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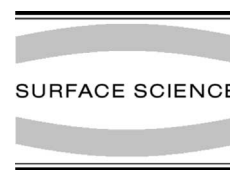
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# Theoretical investigation of the initial steps of the adsorption of N atoms on Si(1 0 0)-2 × 1

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## Abstract

Structural, energetics, and mechanistics aspects of initial steps of the reaction of a N atom with Si(100)-2 × 1 modeled by the Si<sub>9</sub>H<sub>12</sub> + N system are reported. Hybrid density functional B3LYP calculations predict a barrierless first step leading to an adsorbate where N is bound to one of the dimer Si. Two possible activated routes for internal rearrangements were found, with that leading to the incorporation of Si below the first layer predicted to be kinetically dominant (98%) under the experimental conditions. This structure and frequency calculations are consistent with the experimental finding of a planar NSi<sub>3</sub> moiety and with the experimental SiN asymmetric stretching frequency of the NSi<sub>3</sub> groups. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Density functional calculations; Surface chemical reaction; Silicon; Nitrogen atom; Silicon nitride

## 1. Introduction

Silicon nitride is an important ceramic material known for its high thermal stability, mechanical resistance, large electrical resistivity, and chemical stability mainly imparted by the highly covalent nature of the Si–N bonds [1]. Applications can be found in high-temperature engines, in passivation layers in microelectronics, and as insulators in thin-film transistors, among others [2]. Extensive experimental studies for the growth of a thin layer have been carried out using a variety of techniques [3–8], but thermal chemical vapor deposition

(CVD) [9–16] has predominated over the others. The high reactivity and sticking coefficient of NH<sub>3</sub> has made its use preferred over N<sub>2</sub>, however, the high temperature (800–1200°C) needed in these thermal CVD experiments often leads to undesirable processes such as dopant diffusion, and hydrogen in the surface. To avoid these problems, direct ion beam deposition experiments using species like N<sup>+</sup> and N<sub>2</sub><sup>+</sup> have been conducted as an alternative to grow these layers. Penetration of the substrate or reaction with the surface atoms is dependent on the kinetic energy of the colliding particles. In ion implantation studies conducted by Pan et al. [17] with 10 keV N<sup>+</sup> and N<sub>2</sub><sup>+</sup> species, the use of Auger electron spectroscopy revealed a surface stoichiometry close to that of Si<sub>3</sub>N<sub>4</sub> for incident angles between 0° and 30° to the surface normal, with practically identical results for either N<sup>+</sup> or N<sub>2</sub><sup>+</sup>. For low energy N<sup>+</sup> and N<sub>2</sub><sup>+</sup> ions in the

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range of 1–300 eV, investigations carried out by Park et al. [18] revealed a saturation of the silicon surface and a composition also close to that of  $\text{Si}_3\text{N}_4$ . The reaction with the surface is supposed to involve first a neutralization of the ion close to it, followed next by an incorporation of silicon atoms or backscattering of the nitrogen atom or molecule from the surface. The geometry of the silicon nitride formed with low energy ions resembles that of  $\text{Si}_3\text{N}_4$ , with the nitrogen atoms located in  $\text{Si}_3\text{N}$  planes.

As part of an ongoing investigation on clusters of silicon and nitrogen conducted in our group, and in part motivated by the fact that one of the reactions leading to the formation of silicon nitride involves a reaction of  $\text{N}_2$  with Si atoms, and also surprised by the lack of either theoretical or experimental structural and stability information on compounds of silicon and nitrogen, we have recently reported structural, energetics, and spectroscopic results for a series of compounds of molecular formula  $\text{Si}_2\text{N}$  [19],  $\text{SiN}_2$  [20],  $\text{Si}_2\text{N}_2$  [21],  $\text{HSiN}_2$  [22], and  $\text{Si}_3\text{N}_2$  [23]. In this work, in the absence of any theoretical investigation modeling the reaction of nitrogen with a silicon surface, our main purpose is to characterize theoretically the energetics of the approach and adsorption of a N atom to a model silicon surface ( $\text{Si}_9\text{H}_{12}$ ), to follow structural rearrangements on surface adsorption and incorporation below the surface layer, and propose a mechanism for the whole reaction that can help us have a better understanding of this process.

