# Crystalline-to-amorphous transition in $Ti_{1-x}Si_xN$ solid solution and the stability of fcc SiN studied by combined *ab initio* density functional theory and thermodynamic calculations

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Gibbs free energies of the quasibinary $TiN_y$-$SiN_y$ system are constructed to study the relative phase stability of the metastable ternary fcc(NaCl type) and amorphous $Ti_{1-x}Si_xN_y$ solution phases over the entire range of compositions. The predicted cross point at about $x=0.20-0.24$ is supported by the published results from physical vapor deposition and chemical vapor deposition experiments. Based on the calculated properties of fcc-SiN phase, the physical origin of the formation of the amorphous phase is addressed.

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## I. INTRODUCTION

Much interest has been paid recently to the development of nanostructured materials, in particular, superhard nanocomposites with high hardness of 50–100 GPa, high thermal stability, and high oxidation resistance, formed by self-organization.[1–7] The desired nanostructure is formed by thermodynamically driven decomposition from a metastable or from a hypothetical homogeneous, mixed solid solution phase.[2,6–13] The decomposition can occur by nucleation and growth or by spinodal mechanism. Metastable solid solutions of metallic alloys or ternary nitrides, such as $Ti_{1-x}Al_xN$, $Al_{1-x}Cr_xN$, etc., whose demixing energy is relatively small (typically $\leq 20-40$ kJ/mol of atoms), can be prepared by physical vapor deposition (PVD) under conditions which kinetically hinder the phase segregation and formation of the equilibrium phases. Appropriate postannealing at elevated temperature often results in the formation of a nanostructure with improved mechanical properties (so called "age hardening"). An example, which has been studied in much detail, is the fcc-$Ti_{1-x}Al_xN$ system ($x\leq 0.65$) which upon annealing decomposes into the stable fcc(NaCl type) TiN+hcp (wurtzite type) AlN via an intermediate fcc-AlN.[7–11] The reported strengthening by the formation of coherent interface[8] has been clarified by comparing the ideal strengths and bonding nature of fcc- and hcp-AlN.[10] [In the following, the notations fcc and hcp are used for the structure types of NaCl (space group: *Fm*-3*m*) and $\beta$-$Si_3N_4$ (space group: $P63/m$), respectively.]

In the case of strongly demixing systems, such as stoichiometric fcc-TiN and hcp($\beta$)-$Si_3N_4$, the homogeneous fcc-$Ti_{1-x}Si_xN$ solid solution with high silicon content of x $>0.25$ has been, so far, not possible to prepare (note that in Ref. 14, $x$ was $\leq 0.14$). Therefore, when performing thermodynamic calculations, one has to assume a hypothetical solution phase based on the structure of the terminal phases.[11–13] For the nitrogen-substoichiometric fcc-$Ti_{1-x}Si_xN$ solid solution [which has been deposited by reactive sputtering with relatively low Si fraction of $x\leq 0.14$ (Ref. 14)], a hypothetical metastable fcc-SiN phase has to be assumed in the calculations.[12,14] The fcc-SiN can be stabilized as pseudomorphic 1–2 monolayers thin interface between $\geq 4$ nm thick TiN nanolayers. However, it turns amorphous when the thickness exceeds 2 monolayers.[15–18] The fcc-TiN/SiN heterostructures were regarded[15–18] as prototypes of the superhard nc-TiN/*a*-$Si_3N_4$ nanocomposites[1,19] which are formed during plasma chemical vapor deposition (CVD) by self-organization upon spinodal phase segregation. (Note that "nc" means nanocrystalline, "*a*" x-ray amorphous, and the stoichiometry "$Si_3N_4$" symbolizes that the chemical environment of Si atoms is like in bulk $Si_3N_4$, as observed by the value of the Si 2*p* binding energy of $101.7\pm 0.1$ eV in x-ray photoemission spectroscopy[6,19,20]). The thermodynamic and kinetic conditions needed for that segregation are, however, not always met in PVD experiments, in particular, under the conditions where the heterostructures are prepared.[6,15–17]

