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Features of the electrophysical parameters of silicon serially doped with impurity atoms of phosphorus and boron

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Silicon samples sequentially doped with impurity atoms of phosphorus and boron were studied. These investigations make it possible to study the interaction and distribution of phosphorus and boron impurity atoms in silicon. It has been established that, in such silicon samples, the mobility of electrons and holes changes. From the analysis of the obtained results, it was shown that boron atoms change the type of conductivity of the material to a depth of $2\,\mu$m due to the compensation of phosphorus atoms, which are 4 times higher than the concentration of boron in silicon.

Keywords: semiconductor, silicon, phosphorus, boron, alloying, mobility, diffusion, concentration.

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1. Introduction

Formation of binary unit cells involving atoms of groups III and V in the silicon lattice is of profound scientific and practical interest. This is due to the fact that formation of binary unit cells of the $Si_2A^{III}B^V$ type with controlled parameters can, on the one hand, be a basis for the making of a new class of semiconductor material that allows for control of the fundamental silicon parameters, and, on the other hand, it is an optimal and promising method for the making of bulk-nanostructured silicon with the specified electrophysical parameters [1–3]. Thorough mastering of a reproducible technology for the making of samples doped with elements of groups III and V, with a high solubility in silicon, makes it possible to form binary clusters having the necessary concentration and the given material depth [4–6].

This paper is aimed at developing a diffusion technology for the formation of binary unit cells of the Si_2BP type in the silicon lattice and studying the peculiarity of electrophysical parameters of silicon serially doped with impurity atoms of phosphorus and boron.

Assurance of the maximum contribution by the injected B and P impurity atoms required the determination of thermodynamic conditions that would provide for silicon having a virtually identical concentration distribution of these impurities. The performed theoretical calculations of concentration distribution with account of the diffusion and solubility coefficients for these impurity atoms in silicon under diffusion from an unrestricted source have shown that fulfillment of this thermodynamic condition requires rather fine and complex process operations.

A study of boron and phosphorus atoms' interaction in the silicon lattice allows for looking into the physical mechanism of interactions during formation of binary nanoclusters having a different composition, structure, and nature. The very high solubility of B and P ($N \geq 10^{20}-10^{21}\,\mathrm{cm}^{-3}$) in silicon allows for creating binary clusters having rather a high concentration, which considerably affect the silicon energy structure and electrophysical properties. Moreover, due to the rather low diffusion coefficient of these elements in silicon ($D \sim 10^{-12}-10^{-13}\,\mathrm{cm}^2/\mathrm{s}$) it is possible to form binary clusters both in the near-surface region and in the bulk of the crystal with the required thickness [7,8].

An analysis of the obtained results has shown that silicon doping with elements of groups III and V or formation of their epitaxial layers on the silicon surface causes a change in the silicon photoelectric and optical characteristics. Such a material will make it possible to create efficient solar cells and to develop a new class of sensors [9–12].

2. Sample making technology and study methods

The initial material was single-crystal silicon KDB-10 with initial boron concentration $N_\mathrm{B} \sim 2 \cdot 10^{15}\,\mathrm{cm}^{-3}$ [13]. The samples were subdivided into three groups for the experiment (Fig. 1). The samples of the first group were doped with impurity atoms of phosphorus. The samples of the second group were doped with impurity atoms of boron. The samples of the third group were doped first with atoms of phosphorus and then with atoms of boron.

Prior to diffusion, all silicon samples were cleaned by etching in $HNO_3 + HF$ acid solution. Cleaning removed the oxide layer from the silicon monocrystal surface.

Diffusion of P into KDB-10 silicon was performed from the formed P_2O_5 layer at $T = 1100^\circ\mathrm{C}$ for $t = 4\,\mathrm{h}$ (the first group). The silicon samples were doped with boron atoms at $T = 1100^\circ\mathrm{C}$ for $t = 4\,\mathrm{h}$ (the second group) and

