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# Effects of electrically active impurities on the bond energy in silicon: *Ab initio* total energy cluster study

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The influence of electrically active impurities on the solid phase epitaxy rate in silicon has been studied in terms of the bond energy by the cluster version of the local-density approximation (LDA) method with use of the *ab initio* atomic pseudopotentials. The bond energy (binding energy per bond) was found to be decreased for the one-impurity doped silicon in comparison with the undoped one, but it was almost unchanged for the two-impurities (compensated) systems.

It is known[1–5] that the rate of the solid phase epitaxy (SPE) of silicon increases if the concentration of active dopants (donors or acceptors) is more than $10^{19}$–$10^{20}$ cm$^{-3}$. Because of its activation nature this process is connected with the decreasing of the SPE activation energy $E_a$. A compensation effect was also observed: the regrowth rate of silicon doped by two opposite types of dopant drops to the rate of intrinsic silicon.[2] There are several models of this effect. They can be divided into three categories: (1) Fermi-level shifting,[4,6,7] (2) strains,[8] and (3) local electronic excitations.[9] Each of these models has some explanation of doping effects; however, the direct quantum-mechanical calculation of the doping influence on the binding energy has not been reported thus far, to our knowledge. The given work presents the direct investigation executed by the cluster version of the local-density approximation (LDA) method with use of the *ab initio* atomic pseudopotentials.[10]

Finite-size clusters have often been used to simulate bulk crystals.[11–14] Broken bonds of silicon usually are saturated by hydrogen atoms[15,16] or atoms of quasihydrogen (so-called siligen).[17] Siligen was defined in Ref. 17 as hydrogen with the nonhydrogen Slater exponent $\zeta_S$ of the 1*s* orbital ($e^{-\zeta_S r}$). Lutrus *et al.*[14] used siligen to simulate bulk silicon and have found the silicon binding energy close to experimental data. The quasihydrogen approach has been used by the author and co-workers[18,19] for investigation of the electronic structure of some silicon and metal-silicon systems, and now the same approach is applied to study the influence of active impurities on the binding energy of silicon.

Several types of clusters with the number of silicon atoms up to 22 were tested (Fig. 1). Dopant atoms were phosphorus and aluminium ones. This choice is stipulated by the affinity of the size and electronic structure of Si, P, and Al; that allows us to minimize an error that may be caused by incompleteness of the basis set and the neglecting of the lattice relaxation. Because of the rather small size of tested clusters the vacancy relaxation effects could not be studied. They can be essential for the correct computing of the energy of silicon-silicon or silicon-impurity bonds, but they will almost compensate each other at calculation of a difference of these energies, if the size of an impurity atom is close to the size of a silicon atom.The basis set of the Al, Si, and P 3s, 3p numeral pseudo-wave-functions and the Hedin-Lundquist exchange-correlation potential[20] were chosen. As for the Slater exponent of siligen, some special comments are necessary.

In Refs. 17 and 18 the equivalence of the Mulliken's charges on Si atoms was controlled and resulted in $\zeta_S = 1.22$ a.u., leading to good results in electronic structure calculations. However, it is not obvious that this value of $\zeta_S$ will be correct to describe the interatomic binding. As a matter of fact, the 1.22 value of $\zeta_S$ does not minimize the total energy of the $Si_5\overline{H}_{12}$ cluster but the 1.05 one does. Thus both values of $\zeta_S$ (1.05 and 1.22) were used to compare results.

Neither of the SPE models connects the SPE activation energy $E_a$ and the bond energy $E_{\mathrm{bond}}$ directly. However, one can suppose that the silicon-dopant bonds are responsible for the change of $E_a$. If the energy of the destruction of the silicon-dopant (Si-$D$) bonds is less than the energy of the destruction of the silicon-silicon (Si-Si) bonds the presence of impurity results in increased quantities of vacancies, broken bonds, and other things, promoting acceleration of the SPE process.

Using the $Si_5\overline{H}_{12}$, $Si_8\overline{H}_{18}$, $Si_{16}\overline{H}_{24}$, and $Si_{22}\overline{H}_{36}$ clusters, the bond-energy difference $\Delta E_{\mathrm{bond}} = E_{\mathrm{Si}-D} - E_{\mathrm{Si-Si}}$ between the doped and undoped systems was found. The dopant atoms were placed at the sites marked as large full circles in Fig. 1 (P or Al). The $\Delta E_{\mathrm{bond}}$ values for one-impurity doped systems were calculated as follows:

$$\Delta E_{\mathrm{bond}} = \frac{E_{\mathrm{Si}_{n-1}D_1\overline{\mathrm{H}}_m} - E_{\mathrm{Si}_n\overline{\mathrm{H}}_m} + E_{\mathrm{Si}_1} - E_{D_1}}{4,} \qquad (1)$$

where $E_{\mathrm{Si}_{n-1}D_1\overline{\mathrm{H}}_m}$, $E_{\mathrm{Si}_n\overline{\mathrm{H}}_m}$, $E_{\mathrm{Si}_1}$, and $E_{D_1}$ are the total energies of the doped $\mathrm{Si}_{n-1}D_1\mathrm{H}_m$ cluster, the undoped $\mathrm{Si}_n\overline{\mathrm{H}}_m$ cluster, and of the single $\mathrm{Si}_1$ and $D_1$ atoms, respectively. $D$ is P or Al.