There are several questions which we would like to address in this paper: The fcc-$Ti_{1-x}Si_xN$ solid solution and the hypothetical metastable fcc-SiN phase are not thermodynamic equilibrium states under conditions of a sufficiently high nitrogen activity (nitrogen pressure of $\geq 10^{-3}$ mbar and temperature of 500–600 °C), as typically used during the deposition of the nanocomposites by CVD.[6,19] Therefore, it is difficult to understand why the stoichiometric fcc-$Ti_{1-x}Si_xN$ phase could be stable upon annealing up to 900 °C, as reported in Ref. 14, when, according to combined *ab initio* density functional theory (DFT) and thermodynamic calculation, it should spinodally decompose.[12] Why does this phase transform into an amorphous one with a high stability above 1000 °C when the Si fraction increases above about $x\geq 0.25$, as reported for a series of Me-Si-N systems (Me=Ti, Zr, Ta, Mo, W)?[21–27] Here, we focus mainly on the crystalline-to-amorphous transition in the Ti-Si-N system and on the phase instability of the fcc-SiN.

## II. COMPUTATIONAL METHODS USED

We used a combined *ab initio* DFT and thermodynamic calculation as outlined in detail in our earlier papers.[11–13] For the *ab initio* DFT calculation, the VASP code[28,29] has been used (for details, see Refs. 11–13). In order to check the reliability of our calculations, the lattice parameter and bulk modulus and its first derivative (pressure dependence) were calculated for fcc-TiN and hcp-$Si_3N_4$. The obtained results agree within few percent with published experimental and

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theoretical data (see Tables I and II in Ref. 12). It should be noted that for ternary $Ti_{1-x}Si_xN_y$ solution phases in fcc and hcp structures, Ti and Si atoms are assumed randomly distributed over the metal sublattice. The exact choice of the position of metal sublattice in substitution was found to have no significant effect on the results in our calculations. This is in agreement with the finding of Hugosson *et al.* who studied many $TM_{1-x}Al_xN$ (TM is transition metal) systems.[30]

In their *ab initio* DFT studies of the Ti-Al-N system, Mayrhofer *et al.*[9] considered the clustering in the fcc-$Ti_{1-x}Al_xN$ solid solution and found that it decreases the (positive) value of the Gibbs free energy, i.e., of the instability of the solid solution. This is not surprising because the clustering represents the onset of the phase segregation, i.e., of the decomposition of the unstable, immiscible system. This can be understood by considering the simple form of the interaction parameter $L_{AB}$ for a binary, regular solution $AB$, which can be approximated by the difference in the binding energies in the fully mixed solution, $E^b_{AB}$, and the average binding energy of the pure phases, $(E^b_{AA}+E^b_{BB})/2$, as $L_{AB} \propto -[E^b_{AB} - 0.5(E^b_{AA}+E^b_{BB})]$. Because in the case of an immiscible system $L_{AB}>0$, the binding energy of the solution, $E^b_{AB}$, is smaller than the average binding energy of pure phases, $(E^b_{AA}+E^b_{BB})/2$. Thus, clustering of pure phases will decrease the demixing energy of the solid solution and results in higher stability of the inhomogeneous, clustered phase.[11]

In our calculation, we neglect the effects of point defects for the following reasons: Both fcc-TiN and hcp-$Si_3N_4$ are refractory materials. Therefore, the concentration of intrinsic point defects is very small within the temperature range considered here, and it does not influence the stability of the phases. Extrinsic defects, such as nitrogen substoichiometry, impurities, and point defects caused, e.g., by energetic ion bombardment during the deposition of the coatings, are specific for a given deposition experiment, but they are not specified in the published papers. Therefore, it is impossible to quantify their possible effect on the phase stabilities in the given experimental work. Thus, we focus on the fundamental question of the phase stabilities in well-defined systems.

The stress-strain curves have been calculated by incrementally deforming the modeled cell in the direction of the applied strain and simultaneously relaxing both the atomic basis vectors orthogonal to the applied strain, as well as the atoms inside the unit cell, at each step. To ensure that the strain path is continuous, the starting position at each strain step is taken from the relaxed coordinates of previous strain step (see Ref. 10 for further details).

