only possible extension of the work of Hao et al., Zhang et al. and Marten et al. We present in this review results that provide new and deeper insight into the problem of the stability of the interfaces under consideration at finite temperature.

2.2 Computational Aspects

To perform the calculations of the TiN(001)/1 ML B1-XY (XY = SiN, SiC, BN, AlN) heterostructures, we considered 96-atom supercells constructed of the $(2 \times 2 \times 3)$ B1(NaCl)-TiN cubic unit cells each containing 8 atoms. The TiN(111)/1 ML B1-SiN and B1-SiC heterostructures consisted of the 54-atom $(3 \times 3 \times 1)$ supercells, derived from the 6-atom B1-TiN hexagonal unit cells with $[1/2 \ 1/2 \ 0]$, $[0 \ 1/2 \ -1/2]$ and $[1 \ 1 \ 1]$ as the **a**, **b** and **c** basis vectors, respectively. The interfacial XY monolayer has been introduced by replacing Ti atoms with X (Si, B, Al) atoms in the central lattice plane of the given supercell. For the TiN(001)/BN heterostructures, we considered two initial configurations: the first heterostructure (BN1) was generated by replacing the Ti atoms with the B atoms. The second heterostructure (BN2) was constructed by substituting N and Ti with B and N, respectively. Thus, there are eight X atoms and eight Y (C,N) atoms in the (001) interface, and nine X atoms and eighteen Y atoms (8 up and 8 down with respect to X) in the (111) interface. (The TiN(111)/1 ML XY heterostructures are “polar” in the c-direction). A similar procedure was considered to construct the initial TiN(111)/Si₃N₄-like SiN (abbreviated as “top-top” in [16, 17]) and TiN(111)/Si₃N₄-like Si₂N₃ (abbreviated as “Si₂N₃” in [16, 17]) interface, respectively. However in this case, the Si₃N₄-like SiN interface was inserted between two complete TiN(111) units, in which the number of the TiN layers is a multiple of 3 as in perfect TiN. The Si₃N₄-like Si₂N₃ interface was introduced by replacing one TiN layer. The notation and structural characteristics of all the initial heterostructures under consideration are summarized in Table 2.1. All the heterostructures consist of the parallel layers aligned perpendicularly to the c-direction, and one of them is the XY interfacial layer. To clarify a possibility of the formation of stable Si₃N₄ configurations by introducing Si vacancies we removed two Si atoms from both the B1-SiN interfacial planes.

The present calculations were done using the first-principles pseudo-potential DFT MD method as implemented in the quantum ESPRESSO code [55] with

Table 2.1 Structure, composition, number of atoms in supercells (N_a), number of the layers in the TiN unit (N_L), supercell configurations (with respect to the simple cubic TiN unit cell), symmetry of an interface and configuration of Si atoms at an interface (Si- N_i) of all the initial heterostructures under consideration

Denotation	Structure	N_a	N_L	Supercell	Symmetry of interface	X- Y_i
SiN(001)	Ti ₄₀ N ₄₀ (001)/Si ₈ N ₈	96	5	$2 \times 2 \times 3$	B1 (NaCl-type)	Si-N ₆
Si _{0.75} N(001)	Ti ₄₀ N ₄₀ (001)/Si ₆ N ₈	94	5	$2 \times 2 \times 3$	B1 (NaCl-type)	Si-N ₆
SiN(111)	Ti ₁₈ N ₁₈ (111)/Si ₆ N ₉	54	4	$3 \times 3 \times 1$	B1 (NaCl-type)	Si-N ₆
Si _{0.78} N(111)	Ti ₁₈ N ₁₈ (111)/Si ₇ N ₉	52	4	$3 \times 3 \times 1$	B1 (NaCl-type)	Si-N ₆
TOP(111)	Ti ₂₇ N ₂₇ (111)/Si ₉ N ₉	72	6	$3 \times 3 \times 1$	Si ₃ N ₄ -like SiN	Si-N ₄
Si ₂ N ₃ (111)	Ti ₄₅ N ₄₅ (111)/Si ₆ N ₉	105	10	$3 \times 3 \times 2$	Si ₃ N ₄ -like Si ₂ N ₃	Si-N ₄
SiC(001)	Ti ₄₀ N ₄₀ (001)/Si ₈ C ₈	96	5	$2 \times 2 \times 3$	B1 (NaCl-type)	Si-C ₆
SiC(111)	Ti ₁₈ N ₁₈ (111)/Si ₉ C ₉	54	4	$3 \times 3 \times 1$	B1 (NaCl-type)	Si-C ₆
BN(001)	Ti ₄₀ N ₄₀ (001)/B ₈ N ₈	96	5	$2 \times 2 \times 3$	B1 (NaCl-type)	B-N ₆
AlN(001)	Ti ₄₀ N ₄₀ (001)/B ₈ N ₈	96	5	$2 \times 2 \times 3$	B1 (NaCl-type)	Al-N ₆

periodic boundary conditions. The generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof [56] has been used for the exchange-correlation energy and potential, and the Vanderbilt ultra-soft pseudo-potentials were used to describe the electron-ion interaction [57]. In this approach, the orbitals are allowed to be as soft as possible in the core regions so that their plane-wave expansion converges rapidly [57]. The non-linear core corrections were taken into account as described in [55]. The criterion of convergence for the total energy was 10^{-6} Ry/formula unit ($1.36 \cdot 10^{-5}$ eV). To speed up the convergence, each eigenvalue was convoluted with a Gaussian with a width $\sigma = 0.02$ Ry (0.272 eV).

All the initial structures were optimized by simultaneously relaxing the supercell basis vectors and the atomic positions inside the unit cells using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [58]. The QMD simulations of the initial relaxed heterostructures were carried out in the temperature range of 10–1,400 K with fixed unit cell parameters and volume (NVT ensemble, i.e., constant number of particles-volume-temperature) for 2.7–4 ps. Below, we will analyze the heterostructures generated at 0 K (denoted L0), at 300 K (called further in the text “low temperature” and denoted LT) and at 1,400 K (called “high temperature” and denoted HT). In all the QMD calculations, the time step was 20 atomic units (a.u., about 10^{-15} s). The system temperature was kept constant by rescaling the velocity, and the variation of the total energy was controlled during each QMD time step. During the initial 1–1.5 ps, all structures reached closely their equilibrium state and, afterwards, the total energy of the equilibrated structures varied only slightly around the equilibrium value with a small amplitude of 0.005 eV/atom. We verified the convergence of the final QMD equilibrated structure with respect to the simulation time and the total energy of an equilibrated structure by choosing two B1-SiN(001) heterostructures at later stages of simulation at 1,400 K with simulation time and total energy differences of 0.2 ps and 0.01 eV/atom, respectively. Their pair correlation functions and atomic

configurations practically coincided, and the total energy difference was only about 0.27 mRy/unit cell (0.038 meV/atom; not shown here). Thus, the resultant relaxed structures are only very weakly sensitive to structural changes during the last stage of the QMD simulation.

After QMD equilibration, the geometry of all LT and HT heterostructures was optimized by simultaneously relaxing the supercell basis vectors and the atomic positions inside the unit cells using the BFGS algorithm [58]. The cut-off energy for the plane-wave basis $E_{\text{cut}} = 30$ Ry (408 eV) and the Monkhorst-Pack [59] (2 2 2) mesh (4 k -points) were used. The relaxation of the atomic coordinates and of the unit cell were considered to be complete when the atomic forces were less than 1.0 mRy/Bohr (25.7 meV/Å), the stresses were smaller than 0.05 GPa, and the total energy during the structural optimization iterative process was changing by less than 0.1 mRy (1.36 meV).

The calculations of the amorphous silicon nitrides a-SiN and a-Si₃N₄ were carried out by analogy with those of the HT nanolayered systems, with only small differences. The initial 96-atom and 112-atom samples of SiN and Si₃N₄, respectively, were constructed on the basis of the (2 × 2 × 2) β-Si₃N₄ supercell. These initial structures were heated up to 5,000 K, where the systems showed a diffusive behavior characteristic of liquids. QMD simulations of the amorphous samples were carried out in the NVT ensemble by taking into account the sample density ρ_s of β-Si₃N₄ (3.12 g/cm³). The liquids were cooled down to 300 K within about 3.5 ps. The final amorphous samples were equilibrated at 300 K for 2.0 ps and then relaxed. In molecular dynamics simulations of the large-scale systems, only the Γ point was taken into account in the BZ integration, and the cut-off energy for the plane-wave basis was set to 24 Ry (~326 eV). The application of a reduced E_{cut} in large-scale QMD calculations was validated by Wang, Gudipati, Rao et al. [60] who successfully used a plane wave energy cutoff of 348.1 eV for the pseudopotential calculations of the elastic constants C_{ij} of the TiN/Si_xN_y superlattices.

The above-described pseudopotential procedure was used to study the phonon spectra of the B1-type XY in the framework of the density-functional perturbation theory (DFPT) described in Ref. [61]. The first-principles DFPT calculations were carried out for a (8 8 8) q-mesh, and afterwards the phonon densities of states (PHDOS) were computed using a (12 12 12) q-mesh by interpolating the computed phonon dispersion curves. Both the EDOS and PHDOS were calculated with the tetrahedron method implemented in the “Quantum-ESPRESSO” code [55].

For the Ti-Si-N system, the heat of formation of the bulk materials, H^f , has been calculated as $H^f = E_{\text{tot}} - \sum n_i E_i$, where E_{tot} is the total energy of the bulk compound with n_i atoms of all involved elements i (Si, Ti and N) and E_i is the total energy of the bulk Si and Ti atom, and half of the energy of N₂ molecule, respectively. The conditions of the calculations for bulk Ti and Si are summarized in Table 2.2. The total energy and equilibrium bond length of N₂ molecule were calculated using the extended two-atom cubic cell. The bond length of N₂ molecule was in agreement with the experimental value (1.098 Å) within 1 %.

Table 2.2 Structural and energetic characteristics of the computed phases in comparison to those of other experimental (in parentheses) and theoretical (in braces) investigations taken from Ref. [17, 42] that were used in this work for the interpretation of the heterostructures

Phase	Symmetry	N	<i>k</i> -mesh	Lattice parameters <i>a</i> , <i>b</i> , <i>c</i>	<i>H</i> ^f
				(Å)	(eV/f.u.)
TiN	Fm-3 m	2	(8 8 8)	4.249 (4.24) ^a {4.239–4.275} ^a	−3.46 (−3.46) ^b {−3.43, −3.56} ^b
β-Si ₃ N ₄	P6 ₃ /m	14	(4 4 12)	7.670, 7.670, 2.930 (7.607, 7.607, 2.911) ^b {7.652, 7.652, 2.927} ^b	−6.85 (−6.44 ± 0.83 to −8.73 ± 0.03) ^b , {−7.81} ^b {−9.89} ^c
TiSi ₂ -C49	Cmcm	6	(4 4 4)	3.538, 13.418, 3.590 (3.62, 13.76, 3.60) ^b {3.571, 13.573, 3.556} ^b	−1.69 (−1.77 ± 0.09) ^f
TiSi ₂ -C54	Fddd	6	(4 4 4)	8.259, 4.795, 8.521 (8.269, 4.798, 8.553) ^b {8.270, 4.801, 8.553} ^b	−1.71
Ti	P6 ₃ /mmc	2	(8 8 6)	2.913, 2.913, 4.614 (2.951, 2.951, 4.683) ^c	–
Si	Fd-3 m	2	(8 8 8)	5.465 (5.43) ^d	–

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^aRef. [62]

^bRef. [17]

^cX-ray powder diffraction file [044–1294]

^dX-ray powder diffraction file [027–1402]

^eRef. [27]

^fExperimental data for TiSi₂ [63]

The interfacial formation energy E^f , that yields information about the relative stabilities of various interfacial structures in the TiN/Si_xN_y heterostructures, is calculated as

$$E^f = S^{-1} \times \{E_H(N_{TiN}, N_I) - E_L(N_{TiN}) - n_{Si}E_{Si} - n_N E_N\}, N_I = n_{Si} + n_N, \quad (2.1)$$

where E_H is the total energy of the heterostructure under consideration, N_{TiN} and N_I are the numbers of atoms in the TiN slab and Si_xN_y interface, respectively, and $E_L(N_{TiN})$ is the total energy of the TiN unit. To calculate E_L we used two approaches: in approach A), $E_L(N_{TiN}) = N_{TiN} \times E_{TiN}$, where E_{TiN} is the total energy of bulk TiN per atom. For the approach B), the TiN unit is constructed by means of: i) a removal of the interface with interfacial area S from the TiN/Si_xN_y heterostructure, and ii) optimization of the resultant TiN structure as described above; n_S and n_N are the numbers of interfacial silicon and nitrogen atoms, respectively; E_{Si} and E_N are the energies (per atom) of the Si and N interfacial atoms.

Equation (2.1) is similar to Eq. (3) in Ref. [17], where slab structures were considered. In our case, the expression (2.1) is applied to periodic bulk structures. We used the approximations for values of E_{Si} and E_N as suggested by Hao et al. [17], who considered E_{Si} and E_N for so-called nitrogen-rich and nitrogen-poor (Ti-rich) conditions. For N-rich conditions, $E_{Si} = 1/3\{E_{tot}(\beta - Si_3N_4) - 2E_{tot}(N_2)\}$, $E_N = 1/2E_{tot}(N_2)$, where $E_{tot}(\beta - Si_3N_4)$ and $E_{tot}(N_2)$ are the total energy of bulk $\beta - Si_3N_4$ and half the energy of an N_2 molecule, respectively. For the N-poor conditions, $E_{Si} = 1/2\{E_{tot}(TiSi_2) - E_{tot}(Ti)\}$, $E_N = E_{tot}(TiN) - E_{tot}(Ti)$, where $E_{tot}(TiSi_2)$, $E_{tot}(Ti)$, $E_{tot}(TiN)$ are the total energies of bulk $TiSi_2$ -C54, hexagonal Ti and TiN, respectively [17].

In order to interpret the structures of the interfaces, the structural parameters of the Ti-Si-N phases and the most stable XY structures were calculated: B1-XY (space group Fm-3 m), B3-XY (space group F-43 m), h-XY (space group P6₃/mmc) and B4-XY (space group P6₃/mc). The resulting structural parameters and heat of formation of the above mentioned crystalline solids are summarized in Tables 2.2 and 2.3. One can see that our results compare well with the published experimental and theoretical values, whenever available, for all compounds. Also our results for a- Si_3N_4 (not shown in Table 2.2) compare well with those of Giacomazzi and Umari [67], except of a small difference in the pair correlation function (PCF): our average Si-N bond length of 1.77 Å is somewhat larger than the value of 1.73 Å reported in Ref. [67], and the experimental values of 1.73–1.75 Å reported in Refs. [68]. This is due to the different approximations for the exchange-correlation potential used: GGA in our investigation, and LDA in Ref. [67]. It is well known that the GGA usually overestimates bond lengths, whereas the LDA underestimates them [55].