## 2. Methods

To model the reaction of a nitrogen atom on the  $\text{Si}(100)\text{-}2 \times 1$  surface, we have used the  $\text{Si}_9\text{H}_{12}$  cluster which has been extensively employed in the literature to model various types of reactions on this surface [24–26]. This cluster basically consists of four layers of Si atoms. The first one contains two Si atoms representing the surface dimer, which are connected to the Si of a second layer of four atoms; the third and fourth layers contain, respectively, two and one Si atoms. The valence of the terminal Si is saturated with a hydrogen atom.

The split-valence basis set 6–31G(d) was used for the atoms of the first and second layers [27], and the nitrogen [28], with five pure components for the d-type function; the 6–31G basis was used for the remaining silicons, and the hydrogens. This choice was made to make the calculation less computational demanding, since previous complete optimizations of the  $\text{Si}_9\text{H}_{12}$  cluster have shown that changes in the Si–Si distances between atoms in these two layers are very small with these two basis sets. The hybrid density functional method B3LYP, which includes Becke's three parameter non-local exchange functional with the correlation functional of Lee–Yang–Parr, was used for the electronic structure investigation [29,30]. Complete geometry optimizations were done with the analytical gradient technique as implemented in the GAUSSIAN 98 suite of programs [31]. For the Si cluster plus N atom system, the Si–H bond distances were kept fixed at the optimized values obtained for the isolated cluster. In the final results, except for one of the structures,  $C_s$  symmetry was imposed, since initial trials with the  $C_1$  symmetry have shown the optimized geometry to converge to a structure with  $C_s$  symmetry. The nature of the optimized stationary points on the potential energy surface was analyzed through the calculation of vibrational frequencies in the harmonic approximation. Transition state structures were searched by the synchronous transit-guided quasi-Newton method QSTN [32].

Finally, we note that for a more realistic cluster representation of larger areas of the solid, properly accounting for mechanical relaxation, the ONIOM technique seems to be very promising [33].

## 3. Results and discussion

The reaction path for the adsorption of a N atom onto a single dimer and the energetics involved in the various steps are depicted in Fig. 1. For an N ( $^4\text{S}$ ) atom approaching the  $\text{Si}_9\text{H}_{12}$  ( $^1\text{A}'$ ) system, a simple angular momentum addition rule imposes the quartet spin symmetry for the whole system. An alternative approach, leading to a doublet spin symmetry for the whole system in-