The thermodynamic calculations were done by means of the sublattice model,[31,32] which has been adapted for the quasibinary $TiN_y$-$SiN_y$ system as described in Ref. 12. Accordingly, a ternary solution compound $(A,B)_aC_c$ with the assumed structure $\psi$ can be considered as a continuous solution composed of two "pure" phases $A_aC_c$ and $B_aC_c$ (TiN and $SiN_y$). The Gibbs energy of regular solution is given by Eq. (1).[11–13,31,32]

$$G^{\psi}_{(A,B)_aC_c} = y_A({}^0G^{\delta}_{A_aC_c} + G^{\psi\to\delta}_{A_aC_c}) + y_B({}^0G^{\gamma}_{B_aC_c} + G^{\psi\to\gamma}_{B_aC_c}) + aRT(y_A \ln y_A + y_B \ln y_B) + a y_A y_B L^{\psi}_{A,B:C}. \quad (1)$$

Here, ${}^0G^{\delta}_{A_aC_c}$ and ${}^0G^{\gamma}_{B_aC_c}$ are the Gibbs free energy of $\delta-A_aC_c$ and $\gamma-B_aC_c$ phases in the stable structures whose thermodynamic data are accessible in the literature. $G^{\psi\to\delta}_{A_aC_c}$ and $G^{\psi\to\gamma}_{B_aC_c}$ are the lattice instability of metastable phases of $\psi-A_aC_c$ and $\psi-B_aC_c$ (e.g., hcp-$Ti_3N_4$ and fcc-SiN [Ref. 12]) with respect to the stable phases of $\delta-A_aC_c$ and $\gamma-A_aC_c$ (e.g., fcc-TiN and hcp-$Si_3N_4$), respectively, and $a$ gives the numbers of sites of the sublattice $(A,B)$ per formula unit. The site fractions of elements $A$ and $B$ in the sublattice $(A,B)$ are defined by $y_A=x_A/(x_A+x_B)$ and $y_B=x_B/(x_A+x_B)$, where $x_A+x_B+x_C=1$ are the fractions of the elements.[11–13] The first two terms in Eq. (1) are the contributions of the pure phases, the third one is the mixing entropy contribution, and $L^{\psi}_{A,B:C}$ in the last term is the interaction parameter. The *ab initio* DFT allowed us to calculate the total energies of the stable crystalline phases fcc-TiN, ${}^0G^{fcc}_{TiN}$, and hcp-$Si_3N_4$, ${}^0G^{hcp}_{Si_3N_4}$, of the hypothetical crystalline fcc-SiN, ${}^0G^{fcc}_{SiN}$, and of the interaction parameter for the fcc- and hcp-$Ti_{1-x}Si_xN_y$ solution phases.[12]

In order to calculate the free energy of the amorphous $Ti_{1-x}Si_xN_y$ phase, Eq. (1) transfers to Eq. (2).

$$\begin{aligned} G^{amorphous}_{(Ti,Si)N} = {} & (1-x)({}^0G^{fcc}_{TiN} + G^{amorphous\to fcc}_{TiN}) \\ & + x({}^0G^{hcp}_{SiN_{4/3}} + G^{amorphous\to hcp}_{SiN_{4/3}}) \\ & + RT[(1-x)\ln(1-x) + x\ln x] \\ & + x(1-x)L^{amorphous}_{Ti,Si:N}. \end{aligned} \quad (2)$$

The energies of the transition of the crystalline-to-amorphous state, $G^{amorphous\to fcc}_{TiN}=33.47$ kJ/mol of atoms and $G^{amorphous\to hcp}_{Si_3N_4}=9.86$ kJ/mol of atoms, are obtained from the published values of the crystallization energy at high temperature.[33,34] The composition-dependent interaction parameter of the $a$-$Ti_{1-x}Si_xN_y$ is assumed to be the average value of the fcc- and hcp-$Ti_{1-x}Si_xN_y$ solution phases which were also calculated by *ab initio* DFT in a similar way as described in Ref. 12, i.e., $L^{amorphous}_{Ti_{1-x}Si_xN_y}=\frac{1}{2}(L^{fcc}_{Ti_{1-x}Si_xN} + L^{hcp}_{Ti_{1-x}Si_xN_{4/3}})$.

