Effect of the presence of a sufficiently high phosphorus concentration on the concentration distribution of gallium in silicon

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It was found that the silicon preliminarily doped with a high concentration of phosphorus during the diffusion of gallium, there is a significant increase in the solubility of the gallium. The results obtained are explained by the interaction of gallium and phosphorus atoms, as a result of which quasi-neutral molecules $[P^+Ga^-]$ are formed. It is assumed that the formation of such quasineutral molecules $[P^+Ga^-]$ stimulates the formation of Si_2GaP binary unit cells in the silicon lattice. It is shown that a sufficiently high concentration of such unit cells can lead to a significant change in the electrophysical parameters of silicon, i.e. the possibility of obtaining a new material based on silicon.

Keywords: silicon, gallium, phosphorus, binary cell, diffusion.

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1. Introduction

The interaction of impurity atoms with each other in a crystal lattice is of special scientific and practical interest. Thanks to such interactions, the formation of various types of monoatomic nano- and microclusters [1–3] is stimulated, on the basis of which it is possible to create bulk nanostructured semiconductor materials that are practically impossible to obtain by other technological methods. Clusters of impurity atoms of different nature (electrically neutral, magnetic, multicharged, etc.) make it possible to obtain a material with unique electrophysical parameters and functionality [4–7].

The study of the interaction of elements of III and V groups in the silicon lattice is of great interest. Firstly, as a result of such interactions it is possible to form binary nanoclusters with different composition, structure and nature; secondly, due to the very high solubility of elements of III and V groups ($N \geq 10^{20}-10^{21}\,\mathrm{cm}^{-3}$), it is possible to create binary clusters with a sufficiently high concentration, which can significantly affect the energy structure of silicon. Finally, thirdly, 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 [8–10].

Therefore, the purpose of this paper was to study the interaction of phosphorus (P) and gallium (Ga) atoms in silicon during successive diffusion of these impurities.

2. Technology for samples manufacturing and methods for their study

Single-crystal silicon KEF-100 ($N_P \sim 10^{13}\,\mathrm{cm}^{-3}$) with an oxygen content $N_{O_2} \approx (5-6)\cdot 10^{17}\,\mathrm{cm}^{-3}$ and dislocation density $N_D \sim 10^3\,\mathrm{cm}^{-2}$ was used as initial material. The sample size was $V \sim 1 \times 4 \times 8\,\mathrm{mm}$. After the necessary mechanical and chemical treatments of the samples, phosphorus diffusion from the applied layer of ammonium phosphate was performed in air at $T = 1000^\circ\mathrm{C}$ for $t = 2\,\mathrm{h}$. After diffusion, phosphosilicate glass was removed from the surface in all samples by etching with HF and NH_4F. At that the phosphorus concentration on the surface of the samples was $N_\mathrm{P} = 2\cdot 10^{20}\,\mathrm{cm}^{-3}$.

Diffusion of gallium in silicon (KEF-100) was carried out from the gas phase at a temperature of $T = 1250^\circ\mathrm{C}$ for 4 h. Such a choice of conditions for the diffusion of gallium was dictated by the fact that the maximum concentration on the surface and in the bulk of silicon to be obtained.

Then gallium was diffused in the phosphorus-doped samples at $T = 1250^\circ\mathrm{C}$ for 4 h. At the same time, samples of phosphorus-doped silicon (without gallium) were simultaneously subjected to thermal annealing, also at $T = 1250^\circ\mathrm{C}$, $t = 4\,\mathrm{h}$, in order to determine the change in the concentration distribution of phosphorus during additional annealings.

Thus, 4 batches of samples were obtained: I — samples after phosphorus diffusion at $T = 1000^\circ\mathrm{C}$, $t = 2\,\mathrm{h}$; II — samples doped with gallium at $T = 1250^\circ\mathrm{C}$, $t = 4\,\mathrm{h}$, which were pre-doped with phosphorus at $T = 1000^\circ\mathrm{C}$, $t = 2\,\mathrm{h}$; III — reference samples doped with phosphorus ($T = 1000^\circ\mathrm{C}$, $t = 2\,\mathrm{h}$), annealed at $T = 1250^\circ\mathrm{C}$, $t = 4\,\mathrm{h}$; IV — reference samples doped with gallium only at $T = 1250^\circ\mathrm{C}$, $t = 4\,\mathrm{h}$, in which phosphorus diffusion was not carried out.

