CALCULATIONS OF CHARACTERISTICS OF IMPURITY-DEFECT COMPLEXES IN SILICON AT HIGH CONCENTRATIONS OF IMPURITIES

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UDC 537.311.322
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Microscopic mechanisms of an influence of point defect — impurity complexes on atomic rearrangements in a silicon crystal which is saturated by defects are theoretically investigated. To achieve the goal, a model that describes the silicon crystals with concentrations of defects more than 10^{21} cm^{-3} has been developed. For the model crystal, electronic structure and energetic characteristics are calculated by the electron density functional method and the first-principle pseudopotentials. Maps of the electron density distribution as well as potential reliefs for a displacement of impurity atoms (boron, phosphorus) are obtained. It is shown that, at critical concentrations of P_s and B_s, $(P_s)_2$ and $(B_s)_2$ complexes appear which turn into $P_iV_2P_i$ and $B_iV_2B_i$ complexes in a non-activation manner and serve as the generators of divacancies.

Electrical activity of impurity atoms in silicon is determined by their distribution within a crystalline lattice. Among a great diversity of configurations displaying electrical activity (impurity — defect complexes, impurity segregations, and others), an important role belongs to isolated atoms of substitutional impurities. An equilibrium concentration of such atoms, which is maximally attainable, is an important technological parameter that, in particular, determines the so-called impurity utilization factor upon the ion implantation [1]. At the same time, the strong doping of a crystal influences the system of intrinsic point defects as well. The authors of a series of papers, which are devoted to the investigation of diffusion, oxidation, and other processes in materials subjected to the ion implantation, come to the conclusion about the existence of a correlation between a doping level and a vacancy concentration, and this especially concerns strongly doped silicon.

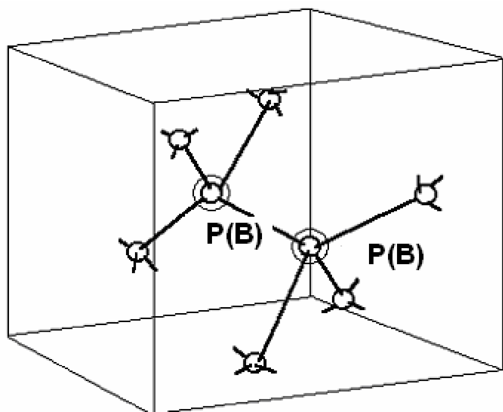


Fig. 1. Unit cell of a silicon crystal with a high concentration of dopants

So, for a solid solution of silicon, the doping by phosphorus with concentrations up to 10^{20} cm^{-3} strongly increases the concentration of thermodynamically equilibrium vacancy defects. This conclusion follows from a rapid rise in the diffusion coefficient of antimony which predominantly diffuses on vacancies in silicon [2] and from an increase in the thermal oxidation rate which is caused by an acceleration of the vacancy self-diffusion [3, 4]. The effect of the radiation diffusion disappearance observed upon a rise in the donor doping is also thought to be associated with increase in the equilibrium vacancy concentration.

To date, the literature data on radiation-induced defects in the boron-doped silicon with a concentration of 10^{19} cm^{-3} are available. As is shown in [5] by means of the infrared spectroscopy technique, boron efficiently passes from lattice sites to the interstitial space during the electron irradiation of the material. The rate of this reaction is so high that, according to the authors' opinion, the annihilation of vacancies with the native interstitial atoms becomes completely suppressed, because the latter fill the boron places at the lattice sites (the Watkins reaction). Similar results were also obtained in other works [6—9].