In large-supercell calculations, the reduced energy cut-off and the mesh of k-points were selected in order to minimize computing time without compromising accuracy, after it was verified that this choice yielded correct values for the lattice parameter a and bulk modulus B of TiN: For the 96-atom sample with $E_{cut} = 24$ Ry (~326 eV) and the one k-point, we obtained $a = 4.228$ Å and $B = 276$ GPa, whereas with $E_{cut} = 30$ Ry (~408 eV) and the (2 2 2) mesh, the lattice constant and bulk modulus were 4.248 Å and 278 GPa, respectively, which is a satisfactory agreement. For the 2-atom TiN cell with $E_{cut} = 30$ Ry (~408 eV) and the (8 8 8) mesh, our calculated lattice constant was $a = 4.249$ Å and bulk modulus $B = 273$ GPa. The calculated lattice constants are close to the experimental value of 4.24 Å and comparable to other theoretical results of 4.239–4.275 Å [62] (cf. Table 2.2), and the values of bulk moduli agree with the experimental and theoretical values of 264–326 GPa [62]. Also the calculated heat of formation for the 2-atom TiN cell is in excellent agreement with the experimental value of H^f (cf. Table 2.2). We compared also the total energy of pure TiN obtained for the 96-atom unit cell with $E_{cut} = 30$ Ry (~408 eV) and (2 2 2) mesh with 2-atom cell, $E_{cut} = 30$ Ry and the (8 8 8) mesh. The total energy difference was only about 0.3 mRy/formula unit (~4 meV/atom), i.e. very small. The calculated surface energy σ (for details see Ref. [17]) for the 5-layer (2 × 2) TiN(001) and 10-layer (3 × 3) TiN(111) slabs

Table 2.3 Lattice parameters (a, b, c), X-Y bond length (R), and total energy (E_T) of the computed XY phases in comparison to those of other experimental and theoretical investigations

XY phase	Lattice parameters a, b, c	R	E_T
	(Å)	(Å)	(eV/atom)
h-BN	2.510, 2.510, 6.713 ^a	1.449 ^a	-178.583 ^a
	2.504, 2.504, 6.661 ^b	1.446 ^b	
	2.491, 2.491, 6.378 ^c	1.438 ^c	
B3-BN	3.621 ^a	1.568 ^a	-178.517 ^a
	3.616 ^d	1.566 ^d	
	3.592 ^c	1.555 ^c	
B4-BN	2.552, 2.552, 4.222 ^a	1.327 ^a	-178.499 ^a
	2.55, 2.55, 4.215 ^c		
	2.531, 2.531, 4.189 ^c		
	2.544, 2.544, 4.208 ^f		
B1-BN	3.499 ^a	1.750 ^a	-176.760 ^a
B4-AlN	3.116, 3.116, 4.996 ^a	1.571 ^a	-221.478 ^a
	3.111, 3.111, 4.980 ^g		
	3.114, 3.114, 4.992 ^h		
B3-AlN	4.384 ^a	1.898 ^a	-221.457 ^a
	4.365 ⁱ	1.890 ⁱ	
	4.380 ^h	1.897 ^h	
h-AlN	3.302, 3.302, 4.147 ^a	1.906 ^a	-221.364 ^a
B1-AlN	4.052 ^a	2.026 ^a	-221.310 ^a
	4.045 ^j		
	4.052 ^h		
B3-SiC	4.378 ^a	1.896 ^a	-142.948 ^a
	4.359 ^k	1.888 ^k	
B4-SiC	3.092, 3.092, 5.063 ^a	1.671 ^a	-142.945 ^a
h-SiC	3.173, 3.173, 4.798 ^a	1.832 ^a	-142.498 ^a
B1-SiC	4.060 ^a	2.030 ^a	-142.211 ^a
	4.080 ^l		
B3-SiN	4.301 ^a	1.862 ^a	-200.476 ^a
B4-SiN	3.312, 3.312, 4.636 ^a	1.530 ^a	-200.328 ^a
h-SiN	3.467, 3.467, 4.111 ^a	2.002 ^a	-200.215 ^a
B1-SiN	4.251 ^a	2.126 ^a	-200.112 ^a

^aThe present Quantum ESPRESSO-GGA calculations
^bX-ray powder diffraction file [073–2095]
^cCASTEP-LDA calculations [25, 64]
^dX-ray powder diffraction file [087–1983]
^eX-ray powder diffraction file [049–1327]
^fCASTEP-GGA calculations [29, 65]
^gX-ray powder diffraction file [065–0832]
^hDFT-GGA calculations [6, 66]
ⁱX-ray powder diffraction file [080–0010]
^jX-ray powder diffraction file [046–1200]
^kX-ray powder diffraction file [029–1129]
^lX-ray powder diffraction file [049–1623]

are $0.074 \text{ eV/\AA}^2$ and $0.203 \text{ eV/\AA}^2$, respectively. These values are in good agreement with those computed in Ref. [17] for the 9-layer (1×1) TiN(001) slab ($0.084 \text{ eV/\AA}$) and 8-layer (1×1) TiN(111) slab ($0.214 \text{ eV/\AA}$). We used larger size of the x-y slab surface as compared to those considered by Hao et al. [17], which explains why our surface energies are slightly lower than those obtained in Ref. [17].

2.3 Characterization of the Structure of the Calculated Interfaces

2.3.1 Structural Properties of SiN and Si_3N_4 -Like Si_2N_3 Interfaces

The geometry optimization of the initial B1-SiN heterostructures at 0 K preserved the hetero-epitaxial arrangement for all interfaces in a similar way as described by Zhang et al. [14, 15] (not shown here; one should keep in mind that the symmetric (001) interface corresponds to a local maximum of the total energy [15] and is dynamically unstable [24]). The geometry of the (001) interface was preserved, but the nitrogen atoms above and below the interface were slightly shifted by $0.26 \text{ \AA}$ toward this interface. However, at finite temperatures, the (001) interfacial structure significantly changed, whereas there were no significant changes in the (111) interface. In Fig. 2.1 we show the atomic configurations of the high-temperature TiN/1 ML SiN/TiN heterostructures after QMD equilibration at 1,400 K and subsequent relaxation. Figure 2.2a shows the corresponding change of the total energy (E_T) of the TiN(001)/SiN heterostructure during the QMD calculations at 10 K, which is sufficient to trigger the structural transformation. The temperature-dependent evolution of E_T for the TiN(001)/SiN heterostructure is shown in Fig. 2.2b. One can see that the structural transformation and concomitant decrease of the total energy occurs at 10 K. Figure 2.3 shows the arrangement of the atoms located in the (001) interfacial plane or close to it for the low- and high-temperature B1-SiN(001) heterostructures.

Because the TiN(001)/B1-SiN structure is strongly influenced by temperature, we need to consider this temperature effect in detail. We note significant atomic re-arrangement caused by thermal motion of the interfacial atoms that occurs predominantly within the interfacial SiN layer. There is an almost symmetrical, “down” and “up” shift of the N atoms in the layer just above and below the SiN (001) interfacial layer, an almost random shift of the Si atoms within the interfacial plane, and a breaking of about half of the Si-N bonds. This leads to the formation of a $\beta\text{-Si}_3\text{N}_4$ -like units that are represented by the SiN_4 , and of SiN_6 units with Si atoms distorted along the (110) directions (cf. Fig. 2.3). One can see from Fig. 2.3 that, along with the new Si_3N_4 -like units, some of the original sixfold coordinated

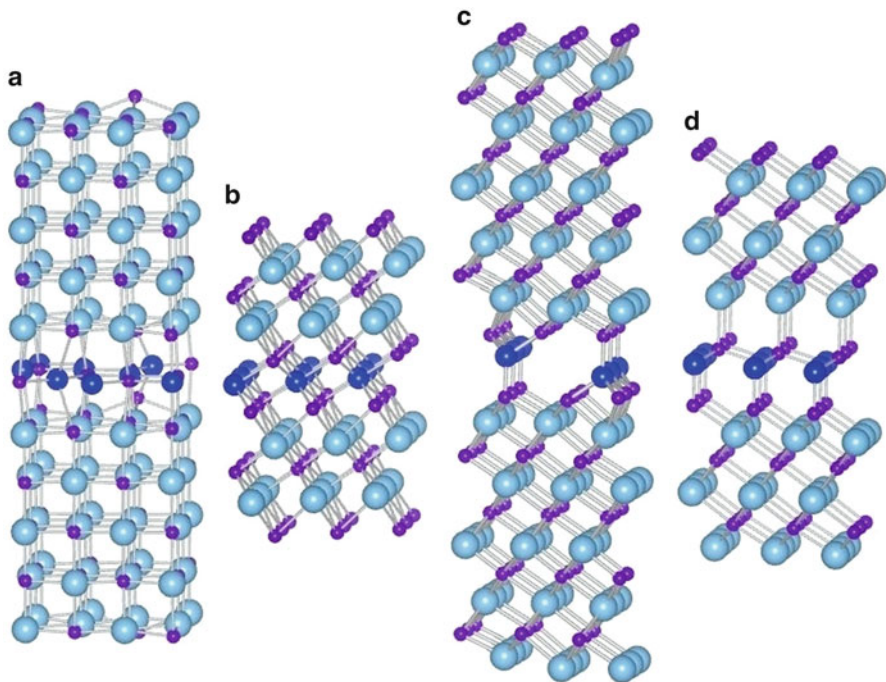


Fig. 2.1 Atomic configuration of the high-temperature TiN/1 ML SiN/TiN heterostructures: HT-SiN(001) (a), HT-SiN(111) (b), HT- $\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_3$ (111) (c) and HT- $\text{Si}_3\text{N}_4\text{-SiN}$ (111) (d). The atomic configurations were computed using the Si-N and Ti-N bond length cut-offs of 2.5 Å. Ti-big blue-grey, Si-medium dark blue and N-small purple

B1-SiN units are still present albeit distorted. We note that only two SiN_4 clusters are present in the interface at 300 K (see LT-SiN(001)) for the Si-N bond length cut-off up to 2.5 Å (which is too long for a covalent bond in Si_3N_4), whereas at high temperature the number of such units increases from two to four (see - HT-SiN(001)). The thermal energy supplied to the TiN(001)/B1-SiN heterostructure during annealing at 1,400 K enhances the formation of the stable SiN_4 units. At slow cooling rate the influence of the Ti-N surrounding around the (001) interface is enhanced and the distortion of the SiN_4 units as well as the total energy slightly increase (not shown here for brevity). This result is similar to that of Zhang et al. who found that the (001) interface lowers its energy by distortion of the Si network so that these atoms become essentially fourfold coordinated [15]. The important difference is the fact that whereas the intentional distortion was regular in the “static” (at 0 K) DFT calculations of Zhang et al. due to the symmetry constraints imposed on their calculations, our present first-principles QMD calculations show that the interfacial layer is distorted randomly, which decreases the strain energy as discussed below.

We also note that the thermal energy supplied to the TiN(001)/B1-SiN heterostructures during evolution at 300 K is not sufficient for a complete relaxation of the

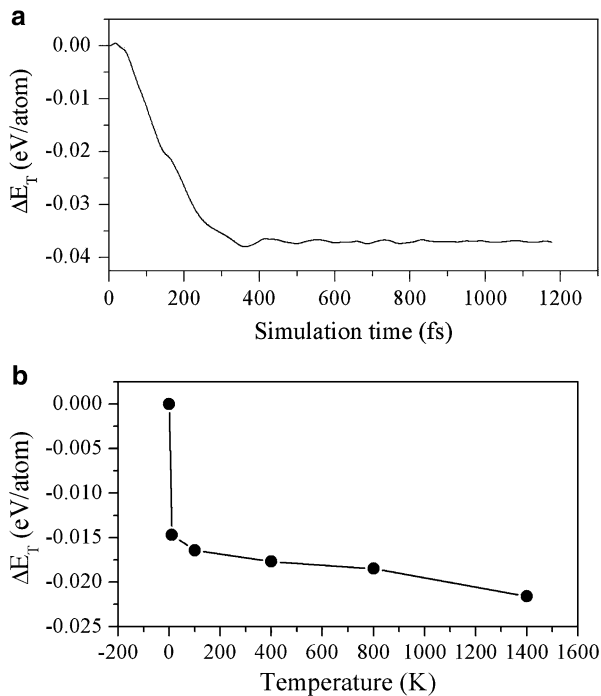


Fig. 2.2 (a) Total energy $\Delta E_T = E_T(t) - E_T(0)$ as a function of the calculation time for the TiN (001)/SiN heterostructure. The calculations were carried out at 10 K. (b) Total energy $\Delta E_T = E_T(t) - E_T(0)$ as a function of temperature for TiN(001)/SiN heterostructure

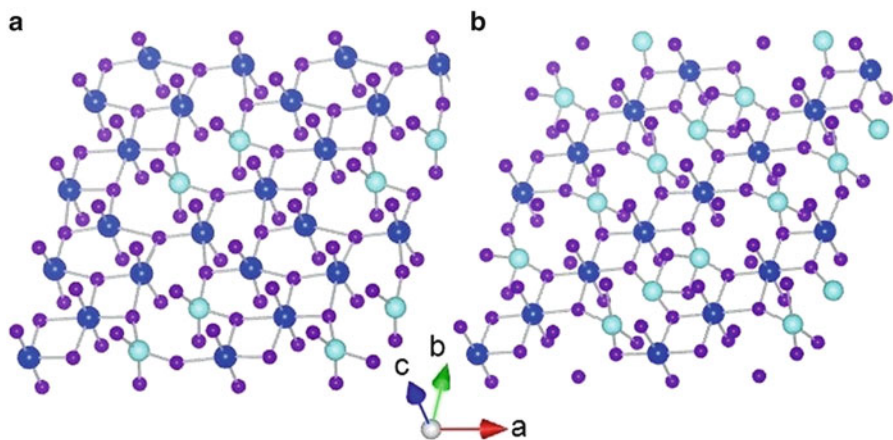


Fig. 2.3 Bond configurations in and around the interfacial planes for LT-SiN(001) (a) and HT-SiN(001) (b). The atomic configurations were computed using the Si-N bond length cut-off of 2.5 Å. Si-medium dark blue, N-small purple, the light-colored large circles are the fourfold coordinated Si atoms (Reprinted with permission from Ivashchenko et al. [30]. Copyright 2012 by the American Physical Society)

system. This interface is characterized by an atomic rearrangement within the interface and a shift of N atoms in the neighborhood as well as in distant TiN planes (cf. LT-SiN(001) in Fig. 2.1). At 1,400 K, the distortions within the interfacial SiN planes are more pronounced, and the shifts of the atoms with increasing distance from it are somewhat relaxed. We note that significantly slower cooling of the (001) heterostructure (HLT-SiN(001)) equilibrated at 1,400 K results in very similar interfacial structures (not shown here).