A better approximation of the interaction parameter may be, in principle, obtained, e.g., from molecular dynamics (MD) simulation of a large system. However, these calculations are not possible now because of insufficient accuracy of the interatomic potentials for the systems under consideration. It will become apparent from the results below that more accurate calculations, which might be possible in future, will not change significantly the phase transition points because it is determined mainly by the large lattice instability of fcc-SiN with respect to hcp-$Si_3N_4$. Moreover, it has been shown by experiments and MD simulations that for metallic immiscible binary systems, the mixing enthalpy of amorphous solution is lower than that of the corresponding supersaturated crystalline solid solution because the amorphous phase is formed by a lattice collapse of the corresponding crystalline one.[35,36] Therefore, the present treatment of the interaction parameter of the amorphous solution gives an upper limit of the mixing enthalpy for amorphous Ti-Si-N solution.

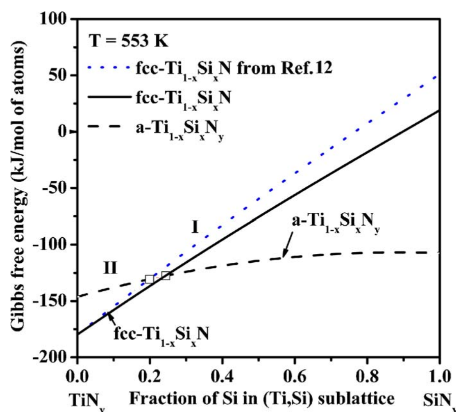


FIG. 1. (Color online) Gibbs free energies of ternary $Ti_{1-x}Si_xN_y$ solution phases in fcc and amorphous structures over the entire compositions at 573 K. The short dashed blue curve is from Ref. 12.

## III. RESULTS AND DISCUSSION

Figure 1 shows the calculated Gibbs free energy as function of the composition for the fcc and $a$-$Ti_{1-x}Si_xN_y$ at temperature of 573 K and atmospheric nitrogen pressure, which is in the lower range of deposition temperatures used by different workers.[21–27] Obviously, a fcc-to-amorphous transition is expected to occur at a silicon fraction of $x \approx 0.24$, in agreement with published experimental observations. (The point $x \approx 0.20$, which was obtained when using the earlier calculation of the Gibbs free energy of fcc-$Ti_{1-x}Si_xN$,[12] is also marked in the Fig. 1 for comparison.) This corresponds to total Si concentration of about 12 at. %, which is slightly higher than the "optimum" Si content of 7–9 at.%, where the maximum hardness has been found in a number of superhard ($H \geqslant 50$ GPa) nc-$Me_nN$/$a$-$Si_3N_4$ nanocomposites which were deposited under conditions that enabled the formation of fully segregated stoichiometric phases.[1,6,19] It has been shown in these papers that under such conditions, the $Si_3N_4$ percolates as about 1–1.5 interfacial monolayer because, due to the lattice mismatch, a thicker layer is unstable.[37] This is in agreement with the finding that the heteroepitaxially stabilized fcc-SiN transform to $a$-SiN when the thickness increases above about 2 monolayers.[15–17]

Shalaeva *et al.*[21] reported the crystalline-to-amorphous transition in Ti-Si-N(O) coatings for Si content of >10–15 at. %. In these coatings, relatively large oxygen impurity content of ⩽20 at. % has been found which decreased to several at. % when the deposition temperature was increased to 700 °C. Oxygen impurities were not reported in the other papers, but they may play an important role in the stabilization of the amorphous structure during annealing to high temperature. Musil and co-workers conducted the annealing either in vacuum or in air.[22–27] The reported high thermal stability of the amorphous phase may be due either to oxygen impurities or to nitrogen substoichiometry, because stoichiometric TiN and $Si_3N_4$ are immiscible, and the crystallization of pure $Si_3N_4$ under oxygen-free, nitrogen rich conditions begins already at about 900 °C and is completed at 1200 °C.[38] (TiN coatings deposited by PVD at much lower temperature grow crystalline.) Therefore, upon annealing to >1100 °C for about 30 min, fcc-TiN (or other transition metal nitrides studied by Musil and co-workers) and a large fraction of crystalline $\alpha$(space group: $P63$)- or $\beta$(space group: $P63/m$)-$Si_3N_4$ would have to be formed if the system were stoichiometric and free of impurities.