Let us describe the basis of the model utilized to find out the configurations of dopant atoms in the silicon matrix as well as the vacancy formation mechanisms in the case where dopant concentrations are sufficiently

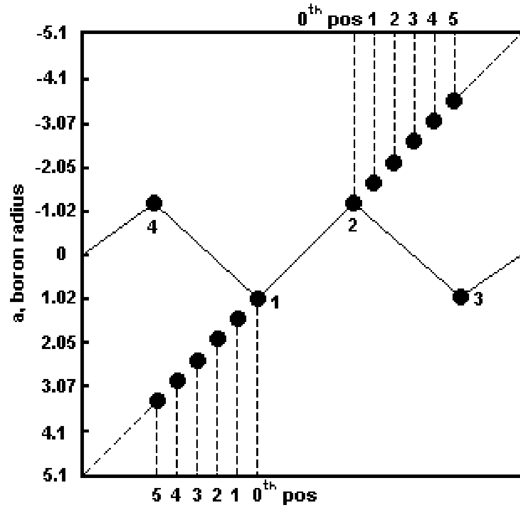


Fig. 2. Path of a displacement of dopant atoms from the lattice sites considered in the calculations of adiabatic potentials

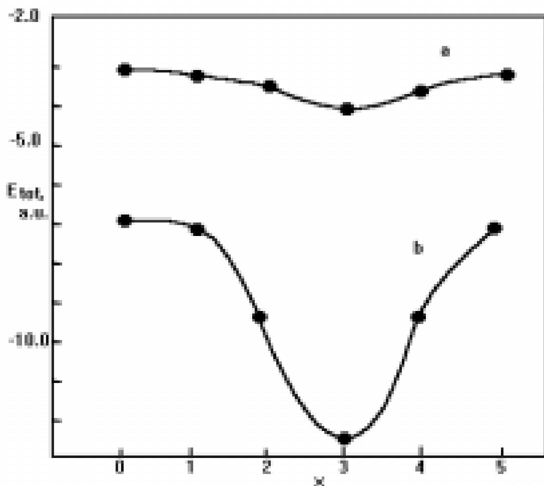
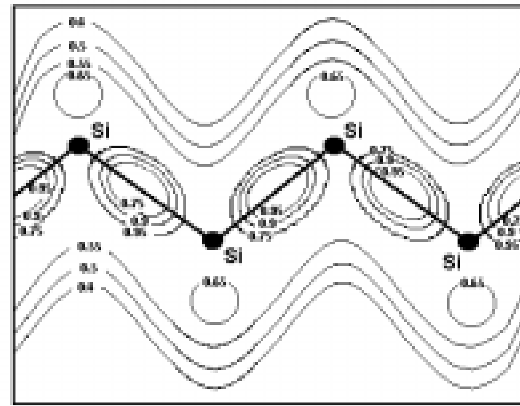


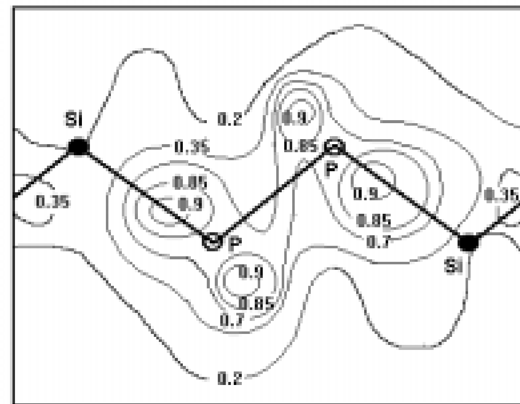
Fig. 3. Potential relief for a displacement of the dopants (phosphorus *(a)* and boron *(b)*) in the case of their high concentrations. Along the x axis — the displacement by $(1/6)a$ units, where a is a distance between atoms

high. The idea of the model consists in the provision of the optimal consistency of the unit cell dimensions (which define the computational time) with the necessary concentration of defects in the crystal which would correspond to the state before a structural transformation. In the case under consideration, two defects fit six matrix atoms. The translation of such eight-atom cell in all directions allows studying an infinite silicon crystal with a defect concentration of the order of 10^{21} cm^{-3} (Fig. 1).

