CURRENT STATUS OF SILICON STUDIES WITH Ge₅₆Si₄₄ BINARY COMPOUNDS AND POSSIBILITIES OF THEIR APPLICATIONS IN ELECTRONICS†

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The paper determines the technological regimes for obtaining GeₓSi₁₋ₓ alloys by introducing germanium atoms into single-crystal silicon by the diffusion method. From the results of the study, it was found that the fundamental parameters of the formed GeₓSi₁₋ₓ alloys differ from the fundamental parameters of the original silicon, in particular, the energy values of the silicon band gap change. Elemental analysis of the surface of the samples showed that the concentration of silicon (in atomic percent) was ~70.66%, germanium ~29.36%. It was assumed that on the silicon surface and in the front part, a thin layer of an alloy of a compound with a composition of approximately Ge₀.₃Si₀.₇ (0.5±2 μm) would be formed. Analysis of the spectra (p) shows that the spectrum contains peaks ~303 cm⁻¹ and ~406 cm⁻¹, corresponding to the Ge-Ge and Si-Ge bonds, respectively. It was also shown that GeₓSi₁₋ₓ binary compounds are a new material for modern electronics, the possibility of creating properties on their basis in electronics was shown. It is proposed on their basis to create devices with new functionality and highly efficient solar cells.

Keywords: Diffusion; Germanium; Silicon; Solubility; Concentration; Binary complexes

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INTRODUCTION

Today, special attention is paid to obtaining new materials with clusters of impurity atoms on the surface and in the bulk of a semiconductor, which is one of the main directions in the development of technology and physics of semiconductor materials [1–3]. In this case, one of the important tasks is the creation of a simple and cheap technology for the formation of clusters (clusters) of impurity atoms in the bulk of a crystal, which makes it possible to create nanoscale structures that change the properties of the base material. The methods of molecular beam epitaxy used to obtain such nanosized structures require expensive equipment.

Obtaining clusters of germanium (quantum dots) in a silicon lattice allows you to significantly expand the spectral region of sensitivity of photodetectors, solar cells. Germanium nanostructures in a solid solution of the GeₓSi₁₋ₓ type can be obtained on the basis of single-crystal silicon by the diffusion method. It is known [4] that germanium forms stable solid solutions in silicon up to a germanium concentration of 1650 K from 80%. At the same time, the maximum solubility of germanium in silicon reaches 1·10²² at/cm³ at a temperature of 1430°C [5].

Upon cooling, the solid solution of germanium in silicon decomposes, and an excess of germanium forms accumulations (clusters) containing mainly germanium (the solubility of silicon in germanium at a temperature of 1550 K is less than 50%) [6].

In this regard, the purpose of research is the development of a diffusion technology for obtaining germanium clusters in the volume of a silicon lattice and the study of the electrical parameters of these materials.

TECHNIQUE AND EXPERIMENTAL

Single-crystal p- and n-type silicon with resistivity of 10 and 100 Ohm cm was chosen as the starting material. The size of all silicon samples was the same 8×4×1 mm³.

The diffusion technology for obtaining GeₓSi₁₋ₓ solid solutions with different ratios of components, although of great interest, is technologically unacceptable. This is mainly due to the very small diffusion coefficient of germanium atoms in silicon (Dₓ ~ 10⁻¹⁴ cm²/s) [7], which requires a long diffusion time (Table 1) to obtain layers with a high concentration of germanium. Here x is the depth at which the concentration of germanium drops by a factor of e, the diffusion time is 20 hours.

We managed to solve the problem of a low diffusion coefficient due to the technology of low-temperature diffusion alloying of silicon with germanium. The technology of two-stage diffusion was used, which makes it possible to obtain a noticeable increase in diffusion coefficients [8–10]. Initial samples of silicon and diffusant - powdered germanium grade GES-1 were placed in quartz ampoules, after which evacuation was performed (residual pressure in the ampule p~ 10⁻³ mm Hg). The ampoules were placed in a diffusion furnace of the Vacuum Tube Furnace 1700°C brand at T = 300K.