Since the relaxed heterostructures are obtained by quenching the different heterostructures to zero temperature, it is interesting to compare their total energy. It was found that the total energy decreased in the following sequence: relaxed zero-temperature (001) heterostructure (as reference) L0-SiN(001) 0.0000 eV/atom $\rightarrow$ LT-SiN(001) -0.0077 eV/atom $\rightarrow$ HLT-SiN(001) -0.0103 eV/atom $\rightarrow$ HT-SiN(001) -0.0193 eV/atom, i.e. the high temperature heterostructure HT-B1-SiN(001), which has the largest random distortion, has the lowest total energy.

This result may appear surprising because in macroscopic systems the ordered, crystalline phase is more stable than the disordered, amorphous one (we shall see later that the disordered (001) interface has similar pair correlation function as for amorphous SiN_x). However, the thermodynamical behavior of nano-sized materials shows differences as compared with the macroscopic ones. For example, the melting point T_m decreases with decreasing size d approaching, in the case of Au, CdSe and other materials, only few 100 °C for crystallite size of about 3 nm [69, 70]. In the case of compact thin films of nanocrystalline silicon, Veprek et al. reported transition to amorphous phase when the crystallite size reached about 3 nm [71]. These authors found that this crystalline-to-amorphous transition is due to increasing elastic strain energy of the nc-Si with decreasing crystallite size, which is seen as a dilatation of the lattice constant, and is driven by the tensile stress within the grain boundaries. The tensile stress within the grain boundaries originates from the density deficit present there. As it has been shown by a simple calculation in Ref. [71], the system reduces this energy by forming amorphous network that eliminates the grain boundaries, and as such it reduces the elastic strain energy originating from the grain boundaries in the nc-Si. Thus, the amorphous phase becomes more stable than the crystalline one for nano-sized compact films, in contradiction to what is happening in a macroscopic system. By analogy, the random distortion of the SiN interfacial layer obtained in the present QMD calculations reduces the strain as compared to the regularly distorted one in the calculations by Zhang et al.

In contrast to the (001) interface, the (111) interface is stable upon heating to 1,400 K and subsequent static relaxation (see HT-SiN(111), HT-Si₃N₄-SiN(111) and HT-Si₃N₄-Si₂N₃ (111) in Fig. 2.1). The structures of the LT- and HT-(111) interfaces are similar to that of the initial (111) interface at 0 K. The total energy of the HT-heterostructures relatively to that of the initial one at 0 K shows only very small changes: it increases by 0.0049 eV/atom for HT-Si₃N₄-SiN(111), by 0.0014 eV/atom for HT-B1-SiN(111), and decreases by 0.0034 eV/atom for HT-Si₃N₄-Si₂N₃(111). Because of the surprisingly high stability of the B1-SiN (111) interface we carried out QMD simulations for the (111) interface by raising the temperature up to 3,000 K (i.e., close to the melting point of TiN of 3,223 K [72]), and found no breaking of old bonds or formation of new bonds. Except for some

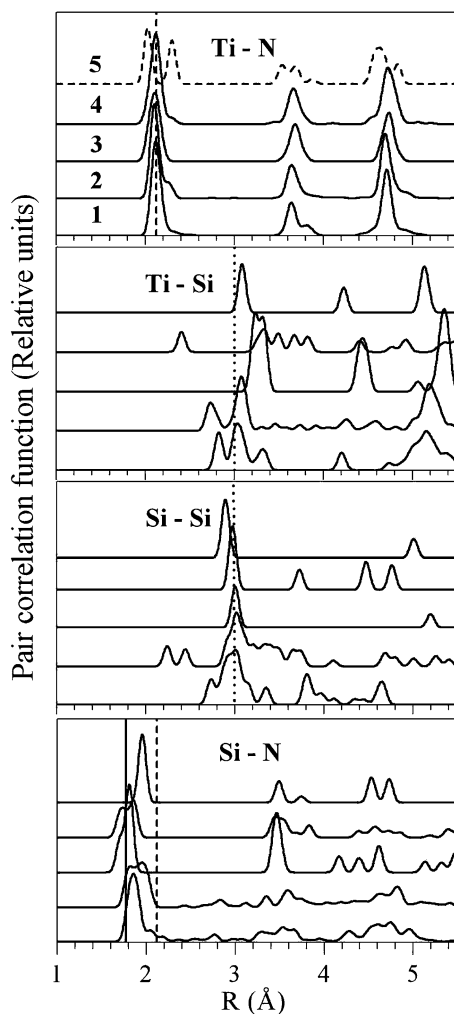
small distortions, there were no significant changes of this structure. To make sure that the high thermal stability of these (111) interfaces is not any artifact of our QMD calculations, we performed QMD calculations for the TiN(111)/B1-SiC heterostructures under the same conditions and found that the B1-SiC interfacial layer transforms to 3C-SiC already above 600 K (see below). Thus, the stability of the B1-SiN(111) interface is intrinsic to this configuration in the SiN-TiN (111) interface. It remains an open question if it is due to hetero-epitaxial stabilization, or due to a different thermodynamics at the nanoscale, or to kinetic limitations because it is well documented that transformations, that require a final nucleation volume, are hindered in nano-sized materials. For these reasons the 1 ML B1-SiN(111) interface should not be excluded when considering the nanocomposites. With this regards, it would be of great interest to conduct experimental studies on the TiN(111)/B1-SiN heterostructures.

To analyze the structural evolution of the interfaces in more details, we computed the pair correlation functions (PCF) and the bond-angle distribution, $g(\Theta)$, for all heterostructures under consideration. The results are shown in Figs. 2.4 and 2.5. We see that the first PCF peak corresponding to the Ti-N nearest neighbor (NN) distance in the (001) interface is located around 2.11 Å that is slightly lower than the Ti-N bond length in pure TiN (2.12 Å). The broadening of this peak can be attributed to small variations in the bond distance as results of the Friedel-like oscillations around the SiN interfaces (SiN(001) and SiN(111)), or to distortions around the Si_3N_4 -like interfaces (Si_3N_4 -SiN(111) and Si_3N_4 - Si_2N_3 (111)) (cf. Fig. 2.2).

The above mentioned shift of the N and Si atoms in the TiN(001)/B1-SiN heterostructures leads to the formation of the many-peak structure of the Ti-Si nearest distances indicating a strengthening of the Ti-Si interaction. This type of interactions shows up in the PCF as a peak associated with the Ti-Si “nearest neighbor” correlations at 2.75–2.82 Å. These values compare well with the calculated and experimental Ti-Si bond lengths of 2.54–2.76 Å found in TiSi_2 (cf. Table 2.2). Also this finding is in qualitative agreement with the results of Zhang et al. because in the case of the (001) interface, there are two different (011) planes running perpendicularly to that interface: “planes I” which pass through Si atoms and “planes II” that pass through N-atoms within that interfacial layer, thus causing a “phase shift” of the Friedel-like oscillations between these planes (see Fig. 2.2 in [15]). One can see from Fig. 2.4 that the splitting of the Ti-Si peak is absent in the PCF of the SiN(111) and Si_3N_4 -SiN(111) heterostructures. Owing to the symmetry of the Si_2N_3 interface, the strong Ti-Si “nearest neighbor” correlations are shown as a peak at 2.4 Å in the Ti-Si PCF of the HT- Si_3N_4 - Si_2N_3 (111) structure.

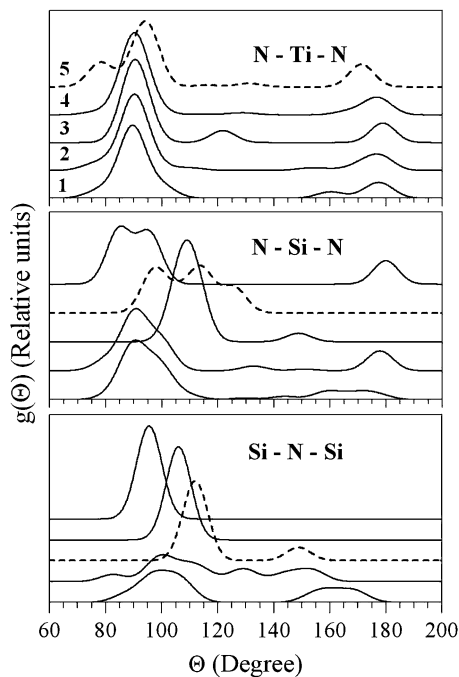
Because the Si-N bond length of 1.75–1.77 Å in β - Si_3N_4 is much shorter than the Ti-N bond length of 2.12 Å in pure TiN, there is a tensile misfit stress within the interfaces. This stress and the tendency of silicon to attain its fourfold coordination to nitrogen as in Si_3N_4 , which is the most stable configuration in the Si-N system, are the main factors that cause the reconstruction of the hetero-epitaxial layers. Figure 2.4 shows that the Si-N bonds are shorter than the Ti-N bonds in all

Fig. 2.4 Pair correlation functions for the low- and high-temperature 1 ML SiN interfaces: 1-LT-SiN(001), 2-HT-B1-SiN(001), 3-HT-Si₃N₄-SiN(111), 4-HT-Si₃N₄-Si₂N₃(111) and 5-HT-SiN(111). The *broken* and *dotted vertical lines* show the Ti-N and Ti-Ti distances in TiN, respectively. The *solid vertical line* corresponds to the Si-N bond length in β -Si₃N₄ (Reprinted with permission from Ivashchenko et al. [30]. Copyright 2012 by the American Physical Society)



heterostructures, and this tendency to shortening is more pronounced for the HT-SiN(001), HT-Si₃N₄-SiN(111) and HT-Si₃N₄-Si₂N₃(111) interfaces which have almost the equilibrium Si-N bond length of 1.77 Å, seen as the shoulders in the Si-N PCF peak. The one-peak Si-N nearest neighbor correlation with the elongated Si-N bonds of 1.85–1.95 Å is seen in all interfaces. An inspection of the atomic arrangement and the PCF for the HT-SiN(001) clearly shows that the bond lengths of 1.76–1.83 Å correspond to the Si-N bonds in the distorted β -Si₃N₄-like units, whereas the peak at 1.95 Å corresponds to the Si-N bond lengths in the SiN₆ units. The shortening of the Si-N bonds causes an elongation of the Ti-N ones, which is more pronounced for the bonds between the interfacial N atoms bonded to Si and the Ti atoms next to it than between Ti and N atoms far away from the interface (cf. Figs. 2.1 and 2.3).

Fig. 2.5 Bond angle distribution $g(\Theta)$ for the low- and high-temperature 1 ML SiN interfaces: 1-LT-SiN(001), 2-HT-SiN(001), 3-HT-Si₃N₄-SiN(111), 4-HT-Si₃N₄-Si₂N₃(111) and 5-HT-SiN(111). The bond angle distributions were computed using the Si-N bond length cut-off of 2.2 Å. The Ti-N bonds were cut at 2.5 Å (Reprinted with permission from Ivashchenko et al. [30]. Copyright 2012 by the American Physical Society)



For the B1-SiN interfaces, the average lengths of the Ti-N bonds adjacent to the interfacial SiN layer are 2.275 and 2.298 Å for the (001) and (111) interfaces, respectively. The average length of the Ti-N bonds between the next neighbor planes parallel to the interfaces is about 2.076 and 2.025 Å for the (001) and (111) heterostructures, respectively. Thus, the broadening of the PCF peaks of the Ti-N next-near neighbor peaks seen in Fig. 2.4 is due to this bond length distribution. The Ti-N bond length increases when moving away from the Si₃N₄-like SiN interface. For the Si₃N₄-like Si₂N₃ interface, we did not identify any regularity in the change of Ti-N bonds in the c-direction (not shown).

It is interesting to compare our results for the B1-SiN based interfaces with those of Zhang et al. who, using a static *ab initio* DFT at 0 K, found fairly regular Friedel-like oscillations of the bond lengths damped with increasing distance from the (111) interface [14]. In the case of the (001) interface, these oscillations were “phase shifted” in planes perpendicular to that interface and passing either through Si or N atoms in that interface [15]. These authors identified the longest Ti-N bonds close to the interface as the weakest links in the heterostructures (and by analogy in the nanocomposites). They could show that for all three interfaces, (111), (001) and (110), studied in their work, the ideal decohesion and shear occurred within the longest and therefore weakest Ti-N bonds and not in the SiN interfacial layer. Our results obtained with more general first-principles QMD at 300 K and at elevated temperatures fully confirm the weakening of the elongated Ti-N bonds adjacent to the SiN interfaces. The disorder due to thermal activation introduces

some broadening of the near neighbor peaks in the PCF. However, the structural instability of the (001) interface discussed above calls for re-considering the stress-strain calculations at finite temperature using the first-principles QMD. Comparing, as an example, the (001) interface one sees that the longest Ti-N bonds adjacent to the SiN layer of 2.206–2.275 Å are shorter than those of 2.35–2.37 Å reported in Ref. [15] for the DFT calculations at 0 K. Also the longest Ti-N bond lengths of 2.298 Å for the (111) interface are shorter than those of 2.32 Å reported in Ref. [14]. This is likely related to a more efficient relaxation of the structure in the present QMD calculations as seen also in the decrease of the total energy discussed above. Because the longest bonds are the weak links where decohesion and shear occurs [14, 15], it would be interesting to see if the somewhat shorter bond lengths found in the present work will reflect larger ideal strengths of the interfaces. This is the subject of our present work.

Let us now examine the PCF for the Si-Si bonds and distances. As one can see in Fig. 2.4, there is one peak at a distance of about 3 Å in all the (111) heterostructures that corresponds to the second nearest-neighbor (Si-N-Si) correlations in the interfaces. In contrast, this peak splits into several shoulders in the case of the LT- and HT-SiN(001) interface due to the random distortion as discussed above. This splitting is much more pronounced for the HT-SiN(001) interface with the appearance of a new peak around 2.35 Å, that are close to the Si-Si bond length in crystalline silicon. This can be understood on the basis of thermodynamic instability of SiN which, in the case of closed system simulated by the QMD, should decompose according to $4\text{SiN} \rightarrow \text{Si}_3\text{N}_4 + \text{Si}$ with a high Gibbs free energy of the reaction of -6.44 ± 0.83 to -8.73 ± 0.03 eV/formula unit (cf. Table 2.2). This value is in a reasonable agreement with the result of Zhang and Veprek who, using a combined DFT and thermodynamic calculations, reported Gibbs free energy for that reaction to be -136.3 kJ/mol atoms (*i.e.*, 9.89 eV/formula unit) [27]. Obviously, there is a kinetic activation barrier for this reaction that must occur at room temperature. Therefore this peak is absent in the PCF of LT-SiN(001) interface (see Fig. 2.4).