The properties of such a crystal were studied by the method of electron density functional in the pseudopo-



a



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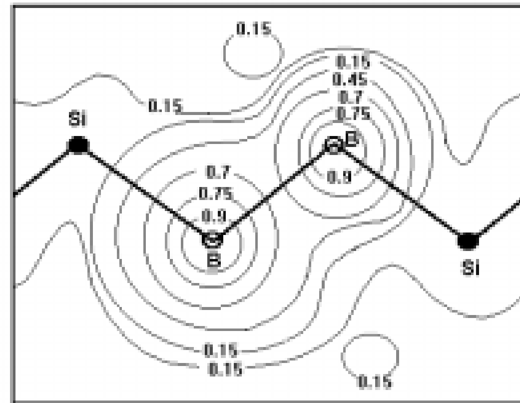

c

Fig. 4. Distribution of the valent electron density in (110) plane for crystals Si (a), Si with P (b), and Si with B (c)

tential approximation [10]. The atomic basis of the unit cell consisted of 8 atoms, 6 of which were silicon atoms, and 2 were the dopant ones. The latter were located

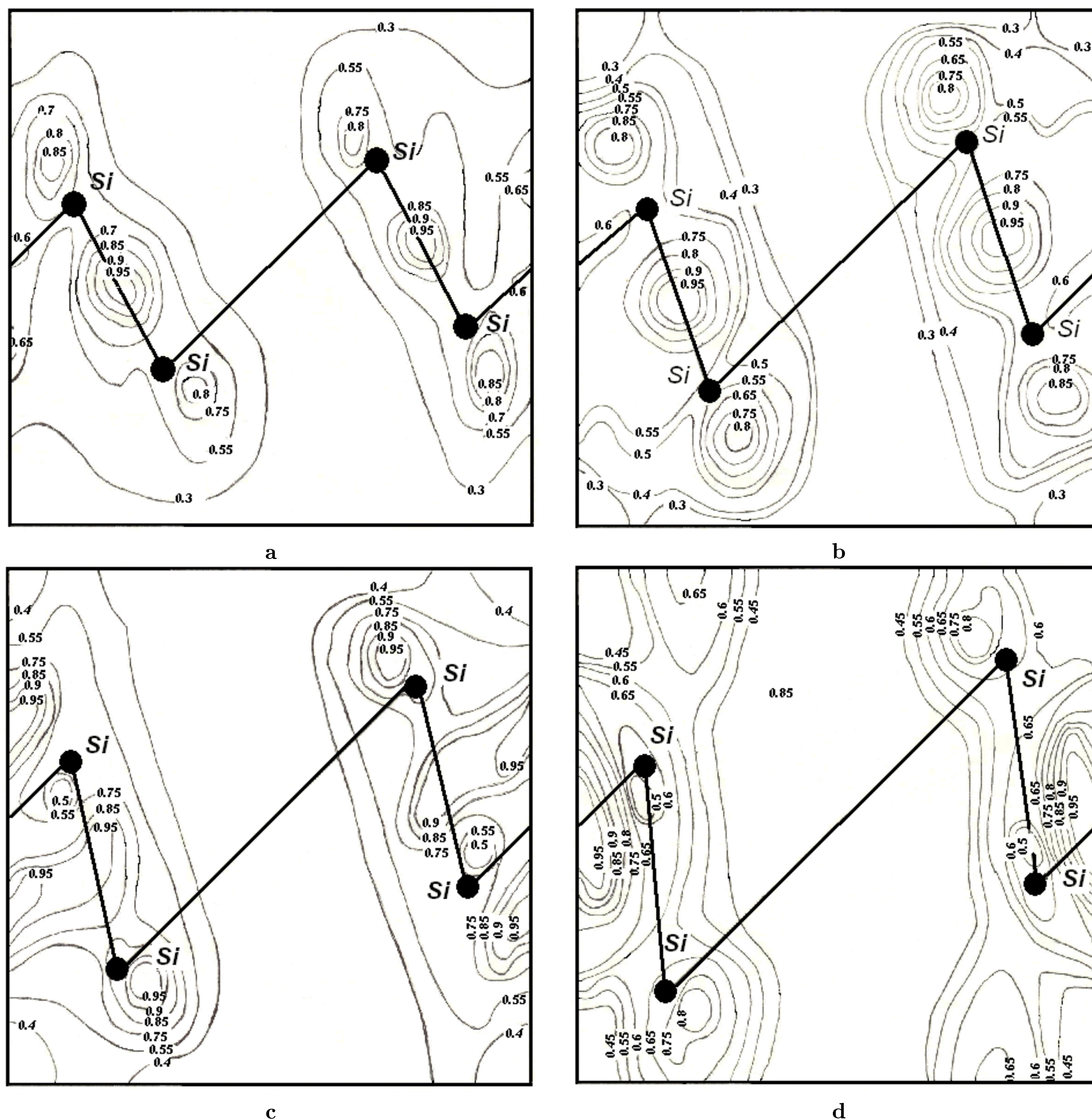

Fig. 5. Distribution of the valent electron density in (110) plane for a Si crystal with Si atoms displaced in [111] direction from one another

at neighboring sites, since such an arrangement is very likely at high concentrations of dopants. It is worth noting that the ionic radii of the dopants considered in this work (boron and phosphorus) are close to those of the matrix. For this reason, the mechanical stress that might appear does not lead to a sufficient lattice deformation. In what follows, the framework consisting of silicon atoms is assumed to be invariable. To find the stable positions for the dopant atoms, the case was considered where these atoms were displaced from one

another in [111] direction (Fig. 2). The full energy $E_{\rm tot}$ of the model crystal was calculated for the intermediate positions of dopant atoms, x. As is seen from Fig. 3, $E_{\rm tot}(x)$ curve contains a minimum, the presence of which implies that, at the given dopant concentration, it is favorable for the dopant atom to be located away from a lattice site. This means that the $P_iV_2P_i$ and $B_iV_2B_i$ complexes are formed in a non-activation way. But, at small dopant concentrations, the isolated boron or phosphorus atom is a substitutional one [11].

