Nitrogen Trapping of Boron and Phosphorus in Silicon

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Using *ab initio* (Hartree-Fock and local density approximation) and semiempirical (Austin Model 1) calculations we have studied the energetics and electronic structures of N+B and N+P complexes. We have found that these complexes are electrically inactive. The energy gains are 1.6 eV for the N+B coupling and 2.4 eV for the N+P pairing. The N-P and N-B interatomic equilibrium distances are about 3.5 Å for the both complexes.

The interest to the study of nitrogen in silicon is stimulated by ideas to use it for formation of nitride and oxynitride buffer layers at the Si/SiO_2 interface by the ion implantation. Since some of the implanted nitrogen atoms penetrate into the bulk of silicon, it is important to know how nitrogen affects the behaviors of active dopants — such as B and P. There are theoretical works devoted to the study of N atoms in silicon [1, 2, 3]. However, as far as we know, the interaction of nitrogen with boron and phosphorus in silicon has not yet been studied. We have studied it using the pseudopotential local density approximation (LDA) method [4], the pseudopotential Hartree-Fock (HF) method and the semi-empirical AM1 method. The last two methods were used within the framework of the PC GAMESS version [5] of the GAMESS (US) QC package [6]. A cluster approach was used in all cases. The outward cluster bonds were terminated by H atoms which were fixed to imitate the ideal solid Si lattice. Coordinates of the other atoms were optimized. To evaluate the size effect, the number X of atoms (Si plus dopants) in the clusters was varied from 5 to 71. Because of the larger computer time required for the HF and LDA calculations, they were performed for the Si_5, Si_8 and Si_{17} clusters, while the AM1 method was used not only for the smaller clusters, but also for the Si_{35} and Si_{71} clusters. All Si_X clusters had the T_d symmetry in the absence of dopants, except for the Si_8 one which had the C_{3v} symmetry.

	N			P			B		
	LDA	HF	AM1	LDA	HF	AM1	LDA	HF	AM1
Si_5	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_{17}	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_{35}			1.78			2.26			1.96
			2.68			2.26			2.91
Si_{71}			1.78			2.25			1.94
			2.67			2.25			2.90

Table 1. Lengths (in Å) of the nearest bonds of N, P and B with Si atoms in various clusters. The bottom numbers in the each line correspond to the bonds directed along the C_{3V} axis.

	N + P			N + B		
	LDA	HF	AM1	LDA	HF	AM1
Si_8	2.4	2.6	1.0	1.6	2.1	1.6
Si_{17}	2.4	2.3	1.0	1.6	2.3	1.5
Si_{35}			0.6			1.5
Si_{71}			0.5			1.4

Table 2. Energy gains (in eV) of the N+P and N+B complexes in various clusters.

First, in order to verify and calibrate our approaches, we have studied the bond geometries of single N, P and B atoms in silicon. Results are collected in Table 1.

Note that for the N and B cases all the methods give approximately the same results. However, the HF method works much worse than the semi-empirical AM1 one for the P case resulting in the C_{3V} symmetry instead of T_d. The T_d symmetry for P in silicon with the 2.45 Å P-Si distance was obtained by Sansores *et. al.* [2] using the AM1 MOPAC optimization with the $Si_{20}P_1$ cluster. Unfortunately, they have obtained the T_d symmetry for the N case also (their N-Si distance was 2.18 Å). The C_{3V} symmetry for N has been obtained by Cunha *et. al.* [1] using the HF calculations with the Si_5 cluster. They have reported only the displacements of N and Si atoms along the C_{3V} axis, and their N-Si bond length in this direction was 3.28 Å. The most trustful results have been published recently by Saito and Miyamoto [3]. Using the local density

approximation they have found the short N-Si distance of 2.08 Å and the longest one of 3.07 Å in good accordance with our above values. For the B case our results correlate with the data of Sansores and Valladares [7] giving 1.98 Å and 2.74 Å for the short and long bonds.

Then we placed two atoms (N+P or N+B) at the same Si_X cluster. It has been found that the total energy was minimal when a D atom (D means P or B) was substituting the Si atom which was the far neighbor of N. We have compared the total energies — ($Si_{X-1}N + Si_{X-1}D$) and ($Si_{X-2}ND + Si_X$) — and 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 the energy calculations are summarized in Table 2.

Comparing the most trustful LDA results with others we can conclude that the HF method describes the N-P interaction more accurately than the AM1 method. In the N-B case the priority belongs to the AM1 method. The size effect is insignificant, i.e. both the N-P and N-B interactions are determined by the nearest surroundings.