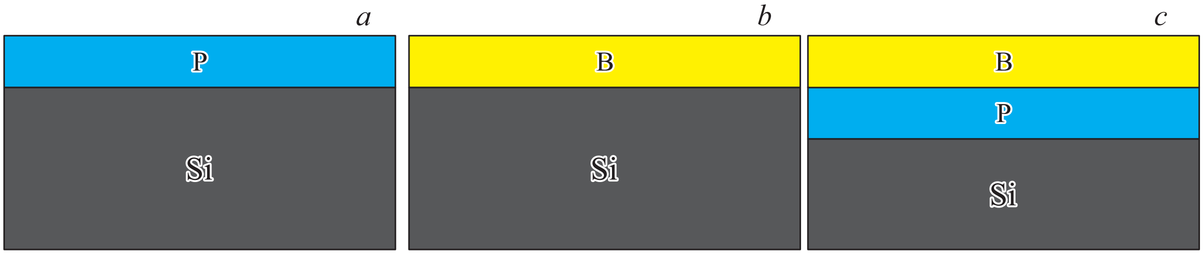

Figure 1. *a*: the first group — samples of silicon (KDB-10) doped with phosphorus; *b*: the second group — samples of silicon (KDB-10) doped with boron; *c*: the third group — samples of silicon (KDB-10) doped first with phosphorus and then with boron.

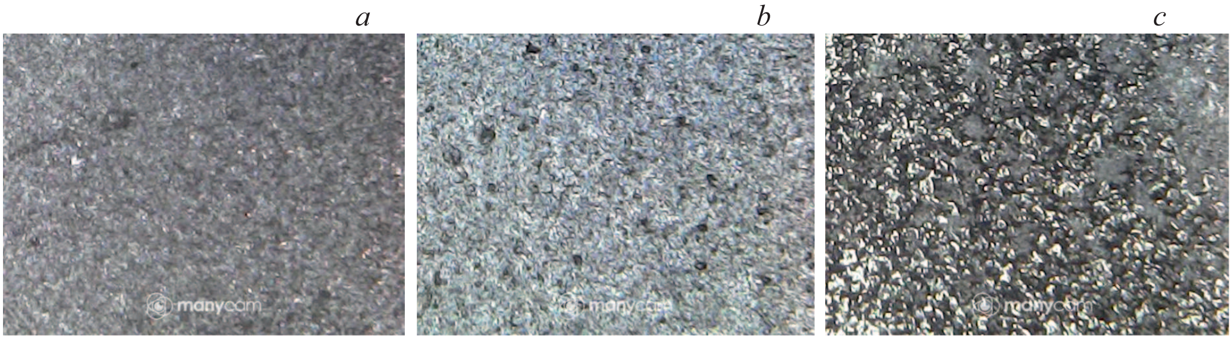

Figure 2. Surface morphology: *a* — the first group of samples of silicon doped with phosphorus; *b* — the second group of samples of silicon doped with boron; *c* — the third group of samples of silicon doped first with phosphorus atoms and then with boron atoms.

the samples of the third group, with boron atoms present, were doped with phosphorus at $T = 1100^\circ\mathrm{C}$ for $t = 4\,\mathrm{h}$.

Concentration distribution of impurity atoms of phosphorus and boron was measured by the 4-probe method, layer-by-layer removal of the layer ($1\,\mu$m each) by chemical etching. It was assumed that all introduced impurity atoms of phosphorus and boron are in an electrically active state. Concentration of phosphorus and boron atoms (electrons and holes) was calculated taking into account the changes in conduction type and mobility of charge carriers. Conduction type was determined using a thermal probe. After diffusion, phosphorus-silicate, borosilicate or boron-phosphorus silicate glass was removed from the surface of all samples by etching in HF.

Figure 2 shows the surface morphology of the silicon samples after diffusion, obtained by means of the Microscope-2 digital microscope. The microscope USB-camera provided object magnification up to 1600 times.