The concentration distribution was recorded using the 4-probemethod by layer-by-layer removal of a layer of $1\,\mu\mathrm{m}$ thick by chemical etching. It was assumed that all introduced impurity atoms of phosphorus and gallium are in an electrically active state. When calculating the concentrations of phosphorus and gallium (electrons and holes),

the change in the mobility of charge carriers depending on concentration of impurity atoms [11] was taken into account. The measurement error did not exceed 10%.

3. Research results

Fig. 1 shows the concentration distribution of phosphorus atoms in silicon after diffusion $T = 1000^\circ$C, $t = 2$ h. The Figure also shows the concentration distribution of gallium after diffusion at $T = 1250^\circ$C, $t = 4$ h in KEF-100 samples. As can be seen from the experimental results, the phosphorus concentration in the near-surface region is $N_P = 2 \cdot 10^{20}$ cm^{-3}, and at a depth of $x = 2.5\,\mu$m, its concentration decreases to $\sim 10^{14}$ cm^{-3} (curve *1*), while the samples always remain of *n*-type. This fully corresponds to the literature data [12–14].

At the same time, the surface concentration of gallium after diffusion at $T = 1250^\circ$C, $t = 4$ h reaches $4 \cdot 10^{19}$ cm^{-3}, it decreases monotonically at the depth of the sample and at $x = 25\,\mu$m is $\sim 10^{14}$ cm^{-3}. It was found that in this case in the gallium distribution region samples keep *p*-type. These data also confirm the papers [15,16]. Thus, the concentration distribution of phosphorus and gallium during their diffusion differ significantly from each other.

Fig. 2 shows the concentration distribution of phosphorus in the reference samples, which were subjected to additional thermal annealing at $T = 1250^\circ$C, $t = 4$ h (curve *1*), and also the concentration distribution of charge carriers in silicon samples doped with gallium at $T = 1250^\circ$C, $t = 4$ h, which were pre-doped with phosphorus at 1000°C, $t = 2$ h (curve *2*). As can be seen from the Figure, as a result

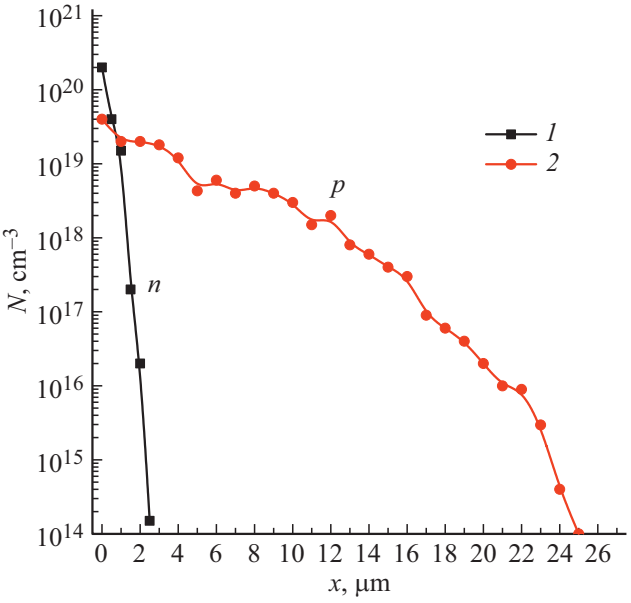

Figure 1. Concentration distribution of electrons (phosphorus atoms) and holes (gallium) in the silicon lattice diffused independently of each other: *1* — distribution of electrons (phosphorus) at $T = 1000^\circ$C, $t = 2$ h; *2* — distribution of holes (gallium) at $T = 1250^\circ$C, $t = 4$ h.