In Fig. 2.5, we show the distributions of the N-Ti-N, N-Si-N and Si-N-Si bond angles. The N-Ti-N angles are between 90° and 94° , which are very close to the angle 90° for pure TiN. For the (001) interfaces, the N-Si-N angles are around 90° and 101° , *i.e.*, close to the angles for the octahedral (90° in B1-SiN) and tetrahedral (109.7° in h-Si₃N₄) configurations, respectively. In the case of the B1-SiN(111) interface, there are two peaks in the N-Si-N bond angle distribution located at 85° and 95° . Because the sixfold octahedral coordination is preserved in these interfaces, such a bond angle splitting indicates its asymmetry, which can be seen by careful observation of Figs. 2.1: the N-Si-N angles oriented up and down (*i.e.* where the N-atoms are further bonded to Ti only) are clearly larger than those oriented to the left or right (*i.e.* where the N-atoms are bonded to the second neighbor Si and Ti). The tetrahedral coordination of the Si atoms in the HT-Si₃N₄-SiN(111) interface is confirmed by the single peak in the $g_{\text{N-Si-N}}(\Theta)$ distribution around 109.7° . The distorted tetrahedral configuration of the Si atoms in the Si₃N₄-Si₂N₃(111) interface is seen as two peaks localized at 98° and 113° . The Si-N-Si bond angle distribution in the HT-SiN(111) interface shows one relatively symmetric peak at about 97° . The Si-N-Si bond angle in the LT-SiN(001) interface shows a

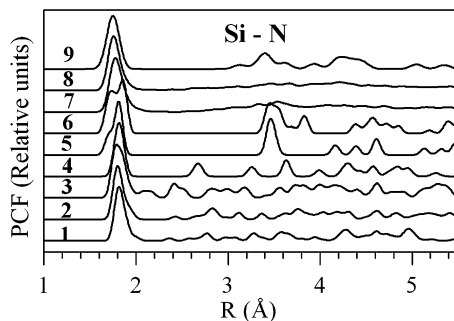


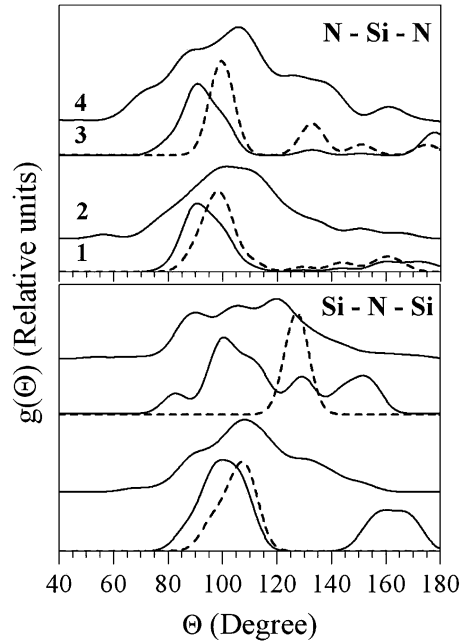
Fig. 2.6 Si-N pair correlation functions for the interfaces with the fourfold coordination of silicon atoms. Denotation: 1-LT-SiN(001), 2-HT-SiN(001), 3-the structure was obtained by slow cooling B1-SiN(001) from 1,400 to 300 K, 4-LT-Si_{0.75}N(001), 5-HT-Si₃N₄-SiN(111), 6-HT-Si₃N₄-Si₂N₃(111), 7-a-SiN, 8-a-Si₃N₄ and 9- β -Si₃N₄. The PCFs of the LT-SiN(001), HT-SiN(001) and HT-Si_{0.75}N(001) were computed for the heterostructures in which the chain of the sixfold coordinated Si atoms was removed (Reprinted with permission from Ivashchenko et al. [30]. Copyright 2012 by the American Physical Society)

broad distribution with a main peak around 101° , whereas in the HT-SiN(001) interface, the distribution is even broader and the main peaks are located around 101° and 128° . Such a distribution shows that nitrogen atoms form mostly the NSi_4 and NSi_3 coordinated units, respectively. The Si-N-Si angles around 106° and 112° in the HT-Si₃N₄-Si₂N₃(111) and HT-Si₃N₄-SiN(111), respectively, indicates the distorted fourfold configurations of the N atoms in the Si-N network of these heterostructures.

To obtain a deeper insight into the structure of the (001) interfaces we calculated the PCF and $g(\Theta)$ functions for β -Si₃N₄, a-SiN and a-Si₃N₄. The results are shown in Figs. 2.6 and 2.7 in comparison with those for the (001) interfaces. A comparison of the PCFs and $g_{\text{Si-N-Si}}(\Theta)$ functions enables us to infer that the Si-N network of the LT(001) interface is more similar to that of a-SiN than to the others. However, the positions of the main peaks in the PCF and $g_{\text{N-Si-N}}(\Theta)$ for both structures differ by 0.08 Å and 7° , respectively, which can be attributed mostly to the presence of a larger number of sixfold coordinated Si atoms in the interface than in the amorphous sample. Therefore, in a first approximation, the LT-B1-SiN(001) interface can be roughly considered as an over-coordinated a-SiN-like structure.

As shown above, in the HT-SiN(001), there are two groups of Si atoms: one forms the SiN_4 coordinated units like in β -Si₃N₄ with the Si-N bond lengths in the range of 1.77–1.85 Å and another one that forms the SiN_6 units with interatomic distances around 1.95 Å. To confirm the formation of the β -Si₃N₄-like units we computed the $g_{\text{N-Si-N}}(\Theta)$ and $g_{\text{Si-N-Si}}(\Theta)$ of the HT-SiN(001) heterostructure using the bond length cut-off of 1.9 Å thus eliminating the contributions of Si-N nearest neighbor correlations with the larger bond lengths. These functions are shown as the curves with broken lines in Fig. 2.7. Obviously, the broad peaks at about 99° and 127° in the N-Si-N and Si-N-Si bond angle distributions, respectively, can be attributed to 106° and to 121° in the corresponding bond angle distributions of a-Si₃N₄.

Fig. 2.7 Bond angle distribution $g(\Theta)$ for: 1-LT-SiN(001), 2-a-SiN, 3-HT-SiN(001) and 4-a-Si₃N₄. The bond angle distributions were computed using the Si-N bond length cut-off of 2.2 Å. The curves with broken lines correspond to the $g(\Theta)$ functions for HT(001) obtained using a Si-N bond length cut-off of 1.9 Å (Reprinted with permission from Ivashchenko et al. [30]. Copyright 2012 by the American Physical Society)



To summarize the results of this section, we showed that the pseudomorphic B1-TiN(001)/1 ML SiN/TiN heterostructure is, at finite temperature, unstable in its highly symmetric arrangement in agreement with earlier results [15, 23] which were obtained by means of DFT at 0 K. At finite temperature, it transforms into a complex interfacial structure with disordered B1-SiN- and β -Si₃N₄-like units. The B1-TiN(111)/1 ML B1-SiN/TiN, B1-TiN(111)/1 ML Si₃N₄-like SiN/TiN, and B1-TiN(111)/1 ML Si₃N₄-like Si₂N₃/TiN heterostructures are stable in the temperature range of 0–1,400 K.

Obviously, the interfacial structures of TiN/Si_xN_y nanocomposites and nanolaminates are much more complex than as it has been considered so far. One has to keep in mind that in nanocomposites consisting of 3–4 nm, randomly oriented TiN nanocrystals of a fairly regular shape [19] connected by about 1 ML thick Si₃N₄-like interfacial layer many different (hkl) interfaces have to coexist [3, 4, 18, 29]. Moreover, the early DFT and the present QMD calculations can consider only closed systems whereas the system is open during the deposition, i.e. the number of nitrogen atoms in the system is not constant. Therefore “nitriding” will occur whenever energetically and structurally preferred. For example, the structural reorganization of the fcc-B1-TiN/1 ML SiN/TiN heterostructure with the SiN₄ and SiN₆ units will be – due to the “nitriding” – transformed so that only the β -Si₃N₄-like SiN₄ units will remain. Therefore studies on heterostructures provide only a limited, although valuable insight into the nature of the interfaces in the nanocomposites. In the following section we discuss only briefly the possibility of the formation of Si₃N₄-like interfaces derived from the SiN ones by means of the formation of Si vacancies.

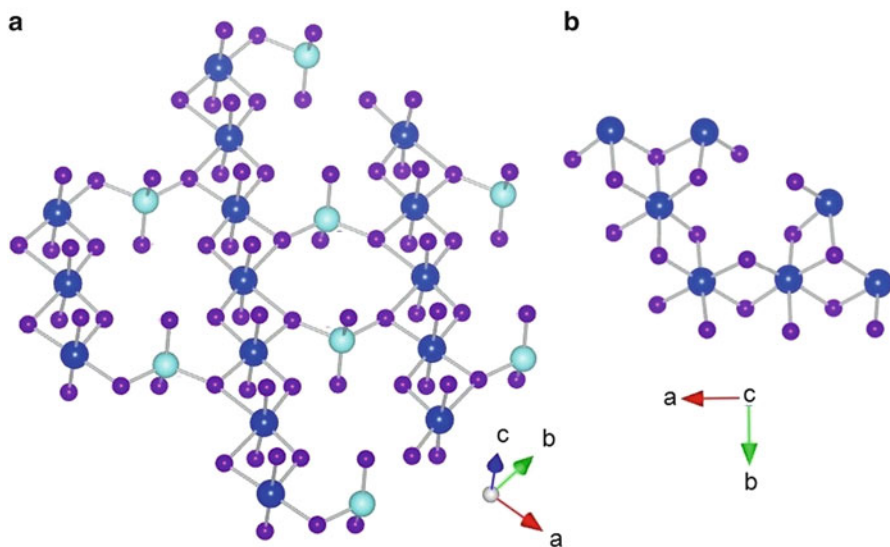


Fig. 2.8 Bond configurations at and around the interfacial planes of the LT-Si_{0.75}N(001) (a), and LT-Si_{0.78}N(111) (b) heterostructures. In Fig. 2.8a, the interface lies in the **a–b** plane. The atomic configurations were computed using a Si–N bond length cut-off of 2.5 Å. Si-medium dark blue, N-small purple, the light large circles are the fourfold coordinated Si atoms

2.3.2 *Si₃N₄-Like Interfaces Derived from SiN by the Formation of Si Vacancies*

Figure 2.8 shows the bond configurations at and around the interfacial planes of the TiN(001)/B1-Si_{0.75}N (a) and TiN(111)/B1-Si_{0.78}N (b) heterostructures at 300 K. (For an easier understanding, the TiN slabs above and below the SiN_x interfaces have been removed.). Figure 2.8a shows the Si₃N₄-like interfacial configurations derived from the TiN/B1-SiN/TiN heterostructure by the formation of Si vacancies at finite temperature of 300 K. The pair correlation functions and bond angle distributions of the substoichiometric heterostructures are shown in Figs. 2.9 and 2.10, respectively. The comparison of the atomic configurations in Figs. 2.3 and 2.8 shows that, for the TiN(001)/SiN heterostructure, the presence of silicon vacancies does not lead to any increase in the number of the SiN₄ units at the interface. The chains of the SiN₆ units are still present.

Let us analyze the temperature-induced changes in the energetics and the structures of the TiN(001)/1 ML B1-Si_{0.75}N(001) heterostructure. The total energy decreases in the following sequence: relaxed zero-temperature (reference) LO-Si_{0.75}N(001) heterostructure 0.0000 eV/atom → LT-Si_{0.75}N(001) –0.0054 eV/atom → HT-Si_{0.75}N(001) –0.0096 eV/atom. The lowering in the total energy with increasing temperature is accompanied by structural changes of the interface (cf. Fig. 2.9b).

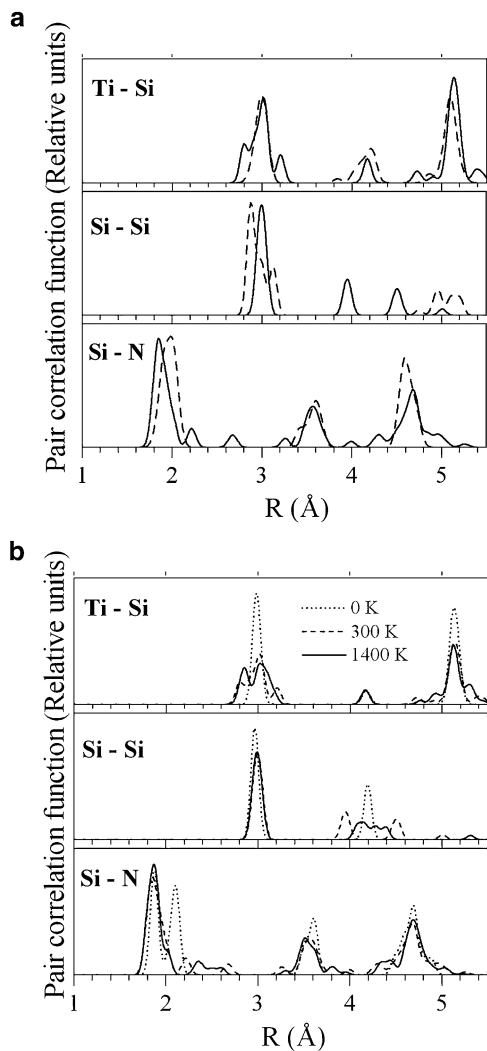
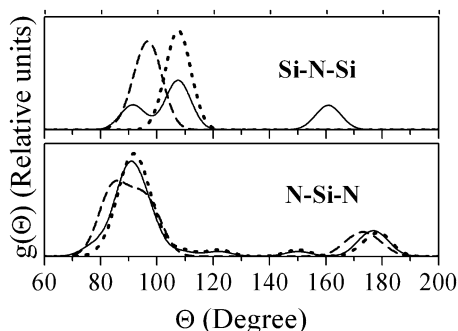


Fig. 2.9 (a) Pair correlation functions (PCF) for the LT-Si_{0.75}N(001) (solid line) and LT-Si_{0.78}N(111) (broken line) heterostructures. (b) Pair correlation functions for the Si_{0.75}N(001) heterostructure as functions of temperature

One can see from Fig. 2.9a that the thermally-assisted motion of the interfacial atoms causes a shortening of the Si-N bond lengths, and this leads to a strengthening of the Ti-Si interactions.

In the case of the Si_{0.78}N(111) heterostructure, the nitrogen atoms shift towards the neighbor silicon and away from the titanium atoms. As a result, a shoulder at 1.95 Å at the peak of Si-N correlations appears, and the peak of the Ti-N correlations

Fig. 2.10 Bond angle distribution $g(\Theta)$ for the LT-Si_{0.75} N(001) (*solid and dotted lines*) and LT-Si_{0.78} N(111) (*broken line*) heterostructures. The bond angle distributions were computed using the Si-N bond length cut-off of 2.1 Å (*dotted line*), 2.2 Å (*broken line*) and 2.4 Å (*solid line*)



shifts towards higher distances by 0.025 Å. The distorted octahedral coordination of the Si atoms is preserved (cf. Figs. 2.8b and 2.10). Thus, the deficit in the silicon atoms in the (111) interface also does not promote any formation of stable Si₃N₄-like configurations at finite temperature.

