

## Energetics of NP and NB complexes in silicon

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### Abstract

Using ab initio (Hartree–Fock and local density approximation) and semiempirical (Austin Model 1) calculations, we studied the energetics and electronic structures of NB and NP complexes. We found that these complexes are electrically inactive. The formation energies are 1.6 eV for the NB coupling and 2.4 eV for the NP pairing. The N–P and N–B interatomic equilibrium distances are about 3.5 Å for both complexes. © 2001 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

The interest to study nitrogen in silicon is stimulated by ideas to build nitride and oxynitride buffer layers at the Si/SiO<sub>2</sub> interface [1] by ion implantation. Since some part of implanted nitrogen atoms penetrates into the bulk of silicon, it is important to know the influence of nitrogen on the behavior of active dopants such as B and P. There are theoretical studies devoted to N atoms in silicon [2–4]. However, up to our knowledge, the interaction of nitrogen with boron and phosphorus in silicon has not been investigated so far.

### 2. Approach

We have studied the interaction of N atoms with B and P donors in Si using the pseudopo-

tential local density approximation (LDA) method [5], the pseudopotential Hartree–Fock (HF) method and the semi-empirical Austin Model 1 (AM1) method. In the last two cases, we used the PC GAMESS version [6] of the GAMESS (US) QC package [7].

A cluster approach was adopted in all three cases. Dangling bonds on the surface of the cluster were terminated by H atoms. Their positions were fixed in order to imitate the ideal lattice of Si bulk. Coordinates of all other atoms were optimized. To evaluate the size effect the number  $X$  of atoms in the cluster (the saturating H atoms are not counted in  $X$ ), the cluster size  $X$  was varied from 5 to 71 atoms. Since HF and LDA calculations are computationally demanding, they were performed on the Si<sub>5</sub>, Si<sub>8</sub> and Si<sub>17</sub> clusters. The AM1 method, which is less accurate but less elaborate, was used in addition for Si<sub>35</sub> and Si<sub>71</sub> clusters. Without dopants, all Si <sub>$X$</sub>  clusters have  $T_d$  symmetry. The only exception is the Si<sub>8</sub> cluster which has  $C_{3v}$  symmetry.

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### 3. Results

#### 3.1. Test calculations

In order to verify and calibrate our approaches, we studied the bond geometries of single N, P and B atoms in silicon. The results are given in Table 1.

Note that all three methods give approximately the same results for N and B. However, for P the HF method works much worse than semi-empirical AM1. HF calculations produce  $C_{3V}$  symmetry instead of  $T_d$ . Sansores et al. [3] reported  $T_d$  symmetry for P in silicon computed by AM1 MOPAC optimization in  $Si_{20}P_1$  cluster; the P–Si distance was 2.45 Å. Unfortunately, for the N case they also obtained the same ( $T_d$ ) symmetry; their N–Si distance was 2.18 Å. In contrast to that, Cunha et al. [2] found  $C_{3V}$  relaxation for N using HF calculations with a small  $Si_5$  cluster. They reported only about the displacements of N and Si atoms along the  $C_{3V}$  axis; their N–Si bond length in this direction was 3.28 Å. The most reliable results have been published recently by Saito and Miyamoto [4]. Using the local density approximation they found the short N–Si distance of 2.08 Å and the long one of 3.07 Å. This is in good agreement with our data listed in Table 1. For the case of B, our results correlate with those of Sansores and Valladares [8] who computed 1.98 and 2.74 Å for the short- and long-bonds, respectively.

#### 3.2. Atomic structures of NP and NB complexes

The nitrogen-dopant complexes were formed by placing two atoms (NP or NB) in the same  $Si_X$

cluster. We found that the total energy was minimal when a D atom (D means P or B) substituted the Si atom which was the distant neighbor of N.

In order to compute formation energies  $E_{ND}$ , we compared the sum of total energies of clusters containing single impurities to the sum of total energies of a “perfect”  $Si_X$  cluster and the cluster with the complex:

$$E_{ND} = E(Si_{X-2}ND) + E(Si_X) - E(Si_{X-1}N) - E(Si_{X-1}D). \quad (1)$$

We found that the combination of B and P with N is energetically favorable. The N–P and N–B interatomic equilibrium distances are about 3.5 Å for the both complexes. Results of these calculations are summarized in Table 2.

Comparing the most reliable LDA results with the HF and AM1 energies, we conclude that the HF method describes the N–P interaction more accurately than the AM1 method. However, in the N–B case the AM1 method works better. The cluster size effect is insignificant. This means that the N–P and N–B interactions are determined by the immediate neighborhood of the impurities.