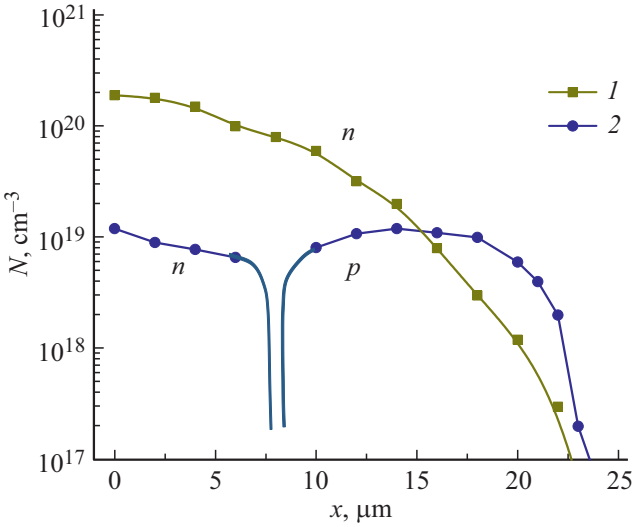

Figure 2. Concentration distribution of electrons (phosphorus) in samples additionally annealed at $T = 1250^\circ$C, $t = 4$ h (curve *1*); concentration distribution of charge carriers in gallium-doped samples pre-doped with phosphorus (curve *2*). *n*- and *p*-type of sample conductivity at a given depth.

of additional annealing at $T = 1250^\circ$C, $t = 4$ h the surface concentration of phosphorus slightly decreases, and the penetration depth reaches $x = 25\,\mu$m (curve *1*), in the region $x = 0-25\,\mu$m the samples acquire the *n*-conductivity type.

Concentration distribution in samples doped with gallium at $t = 1250^\circ$C, $t = 4$ h, after doping with phosphorus at 1000°C, $t = 2F$ h (curve *2*) shows that in the studied samples up to a depth of $x = 7.5-8\,\mu$m there is *n*-conductivity type. In this case, the concentration of electrons (phosphorus) decreases, and at $x > 7.5-8\,\mu$m, the samples acquire the *p*-conductivity type. In $x = 7.5-10\,\mu$m region the hole concentration slightly increases; in $x = 8-15\,\mu$m region the concentration of holes (gallium) practically remains constant, and at $x > 17\,\mu$m it decreases quite sharply. In almost all samples a similar result is obtained. These results show that during gallium diffusion (in the presence of a high phosphorus concentration) the phosphorus concentration in $x = 0-7.5\,\mu$m region decreases by 1–1.5 times, then the gallium concentration becomes greater than the phosphorus concentration, and the material has the *p*-conductivity type. Although, as can be seen from Fig. 2 (curve *1*), the concentration of phosphorus up to $15\,\mu$m region is greater than the concentration of gallium. These results suggest that the phosphorus presence in silicon leads to increasing of the gallium concentration. Based on the obtained results (see Fig. 2, curves *1* and *2*), the value of the gallium concentration over the sample depth in the presence of phosphorus was calculated. The calculation was carried out based on the neutrality equation $N_{Ga} = n_0 - n_1$ in $x = 0-7.5\,\mu$m region, where n_0 is electron concentration in samples doped with phosphorus, annealed additionally at $T = 1250^\circ$C, $t = 4$ h, n_1 is electron concentration in

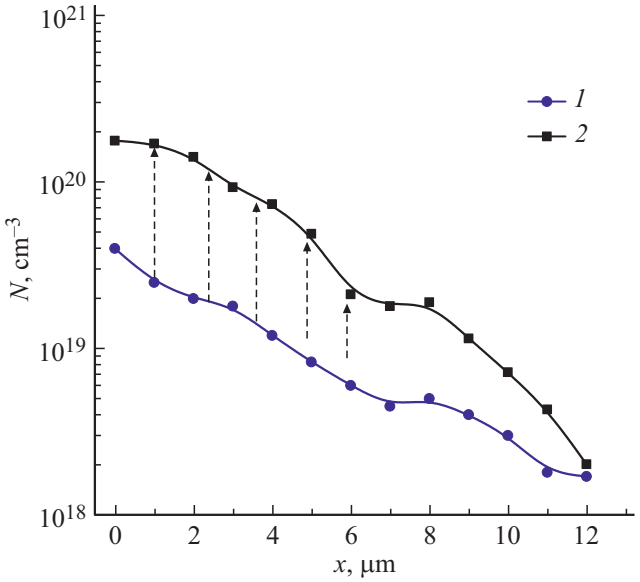

Figure 3. Concentration distribution of holes (gallium) in the absence (curve *1*) and in the presence (curve *2*) of phosphorus.