The results of the calculations are presented in Table I. The bond-energy difference $\Delta E_{\mathrm{bond}}$ is negative for all tested clusters. In other words, the dopant reduction of the SPE process follows from the total-energy calculations for donor P as well as for acceptor Al. The calculated bond-energy difference remains larger for the smallest systems $\mathrm{Si}_4\mathrm{P}_1\overline{\mathrm{H}}_{12}$ and $\mathrm{Si}_4\mathrm{Al}_1\overline{\mathrm{H}}_{12}$ ($|\Delta E_{\mathrm{bond}}| = 0.48/1.20$ eV) and it decreases to 0.18/0.42 eV for the $\mathrm{Si}_{21}\mathrm{P}_1\overline{\mathrm{H}}_{36}$ and $\mathrm{Si}_{21}\mathrm{Al}_1\overline{\mathrm{H}}_{36}$ clusters. The

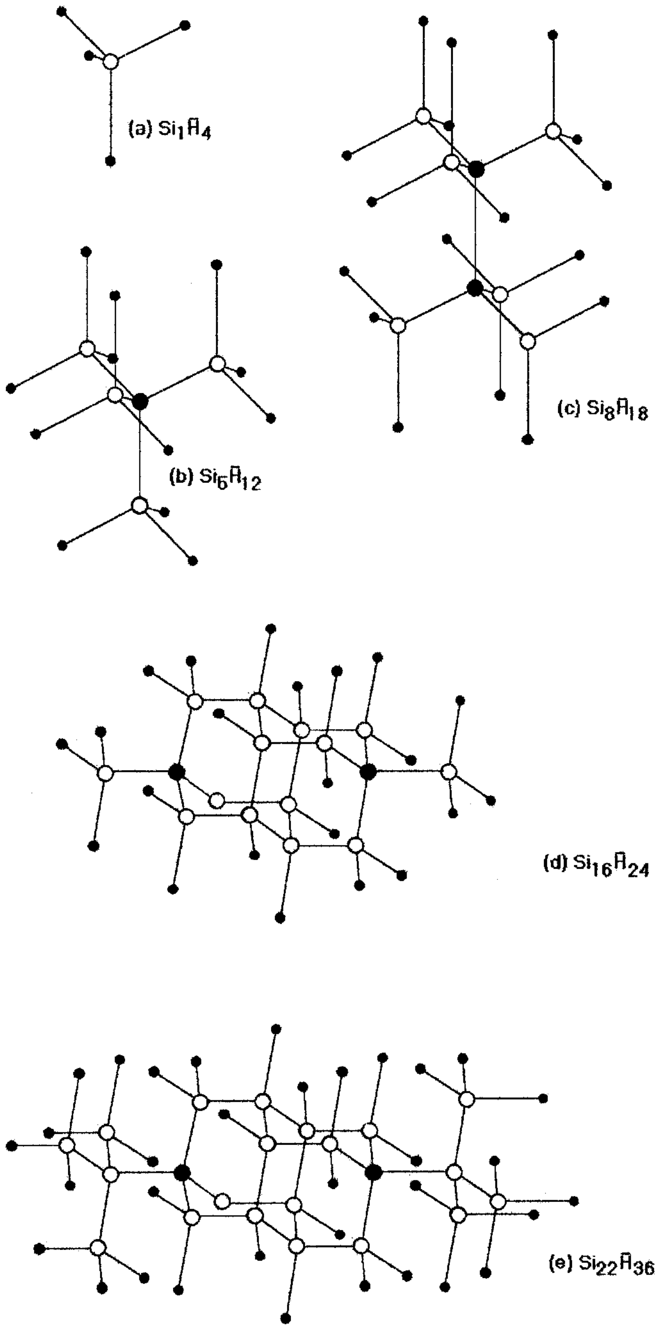

FIG. 1. Various finite-size clusters involving silicons (large circles) and siligens (small circles). The full large circles are the silicon atoms replaced by dopants (phosphorus or aluminum).