The calculation of the formation energy of silicon vacancies in the LT-SiN heterostructures was performed using the equation $E_v^f = 1/2(E_{vac} - E_{ideal} + 2E_{Si})$, where E_{vac} and E_{ideal} are the total energies of the heterostructures with two Si vacancies and without them, respectively, and E_{Si} is the total energy of bulk Si. The values of E_v^f for the LT-SiN(001) and LT-SiN(111) heterostructures were found to be −2.090 and −0.461 eV, respectively, which is close to the values of −1.59 and −0.65 eV obtained by Marten et al. in their calculations at 0 K [24, 25]. It follows that both interfaces are unstable with respect to the formation of Si vacancies. This finding and the results of previous calculations [24, 25] clearly indicate that, for N-rich conditions, the 1:1 Si-to-N ratio for the TiN(001)/ 1 ML SiN_x interfaces is unfavorable in the heterostructures. A careful examination of the atomic configuration and pair correlation functions shows that the observed strengthening of the interfaces caused by Si vacancies is due to a reduction in the coordination of the N atoms at the interfaces, a shortening of the Si-N bond length in the SiN₆ units from 1.95 to 1.85 Å (LT-Si_{0.75} N(001)) and a smaller distortion of the SiN₆ units.

Thus, despite the fact that a formation of Si vacancies at the B1-SiN interfaces does not lead to any increase in the number of tetrahedrally coordinated Si atoms compared to the stoichiometric interfaces, a formation of Si vacancies in the LT-SiN(001) and LT-SiN(111) is energetically favorable. However, in an open system under the conditions of deposition with excess of nitrogen, the stable stoichiometric β-Si₃N₄-like interfacial layers will form (cf. Table 2.4).

2.3.3 TiN/SiC Interfaces

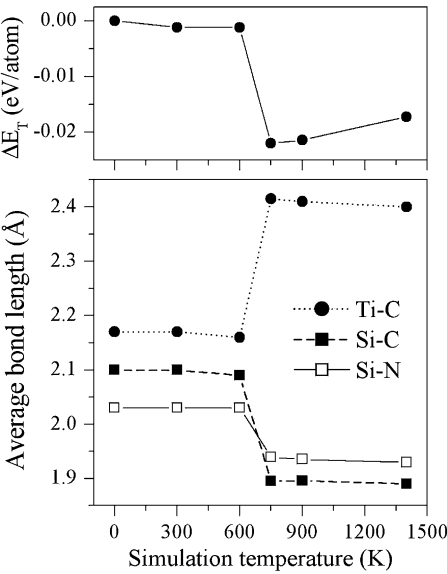
The TiN(001)/SiC heterostructures were investigated at 0, 300, 600, 750, 900, and 1,400 K, whereas the TiN(111)/SiC heterostructures have been studied at 0, 300,

Table 2.4 Interfacial formation energies H^f (in $\text{eV}/\text{\AA}^2$) estimated for the N-rich and N-poor conditions using Approaches A and B

Structure	Approach A		Approach B	
	N-rich	N-poor	N-rich	N-poor
LT-B1-SiN(001)	0.279	0.509	0.127	0.356
HT-B1-SiN(001)	0.264	0.493	0.111	0.341
LT-B1-Si _{0.75} N(001)	0.156	0.426	0.003	0.274
HT-B1-Si _{0.75} N(001)	0.150	0.421	−0.002	0.268
LT-B1-SiN(111)	0.292	0.573	0.142	0.423
LT-B1-Si _{0.77} N(111)	0.205	0.525	0.057	0.378
LT-Si ₃ N ₄ -SiN(111)	0.227	0.489	0.227	0.489
LT-Si ₃ N ₄ -Si ₂ N ₃ (111)	0.165	0.490	0.026	0.351

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Fig. 2.11 Total energy ($\Delta E_T = E_T(T) - E_T(0)$) and average bond lengths for the TiN(001)/SiC heterostructure, determined from the positions of the corresponding first peaks of the pair correlation functions, as functions of simulation temperature



and 1,400 K [36]. Figure 2.11 shows the dependence of the total energy (E_T) and the structural parameters of the TiN(001)/SiC heterostructure on temperature. We note the pronounced changes in the energy and in the structural properties occur between 600 and 750 K. The initial TiN(111)/SiC heterostructure formed after static relaxation at 0 K remains practically unchanged with increasing temperature up to 1,400 K. The total energies of 0.000, -0.079 and -0.098 meV/atom of the L0-SiC(111), LT-SiC(111) and HT-SiC(111) heterostructures, respectively, are, within accuracy of the calculations, essentially the same, and significantly smaller than those seen in Fig. 2.11.

Fig. 2.12 Atomic configuration of the low- (LT) and high-temperature (HT) TiN/1 ML SiC/TiN heterostructures. Ti-big blue-grey, Si-medium dark blue, C-small green-blue and N-small purple. The atomic configurations were computed using Si-C, Ti-C and Ti-N bond length cut-offs of 2.5 Å (Reprinted with permission from Ivashchenko et al. [36]. Copyright 2012 by the American Physical Society)

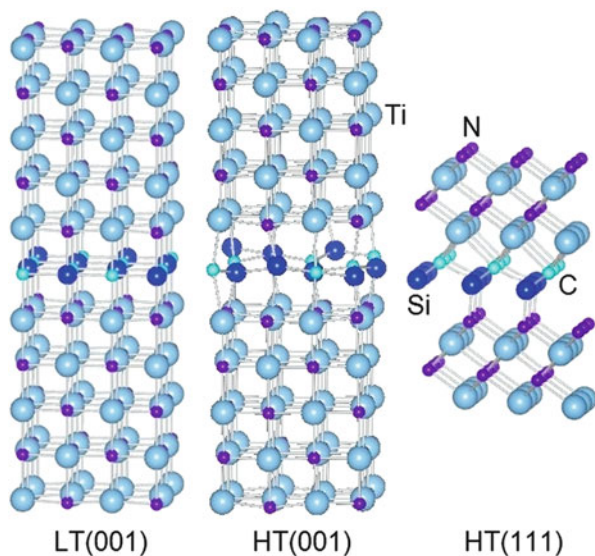


Figure 2.12 shows the structure of the TiN(001)/SiC heterostructures equilibrated at 300 K (LT(001)) and 1,400 K (HT(001)) after subsequent relaxation, as well as the TiN(111)/SiC heterostructure equilibrated and relaxed at 1,400 K (HT(111)). Because the (001) heterostructures are strongly influenced by temperature, we will focus on them. One can see that the LT(001) heterostructure has an epitaxial B1-SiC interfacial layer preserved up to 600 K (see also Fig. 2.11). A further increase in the temperature leads to a significant change in the atomic arrangement caused by thermal motion of the atoms within and near the interface. We note a shift of the N atoms in the layer just above and below the (001) interface. The redistribution of the atoms results in the formation of 3C-SiC-like units, consisting of Si in the tetrahedral N-Si $\equiv$ C₃ coordination. The C atoms form fivefold coordinated Ti₂ = C $\equiv$ Si₃ configurations. The atomic arrangement around the (001) interface in the LT(001) and HT(001) heterostructures is shown in Fig. 2.13. We can see the Si-C₄ and C-Si₄ B1-SiC-like units in the LT(001), and the Si-C₃ and C-Si₃ 3C-SiC-like units in HT(001).

Figure 2.14 shows PCF for the LT(001), HT(001), and HT(111) heterostructures. The bond-angle distribution ($g(\theta)$) for these high-temperature heterostructures is shown in Fig. 2.15. The PCF of the LT(001) displays the peaks of the nearest neighbor (NN) Ti-C, Ti-N, Si-C, Si-N correlations at 2.1–2.2 Å, and of the NN Ti-Si and Si-Si correlations at 3.0 Å, which are very close to the corresponding lengths of the metal-nonmetal and metal-metal correlations in TiN, respectively. The average Ti-C bond length of 2.4 Å in the HT-SiC(001) heterostructure is larger than that in TiC (2.09 Å), whereas the Ti-N bond lengths are close to those in TiN. The NN Si-Si correlations occur at a distance of $\sim$ 3 Å, that is close to that of the second nearest neighbor correlations in the SiC epitaxial layer of the LT-SiC(001) heterostructure. In contrast, additional Ti-Si bonds with $l_{\text{Ti-Si}} \sim$ 2.8–2.9 Å are formed

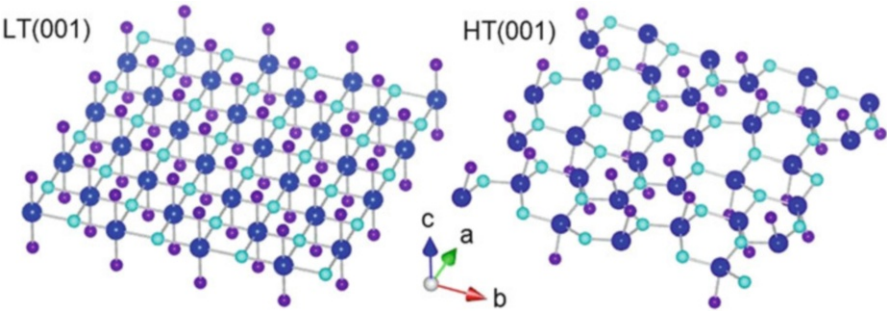


Fig. 2.13 Si-C-N bond configurations in and around the interfacial planes for LT(001) and HT (001). The atomic configurations were computed using Si-N and Si-C bond length cut-offs of 2.5 Å. The two Ti atoms that are neighbor of the C atoms and site above and below the interfaces are not shown. Ti-big blue-grey, Si-medium dark blue, C-small green-blue and N-small purple. (Reprinted with permission from Ivashchenko et al. [36]. Copyright 2012 by the American Physical Society)

Fig. 2.14 Pair correlation functions for the low- and high-temperature 1 ML SiC interfaces: LT-SiC(001) (lower curves), HT-SiC (001) (middle curves) and HT-SiC(111) (upper curves) (Reprinted with permission from Ivashchenko et al. [36]. Copyright 2012 by the American Physical Society)

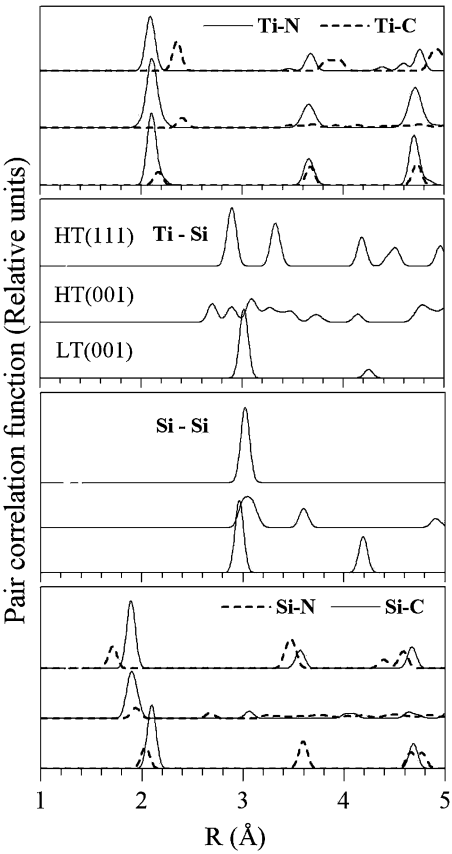
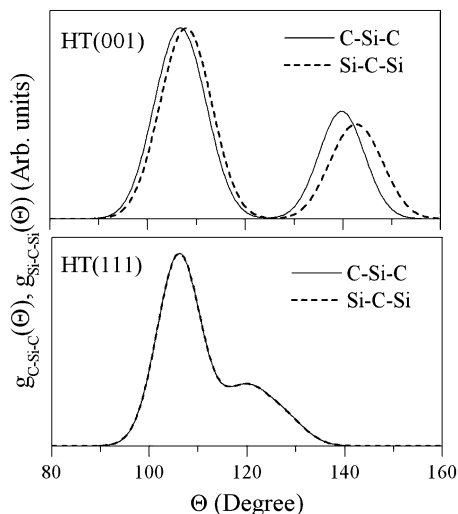


Fig. 2.15 Bond angle distribution $g(\Theta)$ for the high-temperature 1 ML SiC interfaces. The bond angle distributions were computed using a Si-C bond length cut-off of 2.5 Å (Reprinted with permission from Ivashchenko et al. [36]. Copyright 2012 by the American Physical Society)



around the interface of the HT-SiC(001) heterostructure. The peak of the NN Si-C correlations is located at a distance that is equal to $l_{\text{SiC}} = 1.89$ Å in 3C-SiC. The Si-N bonds ($l_{\text{Si-N}} = 1.9$ Å) are elongated compared to those in $\beta\text{-Si}_3\text{N}_4$ ($l_{\text{Si-N}} = 1.76\text{--}1.8$ Å). The bond angle distribution of the HT-SiC(001), $g(\theta)$, in Fig. 2.15, shows a main peak at $\sim 109^\circ$, which means that the interfacial Si and C atoms form a Si-C network similar to that in 3C-SiC. The occurrence of a minor peak at 140° indicates that this network is strongly distorted. These findings show that the B1-SiC-like interfacial layer in the LT-TiN(001)/SiC heterostructures transforms into a 3C-SiC-like interface above 600 K. This interface can be viewed as two Si(111) and C(111) polar layers in 3C-SiC uniaxially deformed in the (111) direction.

Let us now discuss the (111) heterostructure. Figure 2.13 shows that the Si atoms are tetrahedrally coordinated and form $\text{Si-C}_3\text{N}_1$ configurations like the Si-C_4 clusters in 3C-SiC. The Si-C and Si-N bond lengths are 1.89 Å and 1.77 Å, respectively (cf. Fig. 2.14). The C atoms have six neighbor forming $\text{C-Si}_3\text{Ti}_3$ configurations (cf. Fig. 2.12). The Ti-C bonds are strongly elongated ($l_{\text{TiC}} = 2.4$ Å) as compared to those in B1-TiC ($l_{\text{TiC}} = 2.09$ Å). The Ti-N network is weakly distorted by the incorporation of the SiC interface into the TiN(111). The Si-Si and Ti-Si correlations at 2.35 Å and 2.7–2.9 Å, which are present in silicon and TiSi_2 , respectively are absent in the (111) heterostructures (cf. Fig. 2.14). The main peak of $g(\theta)$ in Fig. 2.15 is located at $\sim 109^\circ$, and a small maximum is observed at 120° . Accordingly, the Si-C interfacial layer in the (111) heterostructures is close to that of 3C-SiC and the distortion of the interfacial layer gives rise to a small peak around 120° . In Fig. 2.16 we compare the perfect 3C-SiC structure with a fragment of the Si-C-N network in the (111) interface. We see that three neighbor N(111), Si(111), and C(111) layers are similar to the corresponding layers in 3C-SiC when one C-layer is substituted by one N-layer. This conclusion is consistent with the structural analysis of the (111) interface done above.