samples doped with gallium in the presence of phosphorus, and in $x > 7.5\,\mu$m region. $N_{Ga} = n_2 + p$, where n_2 is the electron concentration in silicon samples doped with phosphorus and annealed at $T = 1250^\circ$C, $t = 4$ h, in the given region x, p is concentration of holes in this region.

Fig. 3 shows the concentration distribution of gallium atoms during diffusion $T = 1250^\circ$C, $t = 4$ h in the absence of phosphorus diffusion, as well as the calculated concentration distribution of gallium atoms under the same diffusion conditions in samples that were pre-doped with phosphorus at 1000°C, $t = 2$ h. It follows from these results that irrespective of the same diffusion doping conditions in all materials the concentration distribution of gallium atoms is by 4–6 times larger in samples additionally doped with phosphorus than in samples without phosphorus. This means that the presence of a sufficiently high concentration of phosphorus significantly increases the solubility of gallium atoms. Also note that the depth of gallium in samples doped with phosphorus is less ($2-3\,\mu$m) than in samples without phosphorus. The experimental data obtained partially confirm the results of the papers [17,18], despite the fact that the interaction of phosphorus with boron was studied there.

4. Discussion of results

The obtained experimental results cannot be explained by the mutual compensation of donor (phosphorus) and acceptor (gallium) impurity atoms. In this case, the phosphorus and gallium atoms in the silicon lattice are distributed randomly, and these atoms are spatially separated. This should not lead to the concentration increasing of gallium atoms in the presence of phosphorus atoms. Therefore, it can be assumed that this phenomenon is associated with the interaction of phosphorus and gallium atoms. Since the phosphorus atoms in the silicon lattice are located in the crystal lattice sites in the form of a positively charged ion P^+, creating additional electrons in the conduction band, the value of which is equal to NP^+. The presence of a sufficiently high concentration of positively charged phosphorus atoms (P^+) practically creates electrical potentials distributed from the crystal surface through the depth of the sample in silicon, which stimulates increasing of gallium atoms during diffusion, which in silicon act as an acceptor impurity in the form negative ion Ga^-. Therefore, it can be assumed that as a result of such interactions the donor-acceptor complexes appear in the silicon lattice, i.e. quasimolecules in the form of $[P^+Ga^-]$.

Such complexes can exist only in cases where the phosphorus and gallium atoms are nearby, i.e. they occupy two neighboring sites in the silicon lattice (Fig. 4, *a*). Another position of the gallium and phosphorus atoms in the silicon lattice does not ensure the stable formation of complexes between these impurity atoms. The formation of such electrically neutral complexes $[P^+Ga^-]$ leads the system to a more favorable thermodynamic state than in the case when the atoms of these impurities are separated from each other. During the complexes formation, firstly, the concentration of charge carriers decreases significantly both in the conduction band and in the valence band, i.e. the degree of defectiveness of the crystal decreases; secondly, the electric potentials that are created around each ion are shielded from each other, which again leads to decreasing of the degree of defectiveness of the crystal.

All these factors stimulate the formation of $[P^+Ga^-]$ complexes, since the presence of the sufficiently high concentration of phosphorus in silicon creates more favorable conditions for increasing the concentration of newly diffusing gallium atoms. The following results of the study serve as proof of this assumption. Diffusion of gallium in silicon was carried out at $T = 1250^\circ$C for $t = 4$ h, but with surface concentration of phosphorus $N_P \sim 10^{17}$ cm^{-3}, i.e. much less than the solubility of gallium at a given temperature. Such samples were obtained by grinding the surface of silicon doped with phosphorus at 1000°C, $t = 2$ h, and then annealed at temperature of $T = 1250^\circ$C, $t = 4$ h. As the experimental results showed, in this case no