#### 3.3. Electronic structures

Finally, we examined LDA electronic structures of the NB and NP complexes. For these calculations the energy optimized coordinates of Si, N, P and B atoms were used. Atoms of quasihydrogen (so-called siligen,  $\bar{H}$ ) were used instead of H atoms in order to saturate the dangling Si bonds on the

Table 1  
Bond lengths (in Å) between N, P and B atoms with their Si neighbors, as computed in various clusters

	N			P			B		
	LDA	HF	AM1	LDA	HF	AM1	LDA	HF	AM1
Si <sub>5</sub>	2.05	2.00	1.96	2.40	2.32	2.32	2.11	2.15	2.07
	3.02	2.99	2.81	2.40	3.36	2.32	2.56	2.82	2.94
Si <sub>17</sub>	2.06	1.93	1.79	2.42	2.29	2.30	2.03	2.16	2.04
	3.05	3.18	2.75	2.42	3.27	2.30	2.62	2.88	2.93
Si <sub>35</sub>			1.78			2.26			1.96
			2.68			2.26			2.91
Si <sub>71</sub>			1.78			2.25			1.94
			2.67			2.25			2.90

The bottom numbers in the each line correspond to the bonds directed along the  $C_{3V}$  axis.

Table 2

Formation energies (in eV) of the NP and NB complexes in various clusters; see Eq. (1)

	N + P			N + B		
	LDA	HF	AM1	LDA	HF	AM1
Si <sub>8</sub>	2.4	2.6	1.0	1.6	2.1	1.6
Si <sub>17</sub>	2.4	2.3	1.0	1.6	2.3	1.5
Si <sub>35</sub>			0.6			1.5
Si <sub>71</sub>			0.5			1.4

cluster surface. Siligen was defined by Redondo et al. [9] as hydrogen with the nonhydrogen Slater exponent  $\zeta_s$  of the 1s orbital and with the Si–Si like Si–H bond of 2.35 Å. This approach, with  $\zeta = 1.22$  (this value assures the equivalence of Mulliken charges on “bulk” and siligen-saturated Si atoms), was already used by us successfully in studies of the influence of impurities on the binding energy of

silicon [10] and for other applications (e.g., see [11,12]).

Unfortunately, for the Si<sub>17</sub> cluster could not be used in these electronic structure calculations because a siligen atom can be placed only in such positions where it saturates a single silicon bond. Thus, we study only the Si<sub>8</sub> cluster – pure and doped.

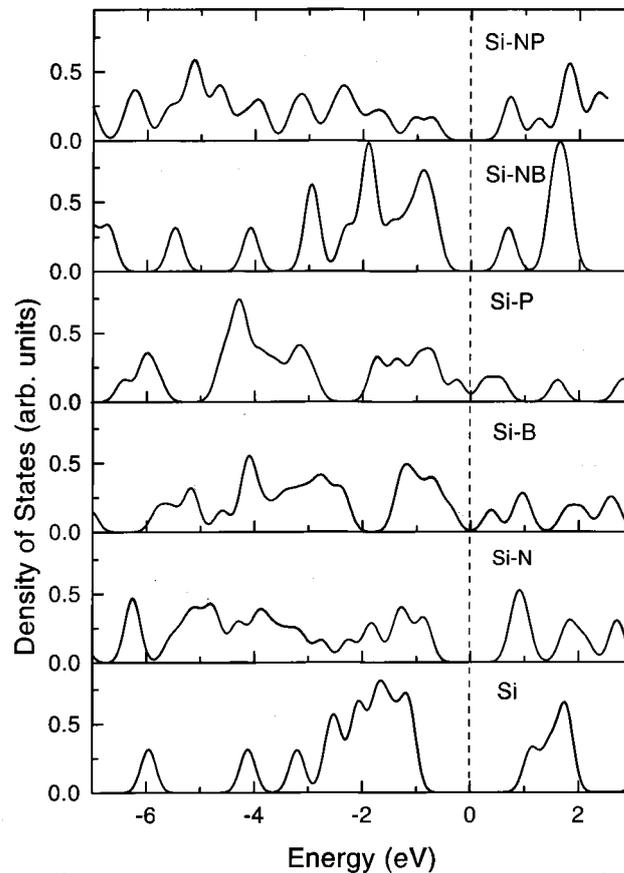


Fig. 1. DOS for the Si<sub>8</sub> clusters (pure and doped). The vertical dashed line represents the Fermi level.

The calculated densities of electronic states (DOS) are plotted in Fig. 1. To make results more transparent, we represented every electronic state in the cluster by a Gaussian with the half-width of 0.1 eV. The forbidden gap in the Si<sub>8</sub> cluster (2.25 eV) is much larger than 1.17 eV of bulk silicon. This is the well-known quantum confinement effect. For the same reason, we found large distances between the Fermi level and the acceptor state in the B-doped cluster (0.38 eV); the same effect is observed for the donor state in the P-doped cluster (0.26 eV). However, we see that in the clusters with the NB or NP complexes the dopant electron states move away from the Fermi level by a significant amount:  $\Delta E = 0.69$  eV for NB and 0.72 eV for NP. As a consequence, all electron states are swept away from the gap. Therefore, we conclude that trapping of boron or phosphorus by nitrogen makes P and B dopants electrically inactive.

#### 4. Summary and conclusions

We reported results of ab initio (Hartree–Fock and LDA) and semiempirical (AM1) calculations for formation energies and electronic structures of NB and NP complexes. The formation energies are 1.6 eV for NB and 2.4 eV for NP. The N–P and N–B interatomic distances are about 3.5 Å. These complexes are electrically inactive.

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