Indeed, no crystalline-to-amorphous transition was reported in the nc-TiN/$a$-$Si_3N_4$ nanocomposite coatings deposited by plasma CVD at 550 °C and nitrogen pressure of several millibars up to the highest Si content of 21.5 at. % used there. The oxygen impurities were below 0.07 at. %.[39] TiN remained crystalline, and only the crystallite size decreased down to about 1.5 nm when the silicon content increased to 21.5 at. %.[40] The thin interfacial $Si_3N_4$ layer was x-ray amorphous.

The question arises about the stability of the $Ti_{1-x}Si_xN$ solid solution free of oxygen impurity (either fcc-$Ti_{1-x}Si_xN$ for $x<0.24$ or $a$-$Ti_{1-x}Si_xN$ for $x \geqslant 0.24$), with the stoichiometry of (Ti+Si):N=1, and what the properties of the fcc-SiN phase may be. Combined *ab initio* DFT and thermodynamic calculation showed that the system should spinodally decompose because the demixing energy (e.g., of about 4 kJ/mol of atoms at 773 K) is sufficiently high and the interfacial strain between fcc-TiN and fcc-SiN of $1.174 \times 10^{-3}$ is small.[12] Because the diffusion at this temperature is fast enough,[12] the system should decompose. According to the calculations of Söderberg *et al.*, the fcc-$Ti_{1-x}Si_xN$ should transform to fcc(ZnS type) phase (space group: $F4$-$3m$) for $x \geqslant 0.63$.[16] However, this hypothetical phase of fcc(ZnS type) SiN and $Ti_{1-x}Si_xN$ has not been found so far.

From the combined *ab initio* DFT calculations of the total energy of fcc-SiN and thermodynamic calculations for the reaction 4 fcc-SiN=hcp-$Si_3N_4$+Si, a high instability of fcc-SiN with respect to hcp-$Si_3N_4$ is calculated to be 136.3 kJ/mol of atoms. The calculated total energy of Si is about −5.43 eV/atom. The previously calculated value of lattice instability of fcc-SiN of about 168.4 kJ/mol of atoms, which was based on the reaction 3 fcc-SiN+0.5$N_2$ =hcp-$Si_3N_4$,[12] is even higher than the present value of 136.3 kJ/mol of atoms. This is due to the different definitions of reaction path and of the reference states with Si and $N_2$, respectively.[12] (Note that the latter reaction corresponds to the conditions of a sufficiently high nitrogen activity, whereas the former one assumes a low activity or even an absence of nitrogen during the annealing.) These results show that under a sufficiently high pressure of nitrogen, the fcc-SiN has to transform to hcp-$Si_3N_4$. This transformation may be suppressed when the annealing experiments are done under argon as in Ref. 14 or in vacuum[22–27] because of the absence of nitrogen. One has to remember that upon annealing to high temperature in the absence of nitrogen, the nitrides will decompose, MeN→Me+0.5$N_2$, the decomposition rate being kinetically controlled in a given experiment.

Next, we study the stability of the fcc-$Ti_{1-x}Si_xN$ solid solution by considering the reaction $Ti_{1-x}Si_xN=(1-x)TiN+(x/4)Si_3N_4+(x/4)Si$, which should occur in the absence of nitrogen for the temperatures considered here.[6] The demixing energy of fcc-$Ti_{1-x}Si_xN$ phase with respect to the stable fcc-TiN, hcp-$Si_3N_4$, and pure Si is expressed by Eq. (3).