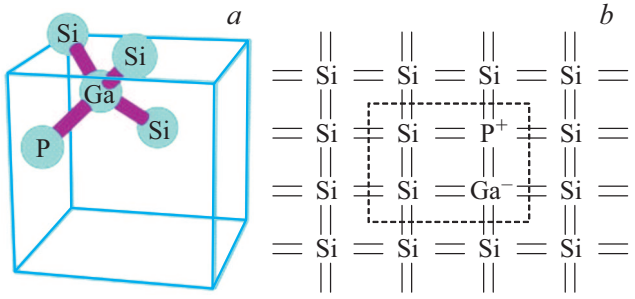

Figure 4. Quasimolecules Ga–P$^+$ (*a*), binary electrically neutral lattices of $Si_2P^+Ga^-$ type in silicon (*b*).

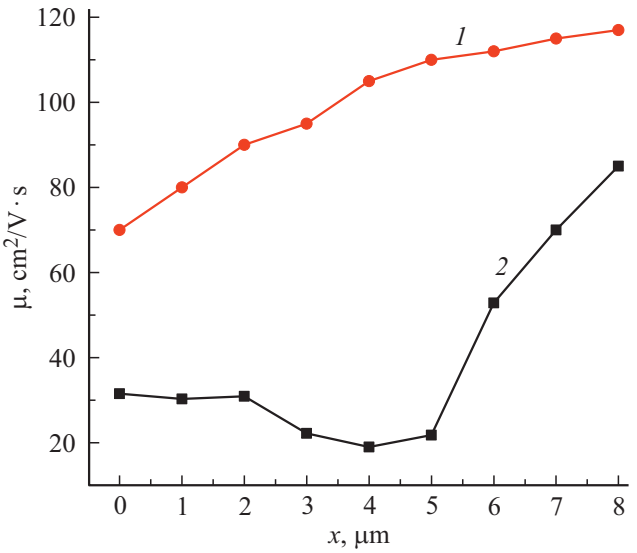

Figure 5. Change in electrons mobility in silicon doped with phosphorus (*1*) and in silicon (pre-doped with phosphorus) doped with gallium (*2*).

increasing of the solubility of gallium atoms was found. As a result of the study, it was found that a noticeable increasing of the gallium solubility occurs only when the concentration of phosphorus atoms is $N_P \geq N_{Ga}$.

Thus, we can state that the increasing of the gallium atoms solubility in silicon with an increased concentration of phosphorus is associated with the formation of complexes in the form of electrically neutral molecules in the silicon lattice. This can be confirmed by the results of study of the charge carriers mobility through the sample thickness by the Van der Pauw method (Fig. 5). As can be seen from the Figure, despite the fact that up to $8\,\mu$m samples of silicon (pre-doped with phosphorus) doped with gallium and of silicon doped with phosphorus without gallium have *n*-conductivity type, but the electrons mobility in silicon with [GaP] complexes is by 2–3 times lower than the electrons mobility in samples doped with phosphorus only. Also note that the electrons concentration in samples doped with phosphorus only is almost by an order of magnitude higher than the electrons concentration in samples doped with phosphorus and gallium.

In this case, also note the following interesting fact related to the formation of $[P^+Ga^-]$ complexes, which are located in neighboring sites of the silicon lattice. When such complexes are formed in the lattice, new binary electrically neutral lattices of $Si_2P^+Ga^-$ type are formed (Fig. 4, *b*).

5. Conclusion

It is shown in the paper that in silicon pre-doped with a high concentration of phosphorus, the gallium diffusion leads to significant increasing of the gallium solubility. The results obtained are explained by the interaction of gallium and phosphorus atoms, as a result of which quasi-neutral molecules $[P^+Ga^-]$ are formed. It is assumed that the formation of such quasi-neutral molecules $[P^+Ga^-]$ stimulates the formation of Si_2GaP binary elementary cells in the silicon lattice. The formation of these binary elementary cells with sufficiently high concentration, and the study of their effect on the fundamental parameters of silicon are of great practical and scientific interest.

Conflict of interest

The authors declare that they have no conflict of interest.

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