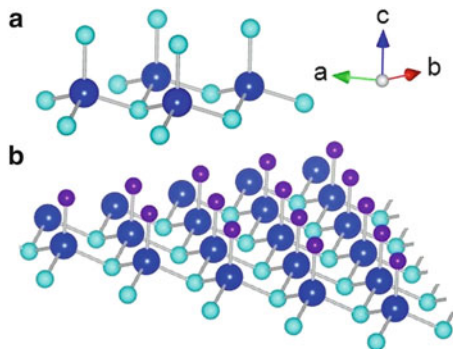


Fig. 2.16 Atomic configuration for 3C-SiC (a) and Si-C-N bond configurations in and around the interfacial planes for HT-SiC(111) (b). The atomic configurations were computed using Si-N and Si-C bond length cut-offs of 2.5 Å. The three Ti atoms that are neighboring to the C atoms and site below the C plane are not shown. Ti-big blue-grey, Si-medium dark blue, C-small green-blue and N-small purple. (Reprinted with permission from Ivashchenko et al. [36]. Copyright 2012 by the American Physical Society)

We also calculated the interfacial formation energy E^f (2.1) for the heterostructure under consideration [36]. The values E^f for the HT-TiN(001)/SiC and HT-TiN(111)/SiC heterostructures are 0.148 eV/(atom $\times$ Å²) and 0.029 eV/(atom $\times$ Å²), respectively, which implies that, in the TiN/SiC nanocomposite and nanolayered coatings, the formation of the TiN(111)/3C-SiC-like interfaces will be preferable already at relatively low temperature. Unfortunately, the TiN/SiC nanolayered coatings in which the TiN(111)/3C-SiC-like interfaces have been predominantly observed [31] were deposited close to room temperature and never annealed.

2.3.4 TiN(001)/BN Interfaces

As already mentioned above, two initial configurations, BN1(001) and BN2(001), were considered for this interface. Both the relaxed heterostructures L0-BN1(001) and L0-BN2(001) were very similar, although the total energy of the second heterostructure was slightly higher by 0.017 eV/atom. Both the L0-BN1(001) and HT-BN1(001) heterostructures are shown in Fig. 2.17, and the atomic configuration around the HT-BN1(001) interface is presented in Fig. 2.18. The pair correlation function (PCF) and bond angle distribution ($g(\Theta)$) for the HT-BN1(001) and HT-BN2(001) heterostructures are presented in Fig. 2.19. An analysis of the results presented in Figs. 2.17, 2.18, and 2.19 shows that the BN interface can be considered as a set of h-BN like sheets connected by BN₃ units. All the boron atoms are threefold coordinated. The HT-BN2(001) network is more disordered than that of HT-BN1(001) (cf. Fig. 2.19). The B-N and Ti-B correlations with the average bond lengths of

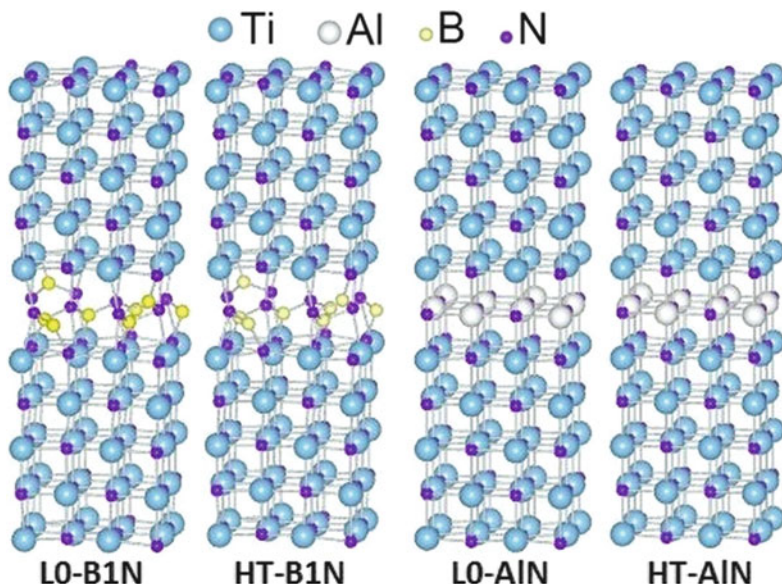
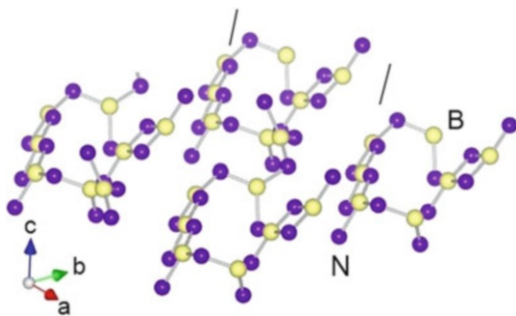


Fig. 2.17 Atomic configurations of the TiN(001)/(BN1, AlN) heterostructures at different temperatures

Fig. 2.18 B-N network at and around the HT-BN1 (001) interface). The dashes denote the distorted h-BN-like sheets



1.5 Å and 2.4 Å, respectively, are seen in Fig. 2.19. These bond lengths are very close to those in h-BN (1.45 Å), TiB₂ (2.37 Å) and TiB (2.34–2.53 Å) that were obtained in the framework of our present DFT calculations (not shown here). The peak at about 3 Å in PCF of Ti-B corresponds to a correlation between B-atoms at the bottom of the interfacial layer and Ti-atoms in the TiN slabs above the interface. These results show that the TiN(001)/BN interface consist of disordered h-BN-like units connected by NBN groups, and it is close to an amorphous state at any temperatures considered here. This conclusion is consistent with the experimental findings for TiN/BN and TiN/BNC heterostructures [39, 74] and nanocomposites [38]. In the nanocomposites, there were always some Ti-B bonds seen in X-ray photoelectron spectroscopy (XPS) even for the stoichiometric system. It has been suggested that the large mismatch

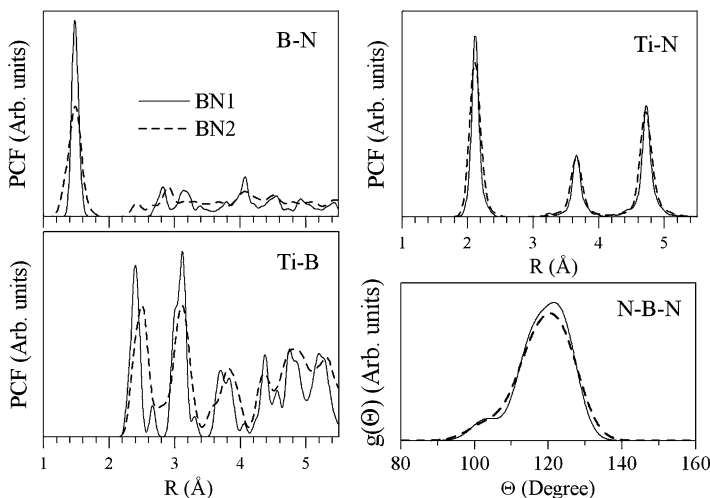


Fig. 2.19 Pair correlation function (PCF) and bond angle distribution ($g(\Theta)$) for the HT-BN1 (001) (solid line) and HT-BN2(001) (dashed line) heterostructures

between the TiN and BN leads to incoherent interface with vacancies within the BN interfacial layer where the Ti-B bonds form (see Fig. 2.12a in [38]). This explanation is supported by the present QMD calculations.

Our results are in disagreement with the static DFT modeling of the TiN(001)/BN interface at 0 K presented in Ref. [49] that predicted that this interface should be epitaxial. According to our QMD results, this interface is not hetero-epitaxial, but it exhibits a distorted h-BN-like structure within the whole temperature range of 0–1,400 K [50]. This discrepancy is obviously due to the use of a too small supercell in the static DFT calculations reported in Ref. [49], and, therefore, it does not allow full relaxation of the lattice. Besides, the large difference in the atom size between titanium (1.47 Å) and boron (0.98 Å) clearly excludes any hetero-epitaxy in this system as discussed already in Ref. [38].

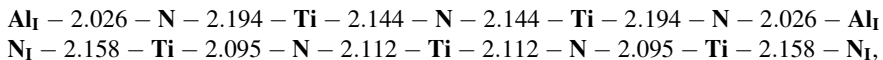
The incoherent nature of the TiN/BN interface rises the question of the mechanism that is responsible for the hardness enhancement found in the nc-TiN/BN nanocomposites, because it must be different from that found in the nc-TiN/Si₃N₄ ones, where it has been attributed to the absence of dislocation activity in 3–4 nm small TiN nanocrystals and a reduction of grain boundary shear due to the formation of pseudomorphic SiN_x interfacial layer that is strengthened by valence charge transfer from TiN [13–15, 20]. A close look at Fig. 2.7 in Ref. [38] reveals that the maximum hardness is achieved when the size of the TiN nanocrystals is around 10 nm, i.e. at the “strongest size” [73], where the strengthening due to a decrease in dislocation activity with decreasing crystallite size (Hall-Petch effect) becomes dominated by a softening caused by an increasing of grain boundary shear, as discussed recently in Ref. [11]. Thus, the fact that only a limited hardness enhancement by a factor of ≤ 2 has been found in this system [38], can be understood. The relatively high hardness of 40 GPa

found in this system is a consequence of high intrinsic hardness of TiN, but not of the formation of a strong semicoherent interfacial layer.

The incoherent TiN/BN interface also explains the insensitivity of the hardness of nc-TiN/BN nanocomposites to oxygen impurities (see Fig. 2.12 in Ref. [18]), whereas the strengthened Si₃N₄-like interfacial layer is strongly sensitive to oxygen already at a level of <2,000 ppm (< 0.2 at.%) [11, 75]. The presence of Ti-B bonds, which is another consequence of the incoherent interface in this system, together with the low melting point of boron oxide of about 460 °C also explains the low oxidation resistance of these nanocomposites reported in Ref. [37].

2.3.5 TiN(001)/AlN Heterostructures

In Fig. 2.17 we show the atomic configurations of the low and high-temperature TiN(001)/AlN heterostructures. As already mentioned above, the interfacial AlN layer in the TiN(001)/1 ML AlN/TiN heterostructures corresponds to a slightly distorted B1-AlN at any temperatures between 0 K and 1,400 K [50]. This is understandable in terms of small differences in atomic radii between Ti (1.47 Å) and Al (1.43 Å), and in agreement with the experimental results [53, 76]. This is also reflected by the relatively small fluctuation of bond lengths in the direction perpendicular to the interface as shown by the following sequence (the bond lengths are given in Å):



where Al_I and N_I are the aluminium and nitrogen atoms located at the interface between TiN and AlN interfacial layer. One notices that the Al-N bond distance within the AlN interfacial layer (i.e. parallel to the interface) is 2.098 Å.

2.4 Dynamical Stability of the Interfaces

In order to understand the origin of the thermal instability of the B1-XY layers in TiN(001)/XY heterostructures we calculated the phonon spectra of the B1-XY phases with lattice parameters corresponding to (a) B1-TiN (a_{TiN}) and (b) to the XY phase in equilibrium (a_0) [50]. Then the question is whether the B1-XY pseudomorphic phases in TiN(001)/B1-XY heterostructures are dynamically stable or unstable when they have the lattice parameter of the prototype TiN. Let us recall that “dynamical instability” means the occurrence of imaginary (“negative”) frequencies in the calculated phonon spectra [77].

The calculated phonon densities of states for the BN, AlN, SiC and SiN phases with the B1-structure are shown in Fig. 2.20. The dependences of the frequencies of

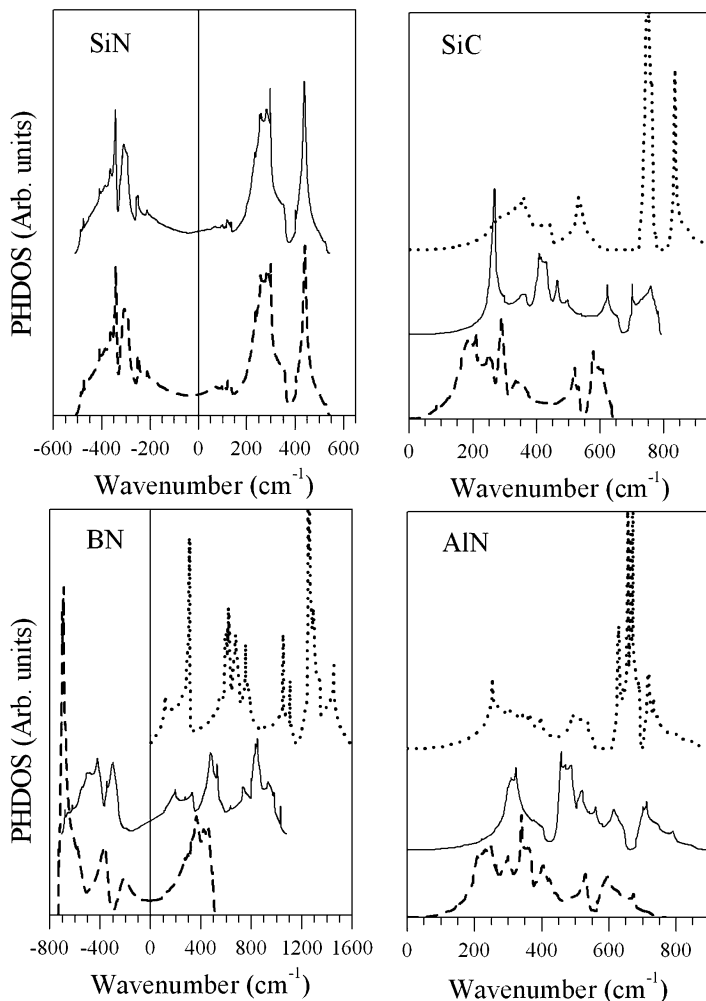


Fig. 2.20 Phonon density of states (PHDOS) for B1-BN, B1-AlN, B1-SiC and B1-SiN structures with the lattice parameters in equilibrium, $a = a_0$ (*solid line*) and with $a = a_{\text{TiN}} = 4.232 \text{ \AA}$ (*dashed line*). For the sake of comparison, the PHDOSs for the most stable XY phases (h-BN, B4-AlN, B3-SiC) in equilibrium are presented in the corresponding figures (*dotted line*)

soft modes on the lattice parameter are shown in Fig. 2.21. We see that the PHDOS of B1-BN and B1-SiN have a wide range of negative (imaginary) frequencies which means that these phases with the B1-structures are dynamically unstable. The phonon spectra of B1-AlN and B1-SiC contain only positive frequencies, although some softening of acoustic phonon modes is observed for both phases with the lattice parameter of TiN. This softening is seen to be larger for B1-SiC than for B1-AlN. To summarize, the B1-BN and B1-SiN layers should be unstable as interfacial layers between the TiN(001), whereas the B1-AlN and B1-SiC

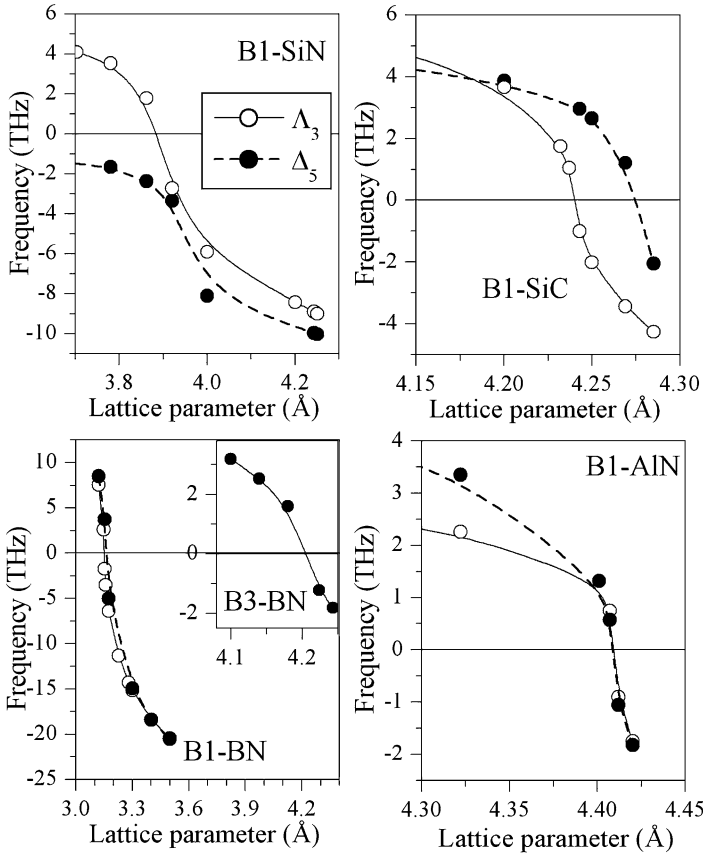


Fig. 2.21 Frequencies of soft phonon modes Λ_3 [$2\pi/a(1/8,1/8,1/8)$] and Δ_5 [$2\pi/a(0,0,1/4)$] as functions of lattice parameters for B1-XY. The results for B3-BN are presented in the insert

interfacial layers are stable and can form. We should recall that the dynamic instability of the B1-SiN(001) has been reported also by Alling et al. who used the static DFT [23].