Using the LDA method we finally examined the electronic structures of the N+B and N+P complexes. For these calculations the optimized coordinates of Si, N, P and B atoms were used. Atoms of quasihydrogen (so-called siligen, $\overline{H}$) were used instead of H atoms to saturate broken Si bonds. Siligen was defined by Redondo et. al. [8] as hydrogen with the non-hydrogen Slater exponent ζ_S of the 1s orbital and with the Si-Si like Si-$\overline{H}$ bond of 2.35 Å. This approach with $\zeta = 1.22$, which controls the equivalence of the Mulliken's charges on Si atoms, was used to study the influence of impurities on the binding energy of silicon [9] and in other applications (for example, see Refs.[10, 11].)

Unfortunately, for the geometry reasons the Si_{17} cluster could not be used in the above electronic structure calculations because a siligen atom can be placed only in such positions where it saturates only one silicon bond. Thus, we study only the Si_8 cluster – pure and doped.

Calculated densities of electronic states (DOS) are plotted in Figure 1. To make the results more graphical, we have diffused each discrete state by the Gaussian function with the half-width of 0.1 eV. Naturally, the semiconductor forbidden gap in the Si_8 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 have found the large distances between the Fermi level and the accepter state in the B doped cluster (0.38 eV) or the donor state in the P doped cluster (0.26 eV). However, we see that in the clusters with the N+B or N+P complexes the dopant states are separated from the Fermi level by larger distances: $\Delta E = 0.69$ eV for N+B and 0.72 eV for N+P. Therefore, one can conclude that the
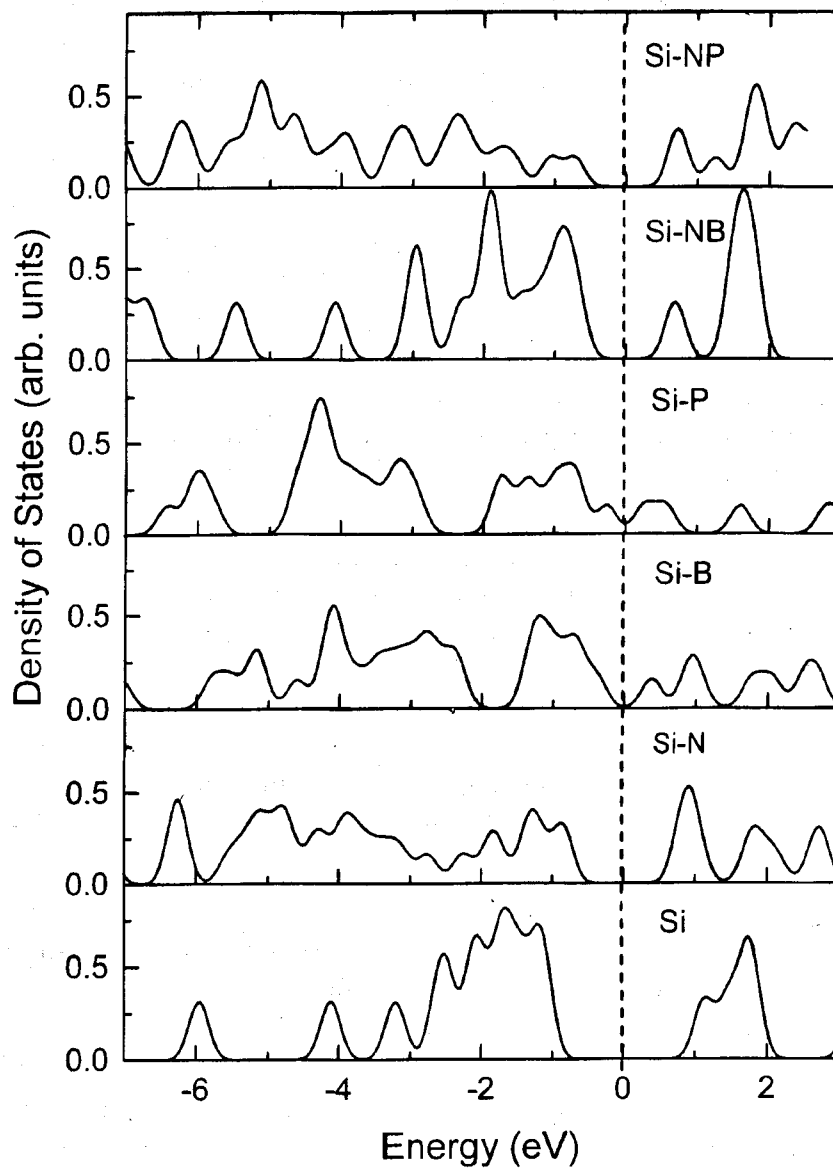
Figure 1. Densities of electronic states for the Si_8 clusters – pure and doped. The vertical dashed line represents the Fermi level.

trapping of boron or phosphorus by nitrogen makes these dopants inactive in silicon.

Acknowledgements

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