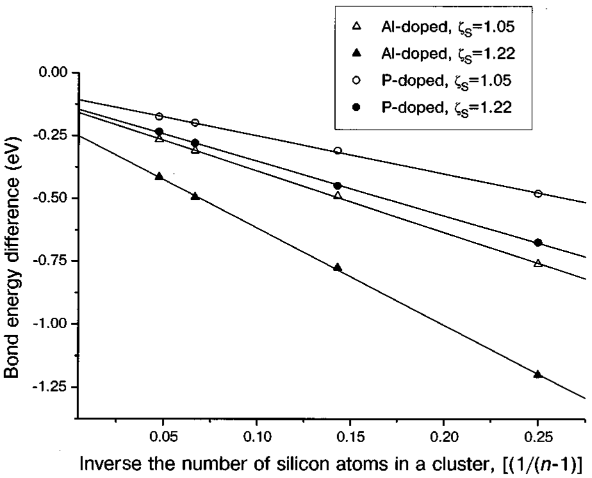

FIG. 2. The difference between the bond energy of the impurity atom in the doped $\mathrm{Si}_{n-1}D_1\overline{\mathrm{H}}_m$ cluster and the bond energy of the silicon atom in the undoped $\mathrm{Si}_n\mathrm{H}_m$ cluster for various values of the siligen Slater exponent $\zeta_S$ as a function of the inverse value of the number of silicon atoms in a doped cluster $[1/(n-1)]$. $D$ is Al or P.

data show a tendency to converge to some constants with increases of the cluster size. To make this tendency clearer the bond-energy difference was plotted in Fig. 2 against the inverse value of the number of silicon atoms in a doped cluster $[1/(n-1)]$. The computed points line up on the direct lines. Extrapolation of these lines to small values of $1/(n-1)$ gives the bond-energy difference in limits from $-0.1$ to $-0.25$ eV compared with the experimental value of the activation energy difference: $\Delta E_a$ for the P-doped ($1.7\times10^{20}$ cm$^{-3}$) and intrinsic silicon is $-0.35$ eV.[2]

Unfortunately, there are no experimental data on the SPE in the Al-doped silicon. However, the general features of the doping influence are the same for all donors and acceptors of III and IV groups,[22] so it is possible to expect that results of testing of Al will not be opposite those obtained for another acceptor.

The basis-set choice error was evaluated by the special calculations for the $\mathrm{Si}_5\mathrm{H}_{12}$, $\mathrm{Si}_4\mathrm{P}_1\mathrm{H}_{12}$, and $\mathrm{Si}_4\mathrm{Al}_1\mathrm{H}_{12}$ clusters using the technique described in Ref. 19, where the binding energy of the Au-Si chemisorption system was studied. The error has not exceeded 4% of the calculated bond energy, about 0.1 eV. Unfortunately, the application of these calculations to all studied clusters was not possible because of a bad convergence of the procedure.

In order to study the influence of the simultaneous doping of silicon by donor and acceptor, the $\mathrm{Si}_8\mathrm{H}_{18}$, $\mathrm{Si}_{16}\mathrm{H}_{24}$, and $\mathrm{Si}_{22}\mathrm{H}_{36}$ clusters were used. Two silicon atoms, shown in Fig. 1 as large full circles, were replaced by P and Al atoms and the total energies of the $\mathrm{Si}_6\mathrm{Al}_1\mathrm{P}_1\mathrm{H}_{18}$, $\mathrm{Si}_{14}\mathrm{Al}_1\mathrm{P}_1\mathrm{H}_{24}$, and $\mathrm{Si}_{20}\mathrm{Al}_1\mathrm{P}_1\mathrm{H}_{36}$ clusters were computed. After that, one of the dopant atoms was removed to infinity and the total energies

TABLE I. The difference $\Delta E_{\mathrm{bond}}$ between the bond energy of the impurity atom in the doped $\mathrm{Si}_{n-1}D_1\overline{\mathrm{H}}_m$ cluster and the bond energy of the silicon atom in the undoped $\mathrm{Si}_n\mathrm{H}_m$ cluster for various values of the siligen Slater exponent $\zeta_S$. $D$ is P or Al.

| | The bond-energy difference (eV) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\zeta_S$ (a.u.) | $\mathrm{Si}_4\mathrm{P}_1\overline{\mathrm{H}}_{12}$ | $\mathrm{Si}_4\mathrm{Al}_1\overline{\mathrm{H}}_{12}$ | $\mathrm{Si}_7\mathrm{P}_1\overline{\mathrm{H}}_{18}$ | $\mathrm{Si}_7\mathrm{Al}_1\overline{\mathrm{H}}_{18}$ | $\mathrm{Si}_{15}\mathrm{P}_1\overline{\mathrm{H}}_{24}$ | $\mathrm{Si}_{15}\mathrm{Al}_1\overline{\mathrm{H}}_{24}$ | $\mathrm{Si}_{21}\mathrm{P}_1\overline{\mathrm{H}}_{36}$ | $\mathrm{Si}_{21}\mathrm{Al}_1\overline{\mathrm{H}}_{36}$ |
| 1.05 | -0.48 | -0.76 | -0.36 | -0.49 | -0.20 | -0.36 | -0.18 | -0.27 |
| 1.22 | -0.68 | -1.20 | -0.45 | -0.78 | -0.28 | -0.50 | -0.24 | -0.42 |