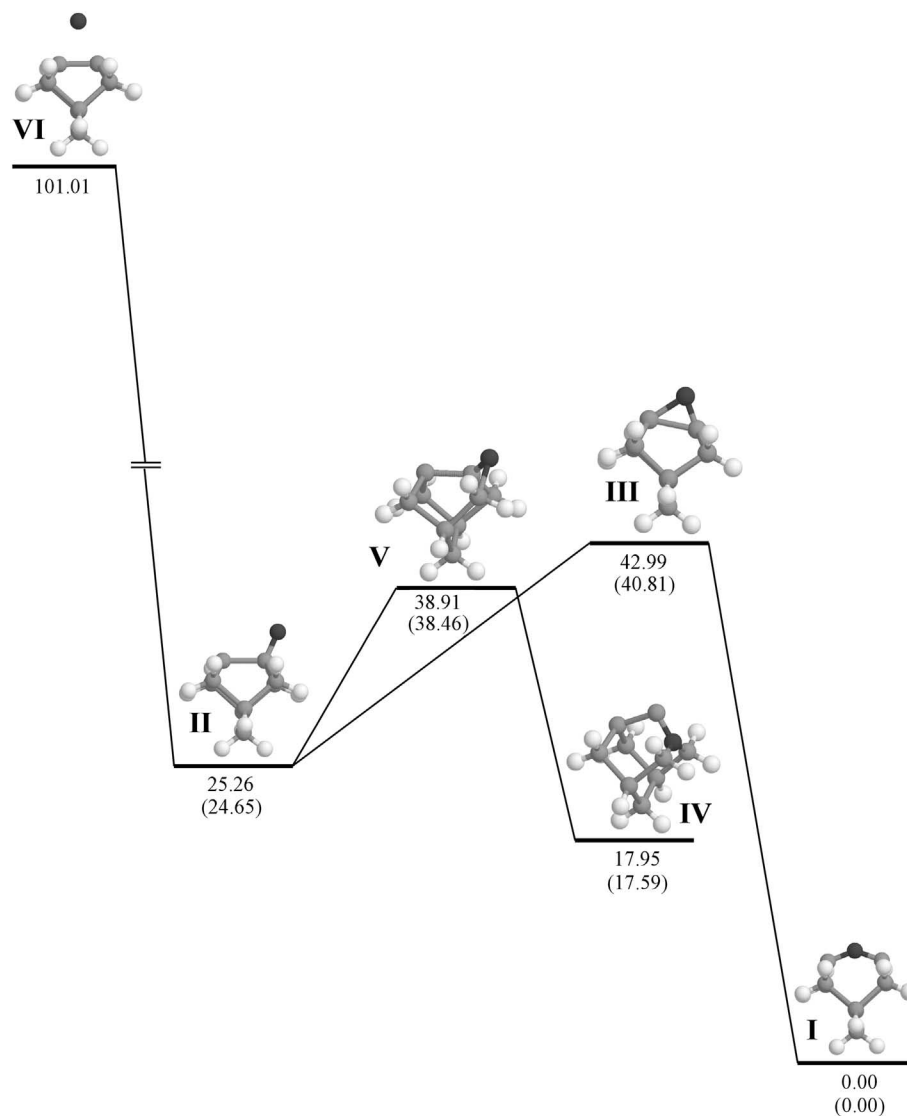


Fig. 1. Predicted energies and Gibbs free energies (in parentheses), in kcal/mol, for representative points along the reaction path leading to adsorption of N on Si (1 0 0) modelled by the cluster Si<sub>9</sub>H<sub>12</sub>.

volves an excited N atom in a doublet state; results for this reaction are expected to be reported soon [34]. In our approach to the problem, we first examined a likely structure (I) for the global minimum, the symmetric binding of the N atom to the two surface Si. Next, to estimate the binding energy involved in the formation of this adsorbate, the energy of separated cluster and N atom system (VI) was evaluated, and a test made to check if the

perpendicular approach of the N atom to the dimer Si would correspond to the minimum energy path. With the only constraint of C<sub>s</sub> symmetry, the perpendicular approach of an N atom to the dimer led to a local minimum 25.26 kcal/mol higher in energy than the symmetric system, with the N atom bound to only one of the dimer Si (II). In attempts to locate a transition state structure connecting these two minima, another stationary point

was found at 42.99 kcal/mol above the global minimum. Frequency calculations revealed this structure (**III**) to correspond to a transition state. Further exploration of a N atom approach to the cluster, now directly facing the plane formed by one Si of the dimer, and the two adjacent Si of the second layer, led to structure **IV**, 17.95 kcal/mol above the global minimum, which is illustrative of the penetration of a Si atom below the surface. The existence of structure **IV** called for the search of another transition state stationary point now connecting **II** and **IV**. Structure **V**, located 38.91 kcal/mol above the global minimum, represents this new transition state.

Geometries for the optimized structures are illustrated in Fig. 2. For structure **I**, the bond distance between the surface Si and the nitrogen is 1.712 Å, slightly shorter than that of a typical Si–N single bond (1.72 Å in  $\text{H}_3\text{Si–NH}_2$ ), and an SiNSi bond angle of 139.1°; the two dimer Si are far apart 3.209 Å, a distance about 15% shorter than that between the surface Si in an unreconstructed surface (3.84 Å) [35]. In structure **II**, the Si–N distance increased to 1.773 Å, still representative of a single bond, while the surface Si are distant 2.397 Å, a value larger than the equivalent one in the isolated symmetric dimer (2.222 Å); the NSi(2)Si(3) (see Fig. 2) bond angle turns out to be 113.8°. In the case of the transition state structure **III**, it takes a buckled form, with the N distant from the lower Si 1.775 Å, and from the upper one 2.180 Å; the surface silicons are now apart 2.481 Å, with an Si(2)NSi(3) angle of 77.3°. For structure **IV**, the N atom is practically located in the plane defined by one of the surface Si and the two adjacent ones of the second layer, but not symmetrically positioned relative to the three silicons; its distances from the surface Si and the lower one are 1.786 and 1.908 Å, respectively, while the Si(4)NSi(8) angle turns out to be 137.3°. For structure **I**, there is a significant increase in the distance between the first and second layers (1.343 Å) when compared with that of the isolated cluster (1.070 Å); for **II**, this change is smaller, 1.222 Å. Finally, structure **V** represents a departure from  $C_s$  symmetry. The distances from Si(2) to Si(3), Si(4), and Si(8) do not differ significantly (2.386, 2.379, and 2.381 Å, respectively), whereas those of NSi(4)

and NSi(8), 2.197 and 3.168 Å, respectively, are much longer than the NSi(2) one, 1.756 Å.