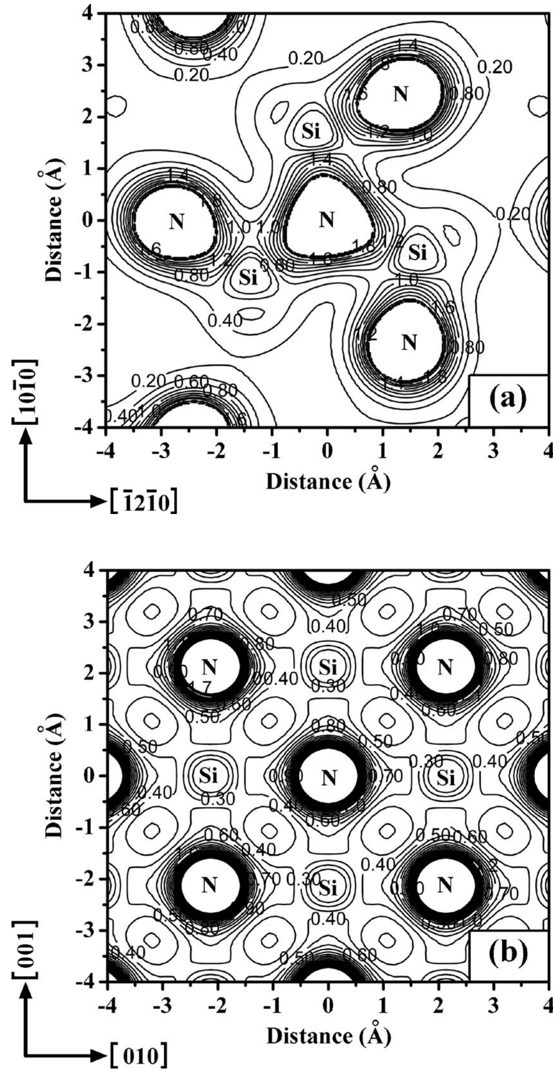


FIG. 2. Electron density distributions for (a) (0001) lattice plane of hcp-$Si_3N_4$ and (b) (100) plane of hypothetical fcc-SiN phases. Note that the apparent threefold symmetry in (a) is due to the fact that not all atoms are exactly in the same plane (Ref. 41).

$$\Delta E_{fcc\text{-}(\mathrm{Ti}_{1-x}\mathrm{Si}_x)\mathrm{N}} = \frac{1}{2}\left[2E_{fcc\text{-}(\mathrm{Ti}_{1-x}\mathrm{Si}_x)\mathrm{N}} - 2(1-x)E_{fcc\text{-TiN}} - \frac{7x}{4}E_{\beta\text{-}\mathrm{Si}_3\mathrm{N}_4} - \frac{x}{4}E_{\mathrm{Si}}\right]. \quad (3)$$

Here, $E_i$ are the total energies in unit of kJ/mol of atoms of the given phases. With the calculated total energies of fcc-$Ti_{0.5}Si_{0.5}N$, fcc-TiN, hcp-$Si_3N_4$, and pure Si by *ab initio* DFT method, the demixing energy of the hypothetical fcc-$Ti_{0.5}Si_{0.5}N$ phase is about 74.25 kJ/mol of atoms. This value is lower than the previous estimation of about 90.6 kJ/mol of atoms[12] due to the same reason as discussed above for the instability of fcc-SiN. However, both values are quite large and suggest that there is a large driving force for fcc-solution phase to segregate into the stable fcc-TiN and hcp-$Si_3N_4$. Therefore, the high thermal stability reported by some workers for this and other solid solutions of transition metal nitrides with $SiN_x$ may be explained either by nitrogen deficiency or by impurities.

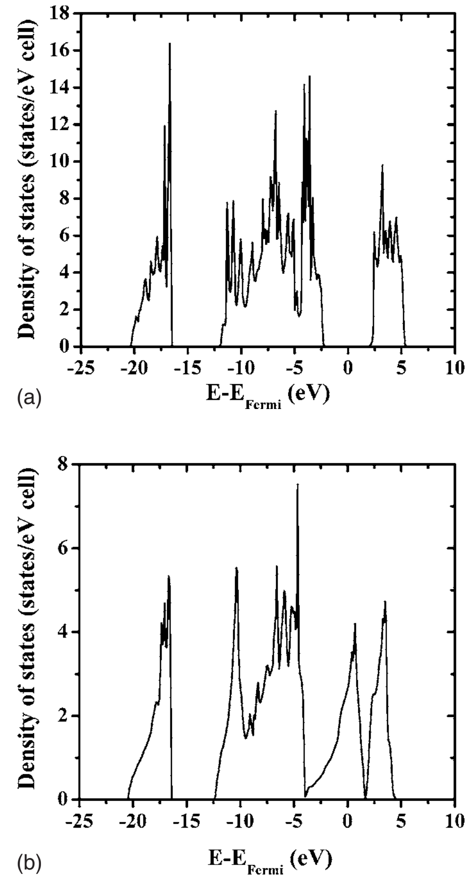


FIG. 3. Total electronic density of states for (a) hcp-$Si_3N_4$ and (b) fcc-SiN. In the calculations, 14 atoms/cell were used for hcp-$Si_3N_4$ and 8 atoms/cell for fcc-SiN.