It has been shown above that the TiN(111)/B1-SiC interface was unstable at 0 K [36], whereas the TiN(111)/B1-SiN interfacial layer was stable up to 3,000 K [30]. For the (001) interfacial layers, we found the opposite picture: B1-SiC(001) is stable at low temperature whereas B1-SiN(001) is unstable. From Fig. 2.21 we see that, for B1-SiC, the condensation of the soft Λ_3 mode, which corresponds to atomic vibrations within the (111) plane, occurs at smaller lattice parameters than the condensation of the Δ_5 mode which corresponds to atomic vibrations within the (001) plane. This means that the reconstruction of the (111) interface will occur at lower temperature than the reconstruction of the (001) interfacial layer, in agreement with earlier results [36]. For B1-SiN, the Δ_5 mode has negative frequencies for a wide range of lattice parameters, whereas the condensation of the soft Λ_3 mode

occurs at a lattice parameter of about 3.88 Å and the frequencies are negative at higher values of a . The QMD calculations of the TiN(111)/B1-SiN heterostructure at various temperatures showed that the Si-N bond lengths were in the range of 1.9–1.96 Å that corresponded to a_{SiN} of about 3.8–3.92 Å in B1-SiN, and did not depend on temperature [30]. However, in this range of lattice parameters, the frequency of the Λ_3 mode is changing from negative to positive (cf. Fig. 2.21), i.e. the (111) interfacial layer should be dynamically stable, which is in agreement with the earlier finding that the TiN(111)/B1-SiN-like interface is stable even at high temperatures. According to the conventional thermodynamics at macroscale, it should undergo the reaction $4\text{SiN} \rightarrow \text{Si}_3\text{N}_4 + \text{Si}$. The possible explanation of this contradiction can be found in the need for nucleation of the new phase that requires a simultaneous motion and rearrangement of several atoms that is difficult to take place within the 1 ML thin interfacial layer. The TiN(001)/B1-SiN interfacial layer reconstructs already at low temperature because the frequencies are negative within the whole range of lattice parameter [30].

The phonon spectrum of B3-BN for $a < 4.206$ Å ($a < a_{\text{TiN}}$) does not contain any soft modes (cf. Fig. 2.21). This means that the B3-BN interface can be quite stable in TiN(001)/BN nanolayers, provided the TiN layers are sufficiently thin, e.g. 5 nm as in Ref. [40], or contain impurity atoms (V, O) which also cause a reduction in the lattice parameter of the TiN slabs. In the nc-TiN/BN nanocomposites the maximum hardness has been found for 1 ML of BN. Although the thermal stability of these nanocomposites was slightly lower (up to 900–1,000 °C) than that of the nc-TiN/Si₃N₄ ones (up to 1,100–1,200 °C), it was fairly high when considering the large lattice mismatch. The present QMD calculations provide a natural explanation.

Because the phonon frequencies are positive for lattice parameter $a \leq a_{\text{TiN}}$, the TiN(001)/1 ML AlN/TiN heterostructures are stable in agreement with the QMD results shown in Fig. 2.17. Considering the dependence of the frequencies of the soft modes on the lattice parameter shown in Fig. 2.21 we note that the B1-AlN interfacial layer should be stable also in B1-VN(001)/AlN/VN heterostructures ($a_{\text{VN}} = 4.14$ Å) since the phonon frequencies are, for this value of the lattice parameter, positive. This is in agreement with the reported experimental results in Refs. [44, 53]. However, it should be metastable in B1-NbN(001)/AlN heterostructures ($a_{\text{NbN}} = 4.4$ Å), because, for the lattice parameter of NbN the phonon frequency is approaching zero. Thus, the VN/AlN/VN heterostructures and nanocomposites are promising candidates for superhard coatings whereas NbN/AlN ones are unlikely to reach high hardness.

We note that the maximum frequency of the soft modes is reached for the X-Y bond length $R_{\text{X-Y}}$ ($R_{\text{X-Y}} = a_{\text{XY}}/2$ in the case of B1-XY) approaches that of the most stable phase of the XY system. The bond lengths of these phases are about 1.5 Å for h-BN, 1.9 Å for B4-AlN, 1.89 Å for 3C-SiC and 1.75 for β -Si₃N₄. For the interfacial layers these lengths increase approximately by 21–22 % for B1-BN and B1-SiN, and by 7 % for B1-AlN and B1-SiC. An increase in the bond length leads to a decrease in frequencies and then to a condensation of the soft modes for systems

with eight valence electrons, and to an increase of the negative (imaginary) frequencies for SiN with nine valence electrons (cf. Fig. 2.21). Therefore the interfacial B1-XY layers with eight electrons can be stabilized at high pressure whereas the B1-SiN with nine electrons is dynamical unstable at any pressure.

To complete this section we should note that the suggested explanation of the thermal instability for the interfaces based on the dynamical stability of the bulk materials does not allow for the availability of Ti-N-Y chains, aligned perpendicularly to the interfacial layer in the heterostructures. Such chains cause an asymmetry in the vibration of the interfacial atoms. As a consequence, soft modes can appear. Nevertheless, despite of the fact that our model is qualitative, it accounts for the thermal stability of the interfaces under consideration in agreement with experiments evidences.

2.5 Electronic Structure and Chemical Bonding of the Calculated Heterostructures

2.5.1 *Electronic Density of States of the B1-XY (XY = BN, AlN, SiC, SiN) Phases*

The next issue to be addressed is the origin of condensed modes in the phonon spectra of the B1-XY phases. To answer this question we calculated the total EDOS of the B1-XY structures shown in Fig. 2.22. The bonding s- and p-states can accommodate eight electrons. For β -Si₃N₄, BN, AlN and SiC which have eight valence electrons the Fermi level ($E_F = 0$ eV) lies between the bonding and anti-bonding states. However, in the case of SiN that has nine valence electrons, E_F lies in a local maximum of the density of anti-bonding states (see Fig. 2.22). This causes a strong screening of vibrations and, consequently leads to a softening of phonon modes.

In summary, the thermal stability of the B1-XY interfaces correlates well with the dynamic stability of the B1-XY phases. Judging from the EDOSs presented in Fig. 2.22, one can see that dynamical instability of the interfaces cannot be assigned to the peculiarities of the electronic density of states, but is caused by the large differences between the X-Y bond lengths in the most stable configurations and in the heterostructures. Besides, the origin of the dynamical instability in B1-SiN can be attributed to the high electronic density of state within the anti-bonding states [23].

2.5.2 *Electronic Density of States and Chemical Bonding of the Heterostructures*

Given the peculiarities of the electronic density of states of B1-XY phases, let us analyze the densities of states related to the (001) interfaces. We calculated the total and local density of states associated with TiN slabs and (001) interfaces.

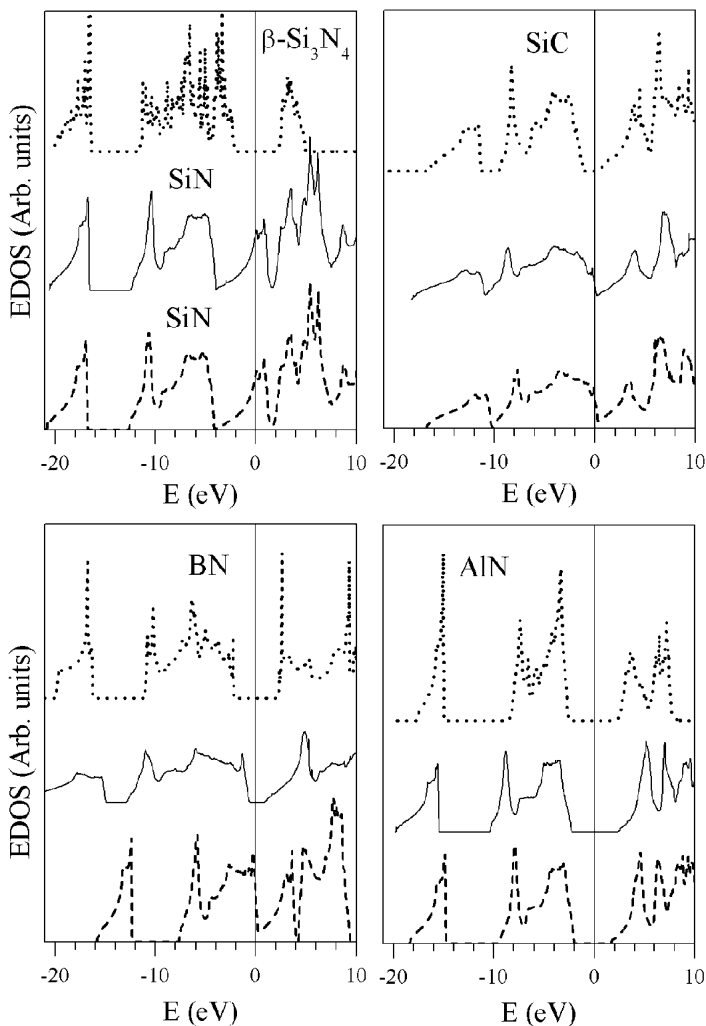


Fig. 2.22 The total electronic density of states (EDOS) of the B1-XY phases (XY = SiN, SiC, BN, AlN) with the lattice parameters at equilibrium, $a = a_0$ (solid line) and with $a = a_{\text{TiN}} = 4.232 \text{ \AA}$ (dashed line). For the sake of comparison, the EDOS of $\beta\text{-Si}_3\text{N}_4$, B3-SiC, h-BN and B4-AlN are presented in the corresponding figures (dotted line). The vertical lines denote the Fermi level

In Fig. 2.23a–d we show only the local EDOS of the interfaces, since the TiN-based EDOS changes insignificantly in comparison with the EDOS of the bulk TiN. We note only that the TiN-related EDOSs of the heterostructures under investigations differ from the EDOS of the bulk TiN by additional small peaks at the low- and high-energy slopes of the main peak located around -5 eV (cf. Fig. 2.23d). These peaks originate mostly from the N-atoms of the TiN layers adjacent to the XY interfaces.

Fig. 2.23 Local density of states (EDOS) related to the (001) interfaces in: LT-SiN (*solid line*), HT-SiN (*dashed line*) and HT-Si_{0.75}N (*dotted line*) (**a**); LT-SiC (*solid line*), HT-SiC (*dashed line*) (**b**); HT-BN (*solid line*), B-partial EDOS in HT-BN (*dashed line*) and N-partial DOS in HT-BN (*dotted line*) (**c**); HT-AlN (*solid line*) (**d**). For a comparison, the EDOS of the bulk TiN is also shown (*dashed line*) (**d**). The vertical lines denote the Fermi level

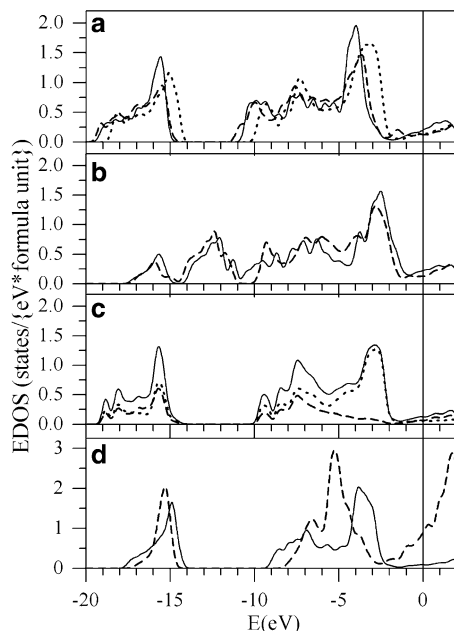


Figure 2.23 shows that, for all the interfaces, the energy gap forms around the Fermi energy. However, gap states are present owing to the defect structure of the interfaces. Since these gap states are localized, interfaces should exhibit conductivity typical of semiconductors. The energy gaps widen and gap states decrease after the thermally-induced structural transformations due to the formation of stable atomic configurations at the interfaces (tetrahedral XY_4 for SiC, Si_3N_4 and AlN, and h-BN-like BN_3 for BN). In the previous section we assumed that the dynamical instability of B1-SiN could be caused by the high EDOS at the Fermi level. The latter results show that the EDOS related to the L0-SiN(001) interface does not show any peaks around the Fermi energy. Therefore we expect that the main cause for the instability of the B1-SiN(001) interface should be found in the large difference between the Si-N bond lengths in the Si_3N_4 structure and TiN(001)/B1-SiN heterostructure. Nevertheless, we do not exclude that, for the multi-layered B1-SiN(001) interfaces, when the interface structure approaches the structure of the bulk B1-SiN, the high EDOS at the Fermi level can be the main cause of dynamical instability for such interfaces.

One can see from Fig. 2.23 that the formation of Si vacancies on the B1-SiN (001) interface leads to a decrease in the number of gap states and to a shift in the bands toward high energies. An analysis of the local EDOSs related to interfaces (we present here only the B- and N-related local EDOS for the H-BN(001)) shows that the nitrogen atoms form mostly the peak just below the Fermi level (cf. Fig. 2.23c).