of the rest clusters, $Si_6Al_1H_{18}$, $Si_6P_1H_{18}$, $Si_{14}Al_1H_{18}$, $Si_{14}P_1H_{18}$, $Si_{20}AlH_{36}$, and $Si_{20}P_1H_{36}$, were calculated. The total energies of the undoped $Si_8H_{18}$, $Si_16H_{24}$, and $Si_{22}H_{36}$ clusters were also calculated as well as the total energies of the undoped $Si_7H_{18}$, $Si_{15}H_{24}$, and $Si_{21}H_{36}$ clusters, representing the silicon system without one silicon atom. The differences between the bond energy of the dopant atoms Al ($\Delta E^{Al}_{Si}$) or P ($\Delta E^{P}_{Si}$) in the compensate-doped clusters and the bond energy of the silicon atom in undoped clusters were obtained from the following equations:

$$\Delta E^{Al}_{Si}=\frac{E_{Si_{n-2}Al_1P_1\bar{H}_m}-E_{Si_{n-2}P_1\bar{H}_m}-E_{Al_1}}{4}-\frac{E_{Si_n\bar{H}_m}-E_{Si_{n-1}\bar{H}_m}-E_{Si_1}}{4}, \qquad (2)$$

$$\Delta E^{P}_{Si}=\frac{E_{Si_{n-2}Al_1P_1\bar{H}_m}-E_{Si_{n-2}Al_1\bar{H}_m}-E_{P_1}}{4}-\frac{E_{Si_n\bar{H}_m}-E_{Si_{n-1}\bar{H}_m}-E_{Si_1}}{4}, \qquad (3)$$

where $n=8$, 16, 22 and $m=12$, 24, 36.

The results of calculations are represented in Table II. For the largest clusters ($Si_{20}Al_1H_{36}$ and $Si_{20}P_1H_{36}$) the differences between the bond energy of the silicon atom and the bond energy of the dopant atom are near zero (between $-0.03$ and $-0.05$ eV). This result is compared to the experimental data of $-0.05$ eV[2] for the silicon doped simultaneously by P and B. The $Si_{20}Al_1H_{36}$ and $Si_{20}P_1H_{36}$ clusters correspond to the bulk impurity concentration of $2\times10^{21}$ $cm^{-3}$. Though additional larger clusters could not be studied, it is clear that the calculated compensation effect would not disappear with increase of the cluster size.

TABLE II. The differences between the bond energy of the dopant atoms Al ($\Delta E^{Al}_{Si}$) or P ($\Delta E^{P}_{Si}$) in the compensate-doped clusters $Si_6Al_1P_1H_{18}$, $Si_{14}Al_1P_1H_{24}$, and $Si_{20}Al_1P_1H_{36}$ and the bond energy of the silicon atom in the corresponding undoped $Si_8H_{18}$, $Si_{16}H_{24}$, and $Si_{22}H_{36}$ clusters for various values of the siligen Slater exponent $\zeta_S$.

| | The bond-energy difference (eV) | | | | | |
|---|---|---|---|---|---|---|
| | $Si_6Al_1P_1H_{18}$ | | $Si_{14}Al_1P_1H_{24}$ | | $Si_{20}Al_1P_1H_{36}$ | |
| $\zeta_S$ (a.u.) | $\Delta E^{Al}_{Si}$ | $\Delta E^{P}_{Si}$ | $\Delta E^{Al}_{Si}$ | $\Delta E^{P}_{Si}$ | $\Delta E^{Al}_{Si}$ | $\Delta E^{P}_{Si}$ |
| 1.05 | -0.07 | -0.09 | -0.05 | -0.06 | -0.02 | -0.03 |
| 1.22 | -0.08 | -0.10 | -0.06 | -0.07 | -0.03 | -0.05 |

To be sure that the electrically active impurities have a special influence on the bond energy the oxygen-doped silicon system was examined on an example of the $Si_4O_1H_{12}$ cluster for the Slater exponent $\zeta_S$ of 1.22. The $Si_4O_1H_{12}$ cluster was constructed to be the same as the $Si_4P_1H_{12}$ (or $Si_4Al_1H_{12}$) cluster described above, but the P (or Al) atom was replaced by the O atom. The bond-energy difference $\Delta E_{bond}$ was found to be positive and equal to $+0.96$ eV. In other words, the oxygen doping increases the bond energy and reduces the SPE rate, as shown in the experiment.[22]

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