Obviously, the hypothetical, bulk metastable fcc-SiN, which can be epitaxially stabilized only up to 2 monolayers during deposition of heterostructures by PVD, is inherently unstable. Figure 2 shows the valence electron density distribution obtained from the *ab initio* DFT calculations for the stable hcp-$Si_3N_4$ [Fig. 2(a)] and for the hypothetical fcc-SiN [Fig. 2(b)]. Note that the crystal planes (0001) for the hcp-$Si_3N_4$ phase and (100) for the fcc-SiN phase were selected as examples because they contain both Si and N atoms. The charge density between the Si and N atoms is larger for the hcp-$Si_3N_4$ than for the fcc-SiN, and the bond length of 1.764 Å in hcp-$Si_3N_4$ is significantly shorter as compared with 2.131 Å for the hypothetical fcc-SiN. Thus, the bond strength is much larger in the stoichiometric hcp-$Si_3N_4$ than in the unstable fcc-SiN.

The instability of the hypothetical fcc-SiN is further illustrated by the density of states shown in Fig. 3. The stoichiometric, stable hcp-$Si_3N_4$ [Fig. 3(a)] is an insulator (or a "wide band semiconductor") with a band gap of about 4.54 eV, in good agreement with published data of 4–4.5 eV.[41,42] The fcc-SiN is a metal due to unfilled valence band because silicon atoms need four N neighbors (i.e., the stoichiometry must be $SiN_{1.33}$) in order to saturate their four valence bonds.

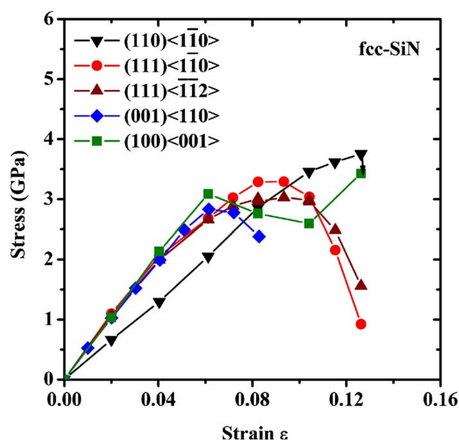


FIG. 4. (Color online) Stress-strain curves calculated by *ab initio* DFT with a full relaxation of the cell parameter after each incremental strain step for fcc-SiN (Ref. 43).

The "weak" nature of the fcc-SiN is finally illustrated by the shear stress-strain curves, obtained from the *ab initio* DFT method by the present authors (for details, see Ref. 43). Because plastic deformation occurs in shear, the shear stress-strain curves provide information about the resistance of a material against plastic deformation. The calculated ideal shear strength of the fcc-SiN of about 3–4 GPa for the five typical slip systems as shown in Fig. 4 is much smaller than that reported for hcp-$Si_3N_4$ (20 GPa).[43,44] This is due to the lack of electrons from nitrogen, which does not allow the silicon atoms to form four strong covalent Si-N bonds in tetragonal configuration and results in low electron density and long bond distance as shown above.

## IV. CONCLUSIONS

The present *ab initio* DFT calculations explain the experimentally observed transformation of fcc-$Ti_{1-x}Si_xN$ into amorphous phase for $x \geqslant 0.24$ to be due to the inherent instability of the substoichiometric fcc-SiN. Similar conclusion applies to other systems consisting of a transition metal nitride in combination with substoichiometric SiN, which were studied experimentally by Musil and co-workers. The fcc-$Ti_{1-x}Si_xN$ has to decompose into fcc-TiN and hcp-$Si_3N_4$ under nitrogen pressure of $\geqslant 10^{-3}$ mbar at elevated temperature. Oxygen impurities probably prevent the $Me_{1-x}Si_xN$ (Me $=$Ti, Ta, Zr, W) solid solution system to reach the equilibrium, but this question could not be addressed in the present work because of the lack of the relevant information in the quoted papers. We only remind the reader that oxygen impurities of few at. % or less cause crystalline-to-amorphous transition in silicon deposited by plasma CVD at about 500 °C,[45] and such impurities are common in nitride coatings deposited by PVD.[46]

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