To better illustrate the charge distribution in the HT heterostructures, we calculated the Löwdin charges by means of the Löwdin population analysis implemented in the “Quantum ESPRESSO” code [55]. (The Löwdin charges reflect the changes in the valence charge density on the atoms upon formation of chemical bond. For example, upon the formation of an Si-N bond where the valence charge density moves from silicon to the more electronegative nitrogen, the charge on Si decreases and that on N increases: the larger the charge density changes the stronger the bond. For more details about the Löwdin population analysis and charges see Ref. [78]). Because the plane-wave basis is not orthogonal, the Löwdin symmetric orthogonalization scheme was applied to convert it back to the orthogonal one [79]. The Löwdin charges (Q_i) (as well as other conventional atomic charges) do not satisfy the sum rule [55]. Therefore, the analysis of a charge state on the same ion in different structures should be done in a comparative way for similar bond configurations.

We calculated the charges Q_i for the ions localized on the (001) interfaces, the TiN layers adjacent to the interfaces and in the centre of the TiN slabs. For the TiN adjacent layers and slabs, we found $Q_{Ti} \sim 2.8$ and 2.9 , respectively, $Q_N \sim 6.0$. For the (001) interfaces the following charges were obtained: $Q_{Si} \sim 2.76$, $Q_N \sim 5.94$ (HT-SiN); $Q_{Si} \sim 2.97$, $Q_C \sim 5.06$ (HT-SiC); $Q_B \sim 2.74$, $Q_N \sim 5.61$ (HT-BN); $Q_{Al} \sim 2.13$, $Q_N \sim 5.97$ (HT-AlN); For the bulk TiN, $Q_{Ti} = 2.85$, $Q_N = 6.02$. We recall that the B and Al atoms have a similar configuration of valence orbitals (ns and np) occupied by three valence electrons. However, on the (001) interface, the ionicity of the B-N bonds is lower compared with that of the Al-N bonds. Also, the positive charge of the Si ions is higher in the HT-SiN(001) than in the HT-SiC(001) interfacial layer. Since the Löwdin charges of the Ti ions in the TiN layers located above and below the interfaces are less than those within the TiN slabs and bulk TiN, one understands the weakening of the Ti-N bonds close to the and XY layers.

Let us now consider the charge states in the Ti-Si-N systems in more details. The calculated Löwdin charges localized on the Si and N ions are: $Q_{Si} = 2.50$, $Q_N = 6.02$ in $\beta\text{-Si}_3\text{N}_4$. For the HT-SiN(001) interface, the calculated average charges are: $Q_{Si} \sim 2.73$ in the Si-N₄ configurations with short bond lengths, $Q_{Si} \sim 2.77$ in the octahedral configurations and $Q_{Si} \sim 3.14$ in the SiN₄ units with long bond lengths, whereas $Q_{Ti} \sim 2.8$, $Q_N \sim 5.94$ for all configurations. For the HT-SiN(111) interface, $Q_{Si} \sim 2.75$, $Q_{Ti} \sim 2.97$ and $Q_N \sim 5.99$. A comparison of the charge distributions in both heterostructures shows that two factors determine the charges localized on Si atoms: the higher the coordination by nitrogen and shorter the Si-N bond, the lower the Q_{Si} . For a given coordination of silicon to nitrogen the following simple rule applies: the shorter the average bond length is, the lower Q_{Si} and stronger the Si-N bonds are. It is also consistent with an increase in the average charge Q_{Si} up to about 3.0 in a-SiN in comparison with the corresponding charge of $Q_{Si} \sim 2.5$ in $\beta\text{-Si}_3\text{N}_4$ caused by a reduction in the average coordination number from 4 to 3 and the Si-N bond length. Q_N decreases insignificantly from 6.0 in $\beta\text{-Si}_3\text{N}_4$ to 5.94 in a-SiN. A low charge on Si means a high stability of that SiN_x configuration. The most stable configuration is the

SiN₄-like one as in β -Si₃N₄. One can see that, whereas the Löwdin charges on Ti and N are similar in TiN and the HT heterostructures, the charges on silicon in the heterostructures are higher than in β -Si₃N₄, thus indicating that the Si-N bonds in these heterostructures are weaker than in β -Si₃N₄, in agreement with the results of Hao et al. [16, 17]. However, because the Löwdin charge on Si in a-SiN of about $Q_{\text{Si}} \sim 3$ is higher than those on most of the atoms Si in the interfaces, the interfacial SiN_x layers are strengthened as compared to a-SiN in agreement with the results of the static DFT calculations at 0 K of Zhang et al. [13–15].

2.5.3 Valence Charge Density Distribution Around the TiN/SiN Interfaces

In this section we investigate the distribution of the valence charge in the TiN, β -Si₃N₄ as well as in the HT-B1-SiN(001) and HT-B1-SiN(111) heterostructures to clarify a possible origin of the lattice distortions and stability of these heterostructures. These heterostructures were selected because the silicon atoms combine six- and four-fold coordination. Figure 2.24a, b show the atomic structure and the valence charge density (VCD) distribution in the b-c planes of the HT-SiN(001) and HT-SiN(111) heterostructures. Obviously, not all atoms are within the same plane (cf. also Fig. 2.1), as seen *e.g.*, in Fig. 2.24a by the different apparent diameters of the atoms within that plane. For the HT-SiN(111) heterostructure, we have chosen the b-c plane consisting of the Si, N and Ti atoms that are located in this plane. In the unreconstructed epitaxial heterostructures, the Si-N bonds are relatively weak because of their large lengths. However, at finite temperatures the atoms are allowed to move and the distances between Si and N atoms decrease so that strong Si-N covalent bonds form. This is reflected in the appearance of a charge polarization towards N atoms (cf. Fig. 2.24a, b). The shifted N atoms interact strongly with Si and to a lesser extent with Ti atoms. Such a redistribution of the valence charge around the interfaces leads to the elongation and weakening of the Ti-N bonds near the interfacial SiN layer as discussed above.

The high stability of the (111) interface in comparison with the (001) one is related to the fact that only Si-atoms are present within the (111) interfacial plane, whereas both Si and N atoms are within the (001) one. In the latter case, the two different atoms with significantly different electronegativities (1.8 for Si and 3 for N, both larger than that of Ti of 1.5 [72]) cause a “phase shift” of the Friedel-like oscillations in neighbor (110) planes perpendicular to that interface and running either through Si or through N atoms within that interface, as discussed by Zhang et al. From the results of their DFT calculations at 0 K [14, 15]. These fairly regular “phase shifts” obtained by DFT at 0 K appear in the present first-principles QMD calculations as an almost random distortion of the Si and N atom positions, re-distribution of valence charge and resulting bond breaking within and near the interfacial layer, as seen in Figs. 2.1 and 2.24a. In the case of the HT-SiN(111) heterostructures, N atoms should

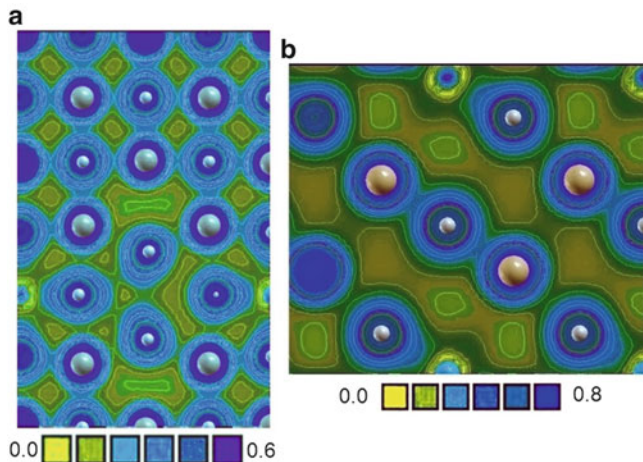


Fig. 2.24 Valence charge density distributions for HT-SiN(001) (a) and HT-SiN(111) (b) heterostructures in the **b-c** plane. Numerals denote the valence charge density scales in electrons/Bohr³. The large balls are Ti, middle balls Si, and small balls N atoms. The cut-off distance of the Si-N and Ti-N bonds is 2.5 Å

move towards the Si interface to form stable SiN₄ configurations. However, the strong Ti-N bonds nearby prevent this motion so that the distorted SiN₆ coordination is preserved and the N atoms are only slightly shifted towards the interfacial Si layer (see Fig. 2.24b).

2.6 Conclusion

We performed first-principles quantum molecular dynamics calculations of the TiN (001)/1 ML B1-derived XY (XY = SiN, SiC, BN, AlN), TiN(001)/1 ML B1-derived Si_{0.75}N, TiN(111)/1 ML B1-derived SiN, TiN(111)/1 ML B1-derived Si_{0.77}N, TiN(111)/1 ML Si₃N₄-derived SiN, TiN(111)/1 ML Si₃N₄-derived Si₂N₃ and TiN(111)/1 ML B1-derived SiC heterostructures at various temperatures. It has been shown that the B1-SiN(001) containing hetero-epitaxial layers were preserved during structural optimization at 0 K in agreement with the earlier “static” DFT calculations of Zhang *et al.* However, the B1-SiN(001) interfacial layer underwent significant reconstruction already at 10 K, and when equilibrated at 300 K, it reconstructed to an over-coordinated a-SiN-like structure. After heating it up to 1,400 K and subsequent static relaxation, the number of the Si₃N₄-like units increased. The interface consists of the octahedral SiN₆ and distorted tetrahedral SiN₄-like units aligned along the (110) direction. In contrast, the B1-SiN(111) interface was stable at 300 K and after heating to 1,400 K and 3,000 K and subsequent relaxation, it only showed small distortions of the atomic positions from their fully symmetric ones and preserved local coordination.

A formation of Si vacancies at zero and finite temperatures in the (001) and (111) interfacial B1-SiN layers is energetically favored. Both interfaces are unstable with respect to formation of Si vacancies due to a reduction of the coordination of the N atoms and Si atoms (in the case of the (001) interface) at the interfaces, a shortening of the Si-N bond length in the SiN_6 units, and a smaller distortion of the SiN_6 units.

An estimate of the interface formation energy shows that, among all the interfaces under consideration, the $\text{TiN}(001)/\text{B1-derived Si}_{0.75}\text{N}$ interface with the six- and four-fold coordinated Si atoms, as well the $\text{TiN}(111)/\text{Si}_3\text{N}_4$ -derived interfaces composed of tetrahedrally N-coordinated Si atoms are most stable.

According to our results obtained at finite temperatures, the 1 ML B1-SiN(001) interface can be stable at high temperatures under nitrogen-poor conditions. We also showed that for both N-poor and N-rich conditions, the B1-derived $\text{Si}_{0.75}\text{N}$ interface between the $\text{TiN}(001)$ slabs is most favorable, whereas the Si_3N_4 -derived interfaces are most stable between the $\text{TiN}(111)$ slabs. The $\text{TiN}(001)/\text{B1-derived Si}_x\text{N}_y$ interfaces cannot exist as hetero-epitaxial layers because they consist of distorted octahedral SiN_6 and tetrahedral SiN_4 units aligned along the (110) direction. Furthermore, despite the fact that according to our QMD calculations, the $\text{TiN}(111)/\text{B1-derived Si}_x\text{N}_y$ interfaces were not favoured under any conditions, they are stable even at high temperatures. This stability may be of kinetic origin because decomposition of SiN into Si_3N_4 and Si requires a nucleation of new phases that is difficult to occur within one monolayer of SiN inserted between TiN slabs.

An analysis of the generated $\text{TiN}(001)/\text{SiC}$ and $\text{TiN}(111)/\text{SiC}$ heterostructures at various temperatures shows that: The B1-SiN(001) interface hetero-epitaxial layers are preserved up to 600 K; Above 600 K, the B1-SiC-like interfacial layer in the $\text{TiN}(001)/\text{SiC}$ heterostructures transforms into the 3C-SiC-like one. This interfacial layer consists of two distorted Si(111) and C(111) polar layers in 3C-SiC uniaxially deformed in the (111) direction; The interface in the $\text{TiN}(111)/\text{SiC}$ heterostructure is stable in the temperature range of 0–1,400 K. Three neighboring N(111), Si(111) and C(111) layers in the $\text{TiN}(111)/\text{SiC}$ heterostructure are identified as the corresponding layers in 3C-SiC, provided one C-layer is substituted by one N-layer. The formation of the $\text{TiN}(111)/3\text{C-SiC}$ -like interfaces is more energetically favorable than the $\text{TiN}(001)/3\text{C-SiC}$ -like interfaces in the temperature range of 0–1,400 K.

Our studies reveal that the $\text{TiN}(001)/\text{BN}$ interface forms an amorphous-like h-BN layer consisting of BN_3 units at any temperatures. For $\text{TiN}(001)/\text{AlN}$ heterostructures, the epitaxially stabilized B1-AlN interfacial layer is preserved over all the whole temperature range.

The thermal stability of the interfaces under consideration has been studied in terms of the dynamics stability of the B1-XY phases that form the interfaces with different lattice parameters a . The phonon calculations showed that B1-BN and B1-SiN interfacial layers are dynamically unstable in a wide range of lattice parameters, particularly close to that of TiN (a_{TiN}). For this reason these interface are drastically modified already during the static relaxation or at 0 K. The hetero-epitaxially stabilized B1-AlN interfacial layer is dynamically stable up to high

temperatures because the phonon spectra of the bulk B1-AlN do not exhibit any soft modes for lattice parameters up to $a = 4.4 \text{ \AA}$. In the case of the B1-SiC interfacial layer, the condensation of the phonon modes occurs for lattice parameters that are slightly above a_{TiN} . Therefore this structure becomes dynamically unstable at high temperatures, and it transforms into the 3C-SiC one above 600 K. It was further shown that B1-BN and B1-SiC interfacial layers could be stabilized at low value of a ("high pressure"), whereas the B1-SiN interfacial layer was dynamically unstable at any pressure due to the high density of states at the Fermi level.

In the electronic densities of states (EDOS) related to the (001) interfaces, the energy gap forms around the Fermi energy. However, gap states are present owing to the defect structure of the interfaces. Since these gap states are localized, interfaces should exhibit a conductivity typical of semiconductors. The gap states decrease after the thermally-induced structural transformations due to the formation of stable atomic configurations at the interfaces (tetrahedral XY_4 for SiC, SiN and AlN, and graphite-like XY_3 for BN). These results point to the fact that the instability of the B1-SiN(001) and B1-BN(001) interfaces is not related to the specific EDOS, but is caused by the large difference between the X-Y bond lengths in the most stable structures and the corresponding heterostructures.

The calculated Löwdin charges (Q_i) for the TiN(001)/XY heterostructures indicate that the N ions on the SiN-, BN- and AlN-based interfaces have lower charges than those in the TiN slabs. Also, the Löwdin charges of the Ti ions in the TiN layers located above and below the interfacial layers are lower compared to Ti-charges inside the TiN slabs. Such charge distribution is supposed to lead to a decrease in the cohesion strength between the TiN and XY layers.

The results of the present theoretical study are consistent with the available experimental data on the corresponding heterostructures and nanocomposite coatings. They provide deeper insight into the choice of new systems that promise to form superhard heterostructures and nanocomposites, and help to identify other systems that are less suitable. We hope that this study will be useful to those who are conducting experimental work in the design of advanced nano-layered heterostructures and of nanocomposite coatings.

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