Phosphorus concentration on the sample surface after diffusion at $T = 1100^\circ\mathrm{C}$ and for $t = 4\,\mathrm{h}$ (the first group) was $N_\mathrm{P} = 3 \cdot 10^{20}\,\mathrm{cm}^{-3}$, while phosphorus concentration at penetration depth $x = 10\,\mu$m decreased to $\sim 4 \cdot 10^{17}\,\mathrm{cm}^{-3}$. These study results agreed well with the literature data [14]. Boron surface concentration after diffusion (the second group) reached $N_\mathrm{B} = 3 \cdot 10^{19}\,\mathrm{cm}^{-3}$, and at depth $x = 9\,\mu$m was $\sim 2 \cdot 10^{17}\,\mathrm{cm}^{-3}$. This data is also confirmed by the experiments from [15]. Phosphorus concentration on the reference samples' surface was ~ 4 times higher than boron concentration. Figure 3 shows the distribution of phosphorus concentration in the reference samples after thermal annealing under the conditions similar to the diffusion conditions (curve *1*), concentration distribution of boron atoms in the samples of the second group (curve *2*) and the third group of samples doped with phosphorus atoms and then with boron atoms (curve *3*). As seen from the plot, the phosphorus surface concentration slightly decreases due to thermal annealing and is $\sim 10^{15}\,\mathrm{cm}^{-3}$ at depth $x = 14\,\mu$m. Thus, the distribution of phosphorus concentration in silicon after diffusion and thermal annealing differs considerably. Thereat, phosphorus concentration in the samples exceeds the boron concentration up to the depth of $11\,\mu$m, under successive diffusion of phosphorus atoms, and then boron atoms there is a compensation of the charge carriers which create these impurities, which causes a decrease of silicon conduction due to the changed concentration of charge carriers and their decreased mobility. Curve *3* in Fig. 3 shows the distribution of charge carrier concentration in the samples doped with boron, after phosphorus diffusion (the third group). Testing of the obtained samples by a thermal probe shows that the silicon samples after diffusion have the *p*-type of conduction up to depth $x = 2\,\mu$m. Concentration of boron atoms in this region is higher than that of phosphorus atoms. The silicon samples at a depth more than $x > 2\,\mu$m have the *n*-type of conduction. At $x = 2{-}6\,\mu$m, the concentration of ionized phosphorus electrons increases insignificantly, while at $x > 6\,\mu$m it decreases sharply.

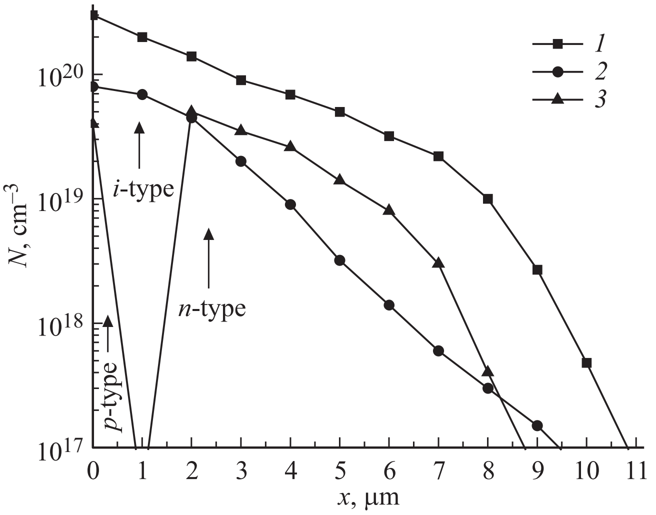

Figure 3. Distribution of concentration of doping atoms in depth: *1* — curve of concentration distribution of phosphorus atoms (electrons) in the samples of the first group; *2* — curve of concentration distribution of boron atoms (holes) in the samples of the second group; *3* — curve of concentration distribution in the samples of the third group doped with phosphorus atoms and then with boron atoms.

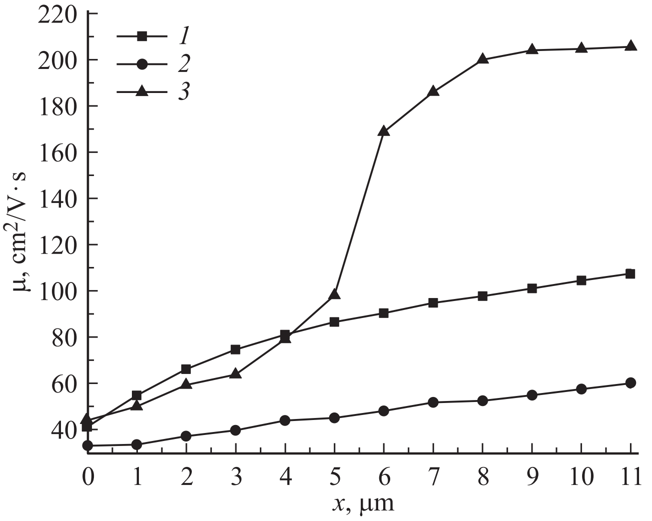

Figure 4. Distribution of mobility of free charge carriers in depth: *1* — the first group of samples of silicon doped with phosphorus; *2* — the second group of samples of silicon doped with boron; *3* — the third group of samples of silicon doped first with phosphorus atoms and then with boron atoms; $T = 300$ K.