It is obvious that the structure of chemical bonds in the vicinity of an impurity-defect complex controls their behavior as well as the properties of the crystal as a whole. To specify the features of this influence, we performed the analysis of a nature of the chemical bonds in Si near P_2 and B_2 complexes. Figs. 4—6 show the electron density distributions for the ideal silicon lattice and for the environment of P_2 and B_2 complexes in Si.

As is seen from Figs. 4,*a, b,* the structure of the bond which is formed between phosphorus and silicon is similar to that of Si—Si. This means that, for the Si−P pair, the conditions necessary for the formation of a covalent bond with sp^3−hybridization are fulfilled. A little displacement of the charge maximum towards phosphorus gives evidence for the presence of the ionic contribution. It is seen that the bond between P—P atoms is sufficiently week. It is such a kind of the electron density distribution that can explain the non-activation character of the displacement of P atoms in [111] direction, which is accompanied by the vacancy formation. Since the distribution of valent electrons in the P—Si bond is similar to that in Si−Si one and the repulsion between the atom cores is greater for the P—P pair than for the latter one, the phosphorus ions are displaced in the crystalline lattice relative to the lattice sites. As a result, the $P_iV_2P_i$ complex is formed. In view of the fact that, at a high-dose implantation of P ions into silicon, there is a great likelihood for the appearance of the $(P_s)_2$ complex or a P atom near the P_iV complex, the following scheme for the atomic rearrangement is very likely: $(P_s)_2 \rightarrow P_iV_2P_i$ or $P \rightarrow P_iV \rightarrow P_2 \rightarrow P_iV_2P_i$.

In the case where boron is included in the silicon matrix, the pattern of the electron density distribution is completely different (see Fig. 4,*c*). There are no localized closed contours characteristic of sp^3−hybridization, and the background ion charges become noticeable. But even in this case, the formation of divacancies in the vicinity of the B_2 complexes can be explained according to the above-described scheme.