Table 1. Diffusion coefficient and displacement length of germanium atoms in silicon

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>1250</th>
<th>1200</th>
<th>1150</th>
<th>1050</th>
<th>950</th>
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</thead>
<tbody>
<tr>
<td>$D$, cm$^2$/s</td>
<td>4.10$^{-13}$</td>
<td>8.10$^{-14}$</td>
<td>6.60$^{-15}$</td>
<td>6.00$^{-17}$</td>
<td>7.10$^{-19}$</td>
</tr>
<tr>
<td>$x$, μm</td>
<td>3.6</td>
<td>3.12</td>
<td>2.12</td>
<td>1.42</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The amount of diffusant was determined by calculation based on the volume of the ampoule and the required vapor pressure (concentration of atoms) of the diffusant at the diffusion temperature.

The furnace temperature was gradually increased at a rate of 5°C/min to a temperature of $T = (900÷940)$ °C. Then the samples were kept $t = (20÷25)$ min at this temperature, after which they continued heating at a rate of 150÷200°C/min to the final diffusion temperature. At this temperature, the samples were kept for $t = 20$ hours, after which the quartz ampoules were removed from the furnace and cooled at a rate of about 200°C/sec. Diffusion annealing of the obtained samples was carried out at the final diffusion temperature $T = 1050; 1150; 1250$ °C for $t = 5$ hours.

**DISCUSSION OF EXPERIMENTAL RESULTS**

The electrical parameters of the samples were measured on an ECOPIA HMS-3000 Van der Pauw setup. The distribution profiles of the electrical parameters of the samples were studied by mechanical removal of layers (by 1 μm), measurement on the Van der Pauw installation, and further calculation of the profiles of resistivity, mobility, and concentration of carriers. The chemical composition of individual points of the samples was studied by energy dispersive X-ray microanalysis on a JSM-IT 200 SEM.

![Figure 1. Changes in silicon resistivity with Ge$_x$Si$_{1-x}$ binary compounds a) sample of no. 2, b) sample of no. 3.](image1)

It is known that Raman spectroscopy is an accurate method for studying the bond states and symmetries of binary compounds of impurity atoms in semiconductors, which depend on the various local modes of vibrations of atoms and molecules formed in the crystal structure. Raman spectroscopy is also widely used to diagnose various structures formed in the bulk of silicon [11-13]. The measurements were carried out using a Raman spectrometer in the spectral range from 100 cm$^{-1}$ to 3400 cm$^{-1}$. The spectra were determined using a diode laser with a wavelength of $\lambda = 785$ nm. During the measurement, a diffraction grating with a period of 1200 lines/mm was used. To clarify the presence and composition of new phases in the samples, X-ray phase analysis was performed on a Shimadzu XRD-100 diffractometer.

The results of (Fig. 1) the study of surface resistance showed that after diffusion, the surface resistance of the sample decreased by 5 orders of magnitude, which indicates a strong doping of the surface layer with antimony contained in germanium.

![Figure 2. a) Topography of the surface of a silicon sample after doping with germanium atoms (sample no. 3). b) X-ray energy-dispersive microanalysis of silicon samples doped with impurity germanium atoms.](image2)

<table>
<thead>
<tr>
<th>Element</th>
<th>Line</th>
<th>Mass %</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>K</td>
<td>70.34±0.24</td>
<td>85.97±0.3</td>
</tr>
<tr>
<td>Ge</td>
<td>K</td>
<td>29.66±0.44</td>
<td>14.03±0.21</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Figure 2a shows the topography of the surface of a silicon sample doped with germanium atoms, obtained on a JSM-IT 200 SEM in the secondary electron mode. The X-ray spectrum obtained at point 3 (Fig. 1,b) showed that the concentration of silicon atoms was 86%, germanium atoms - 14%, which corresponds to the composition of the Ge$_{0.14}$Si$_{0.86}$ solid solution.

From the literature data [14,15], it is known that it is impossible to obtain an equilibrium solid solution of germanium in silicon with a germanium concentration of more than 90%. The result obtained can be explained by the quenching of the solution due to the rapid cooling of the samples after diffusion.