Of the manifold of vibrational modes and associated frequencies possible for this system, we have depicted in Fig. 3 two such modes that seem to be of direct relevance to the IR spectroscopy of silicon nitride. The frequency at 818  $\text{cm}^{-1}$  associated with the asymmetric stretching of the Si–N bond in the NSi(2)Si(4)Si(8) plane of structure **IV** seems to correspond to the observed frequency of 840  $\text{cm}^{-1}$  attributed by Liu et al. [36] to asymmetric vibrations of  $\text{NSi}_3$  groups. Associated now with structure **I**, the mode at 1015  $\text{cm}^{-1}$ , three times less intense than the one at 840  $\text{cm}^{-1}$ , might be associated to the small peak at about 1090  $\text{cm}^{-1}$  in Fig. 2 of Ref. [36], that becomes more prominent for larger gas flow rate ratios.

Despite the adsorption of the N atom on the cluster, structure **I** continues to have the two dangling bonds as in the isolated cluster plus an additional one from the N atom, imparting to the surface a very reactive character. Atomic spin densities turn out to be 0.92 and 0.64 on the N and surface Si, respectively, whereas Mulliken atomic charges are –0.51 and +0.31 on the N and Si, respectively. For structure **II**, the atomic density on the N increases to 1.79, reflecting the presence of more unpaired electrons, but its atomic charge reduces to –0.30. For the non-nitrogen bonded Si, the presence of an unpaired electron is reflected in its spin density of 1.00; atomic charges are predicted to be very small, –0.01. In the case of structure **IV** spin densities on the dimer silicons amount to 1.45 and 1.06, with the larger value associated with the Si bound to the N atom; on the N, it is substantially reduced to 0.22, a likely indication of weak bonds of the N with the silicons of the second layer, also reflected in the value of 1.904 Å for this Si–N distance.

Concerning the mechanism of adsorption of a N atom on the cluster, it can be thought of as involving two steps. First, N is adsorbed (structure **II**) with no barrier; this process is represented by a well depth of 74.75 kcal/mol. Second, internal rearrangements can lead either to structure **I** or **IV**. The reaction leading to **I** is activated, with a barrier of 17.73 kcal/mol, and an exothermicity of 25.26 kcal/mol, while that leading to **IV** encounters