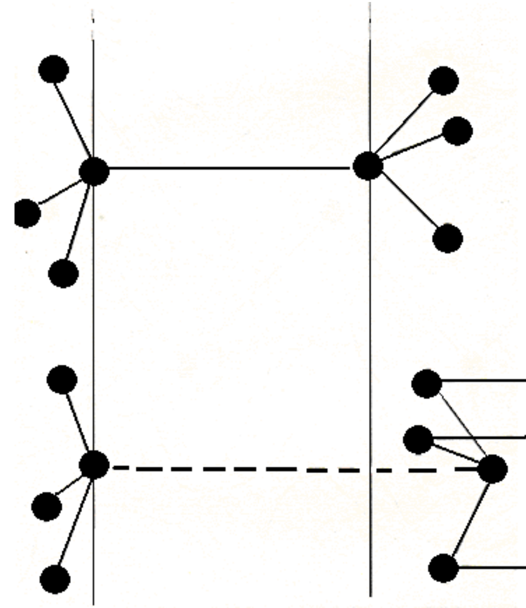

Fig. 6. Scheme of the formation of configurations with turned bonds in silicon

While studying the changes in electron density distributions accompanying a displacement of Si or P atoms from the lattice sites in [111] direction (Fig. 5), we observed a retention of the bonds between the atoms of Si−Si or Si−P pairs, in all the cases where one atom was displaced. This supports the conclusion made by the authors of [12] about the existence of defects with the bonds, which are not broken, but are turned (Fig. 6), and damp displacements. In the given paper, we established that the defects of such kind are likely to be formed at intermediate stages of the formation of the V_2 divacancies in pure Si or the $P_iV_2P_i$ complexes in the doped silicon.

Thus, at high concentrations of the boron and phosphorus dopants, both the $(P_s)_2$ and $(B_s)_2$ complexes become unstable and serve as the generators of divacancies which additionally contribute to the total amount of divacancies near their critical concentration. It is this process that underlies the step-wise transition of silicon from the crystalline to amorphous state, which agrees with a series of experiments [13, 14].

The analysis of the electron density maps shows that

— introduction of the dopants of the III and V groups (B and P) into silicon occurs in different ways: the character of bonds is closer to the typical picture of sp^3-hybridization in the P−Si case than that in the B−Si one;

— when the silicon and phosphorus atoms are displaced, the so-called damping of atomic displacements by chemical bonds is observed in the covalent crystal.

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Received 23.03.04.
Translated from Ukrainian by A.I. Tovstolytkin

РОЗРАХУНКИ ХАРАКТЕРИСТИК ДОМІШКОВО-ДЕФЕКТНИХ КОМПЛЕКСІВ У КРЕМНІЇ ПРИ ВЕЛИКИХ КОНЦЕНТРАЦІЯХ ДОМІШОК

Р.М. Балабай, А.Ю. Ків, Н.В. Моісеєнко

Р е з ю м е

Теоретично досліджено мікроскопічні механізми впливу комплексів точкових дефектів і домішок на атомні перебудови в умовах насичення кристала кремнію дефектами. Для цього було розроблено модель, яка описує кристал кремнію з концентрацією дефектів, не меншою ніж 10^{21} см$^{-3}$. Електронна будова та енергетичні характеристики модельного кристала розраховували із застосуванням теорії функціонала електронної густини і псевдопотенціалу із перших принципів. Були отримані карти розподілу електронної густини і потенціальні рельєфи для зміщення атомів домішок (бору та фосфору). Показано, що при критичній концентрації P_S та B_S виникають комплекси $(P_S)_2$ та $(B_S)_2$, які безактиваційно переходять у комплекси $P_iV_2P_i$ та $B_iV_2B_i$ і відіграють роль генераторів дивакансій.