The obtained study results cannot be explained by a simple compensation of impurity atoms of phosphorus and boron. In this case, the type of material surface conduction must not change (the material bulk at the depth of $2\,\mu$m must be of the *n*-type). In our case we observe an increasing concentration of electrically active boron or a decreasing concentration of electrically active phosphorus in the near-surface region.

We have also studied a change of the mobility of charge carriers in depth in the obtained samples (Fig. 4).

As can be seen from Fig. 4, mobilities of holes and electrons in the silicon samples with impurity atoms of phosphorus and boron are much higher than those in the samples doped with boron or phosphorus only. These results show that the formation of neutral complex of the P^+B^- type considerably reduces the crystal defectiveness degree.

3. Discussion

The revealed changes in electrophysical parameters can occur only due to several physical reasons:

1) an increased coefficient of boron atoms diffusion in silicon due to the presence of phosphorus ions, which cause an expansion of the silicon lattice under the action of phosphorus ions' field (the diameter of the phosphorus ions' field is larger than the size of the silicon lattice constant), which leads to an increase of boron concentration on the surface;

2) due to compression of the silicon lattice, the phosphorus ions enter the interstice of the silicon crystal lattice due to the diffusion of boron atoms (the boron ion diameter is smaller than the lattice constant), which leads to a decrease in phosphorus concentration on the surface;

3) electrostatic interaction of boron and phosphorus ions leads to a decrease of the diffusion coefficient due to the formation of molecules of the P^+B^- type.

An analysis of the study results confirms that the phosphorus concentration in silicon causes an increase in the electrically active boron concentration. Thus, the concentration of electrically active boron atoms on the surface under successive diffusion of phosphorus and boron will be 4 times higher than the one calculated for lightly doped silicon. The experimental data presented in [16] qualitatively confirms our results.

The obtained experimental results cannot be explained only by mutual compensation of impurity atoms of phosphorus and boron. As a result of molecular linking of phosphorus and boron atoms, neutral complexes of the $Si_2P^+B^-$ type form in the silicon lattice; they consist of silicon, phosphorus and boron atoms.

These results do not contradict the conclusions made in [16] and we can assume that a large number of donor-acceptor complexes form in the silicon lattice due to

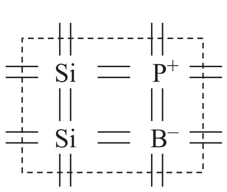

Figure 5. Binary electrically neutral complexes of the $Si_2P^+B^-$ type in silicon.

Band gap and lattice constant

	Boron phosphorus (BP)	Si
Band gap energy (E_g) at 300 K, eV	2.1	1.12
Lattice constant a, Å	4.538	5.43095

interaction, and they cause a change in the fundamental physical parameters of silicon.

Such complexes can exist only when phosphorus and boron atoms are nearby, i.e. they must occupy two neighboring sites in the silicon lattice. The formation of such electrically neutral complexes P^+B^- sets the system to a more favorable thermodynamic state than when the atoms of these impurities are away from each other. Upon formation of such complexes, new binary electrically neutral complexes of the $Si_2P^+B^-$ type form in the lattice (Fig. 5). The further study results have shown that the material must undergo long-term low-temperature annealing in order to increase the concentration of the formed complexes in silicon.

4. Conclusion

Binary electrically neutral complexes of the $Si_2P^+B^-$ type, as distinct from a unit cell, have a partially ionic covalent bond, and their structure differs from the energy structure of pure silicon. When concentrations of such binary complexes are sufficiently high, they may form nano- and microclusters of a new phase, which significantly affects the band gap value (see the table), mobilities of charge carriers, optical absorption and recombination properties of silicon. The study results also demonstrate the possibilities to obtain a new silicon-based material for the making of solar cells with an increased absorption coefficient and an expanded working region of the spectrum, which provide a significant increase of efficiency [17–21].

Conflict of interest

The authors declare that they have no conflict of interest.

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