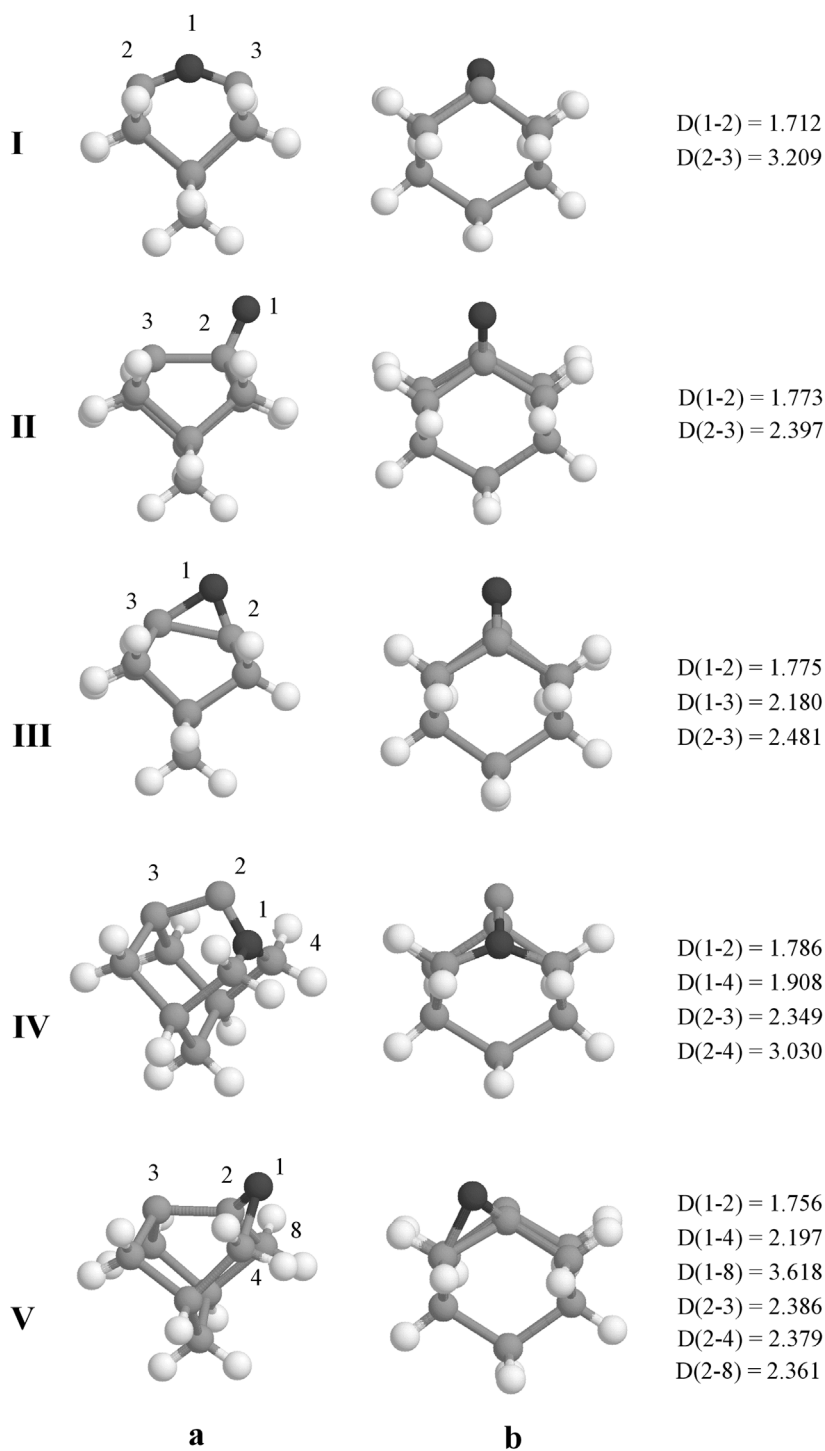


Fig. 2. Calculated geometrical parameters for representative points along the reaction path leading to adsorption of N on Si (100) modelled by the cluster  $\text{Si}_9\text{H}_{12}$ . View **a** is perpendicular to the silicon dimer, and view **b** is along the dimer. Distances are given in Å.

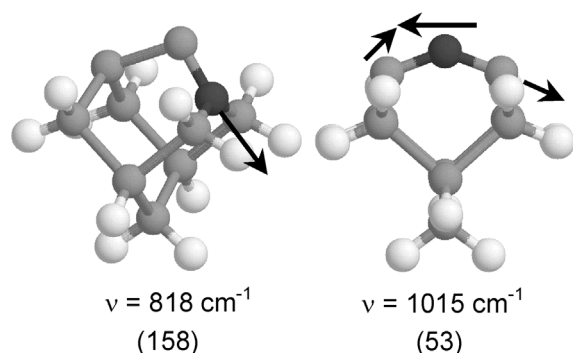


Fig. 3. Calculated frequencies and intensities (in km/mol) for selected vibrational modes of the  $\text{Si}_9\text{H}_{12}\text{N}$  cluster.

a smaller barrier of 13.65 kcal/mol, and is less exothermic, 7.31 kcal/mol. Since the overall exothermicity from reactants to **I** is estimated to be 100.01 kcal/mol, and the largest of the two barrier heights for interconversion to **I** is about 47.0 kcal/mol below the reactants, there is enough energy available for the reaction to proceed without the system being trapped at **II**. The question then arises as to the proportion of final products **IV** and **I** one is more likely to find. Since the reaction in laboratory conditions involves a flow of atoms colliding with a surface, it is expected that this reaction be kinetic controlled. Under this condition, an estimate of product proportion based on the barriers heights, expressed in terms of the Gibbs free energy (see Fig. 2), gives a preference of 98% for the reaction leading to structure **IV**.

#### 4. Conclusions

This work gives the first theoretical description of structural, energetics, and mechanistic aspects of initial steps of the reaction of a N atom with  $\text{Si}(100)\text{-}2 \times 1$  modeled by the  $\text{Si}_9\text{H}_{12} + \text{N}$  system. Our model predicts a barrierless first step leading to an adsorbate where N is bond to one of the dimer Si. Next, of two possible activated routes for internal rearrangement, that leading to the incorporation of Si below the first layer should be kinetically dominant under the experimental conditions. This structure and the frequency calcu-

lated are consistent with the experimental finding of a planar  $\text{NSi}_3$  moiety and with the experimental  $\text{SiN}$  asymmetric stretching frequency of the  $\text{NSi}_3$  groups.

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