Figure 3 shows an enlarged image of the sample area near point 4 and the elemental composition of the surface.

![Figure 3](image1.png)

**Figure 3.** a) Topography of the annealed sample  
   b) X-ray energy-dispersive microanalysis of silicon samples doped with impurity germanium atoms

Judging by the appearance, at this point there is a drop of germanium that has adhered to the surface and has dissolved a significant amount of silicon. The composition corresponds to a solid solution of silicon in germanium Ge$_{0.87}$Si$_{0.13}$. This shows the possibility of obtaining germanium clusters containing a relatively small amount of silicon.

In order to reveal the presence of bonds of the Si-Ge and Ge-Ge type, the samples were studied by Raman spectroscopy. Figure 4 shows the spectrum of Raman scattering in samples of the original silicon (a) and silicon doped with germanium. The spectral measurement range is from 100 cm$^{-1}$ to 3400 cm$^{-1}$. The spectra were determined using a diode laser with a wavelength of $\lambda = 785$ nm.

![Figure 4](image2.png)

**Figure 4.** Raman spectrum: a) initial silicon (SEP-100); b) silicon doped with Ge (no. 3)

Analysis of the spectra (Fig. 3b) shows that the spectrum contains peaks of ~303 cm$^{-1}$ and ~406 cm$^{-1}$, corresponding to the Ge-Ge and Si-Ge bonds, respectively. These results are in good agreement with the data presented in [16, 17]. The amplitude of these peaks is small, and the width is large, which indicates a low volume concentration of these bonds and a significant inhomogeneity of the samples, apparently associated with the "diffusion" inhomogeneity of the composition.
and, consequently, mechanical stresses in the samples. To test this assumption, the samples were annealed at a temperature of 1050 °C degrees for 5 hours. Figure 5 shows the Raman spectrum of this sample. There is no Si-Ge peak in the spectrum, and the Ge-Ge peak is noticeably narrower and higher. This indicates the decomposition of the solid solution with the formation of a new germanium phase containing an insignificant amount of silicon.

Figure 5. Raman spectrum of the annealed sample.

Figure 6 (a,b) shows the diffraction spectra obtained with a step of 0.05° at a scanning speed of 2°/min in the range of scanning angles of 10°-70°.

The diffraction spectra confirm the formation of germanium clusters during the diffusion treatment and the presence of inhomogeneities in the lattice parameter.

Figure 6. X-ray diffraction pattern: a) initial silicon [18]; b) silicon doped with germanium (no.3)

Figure 7. AFM images of the silicon surface doped with impurity germanium atoms
As can be seen from Figure 7, the formation of islands on the silicon surface doped with germanium impurity atoms leads to an increase in the average roughness size. This indicates the formation on the silicon surface of binary compounds Ge\textsubscript{x}Si\textsubscript{1-x}, the electric potential of which is higher than that of the initial silicon.

An analysis of the experimental results showed the formation of binary compounds of the Ge\textsubscript{x}Si\textsubscript{1-x} type in the lattice of single-crystal silicon.

Studies of the state of germanium atoms in diffusion-doped silicon according to the developed technology showed that under diffusion conditions a solid mixture of the Ge\textsubscript{x}Si\textsubscript{1-x} type is formed in silicon [19-21]. It has been established that germanium impurity atoms in the silicon lattice create monoclusters with a certain composition in the formed binary cell.

CONCLUSION

From the analysis of the spectra obtained by the Raman spectrometer and X-ray diffraction analysis, it can be said that binary silicon-germanium (Ge\textsubscript{x}Si\textsubscript{1-x}) compounds are formed in the silicon crystal lattice, the concentration of which will increase from the diffusion conditions and heat treatment (temperatures, time). Comparison of the results obtained with the available literature data established that binary compounds of the Ge\textsubscript{x}Si\textsubscript{1-x} type are formed in the lattices of single-crystal silicon. In addition, the results obtained show that silicon atoms enriched with germanium atoms lead to a change in the fundamental parameters of the initial silicon. Changing the fundamental parameters of the original silicon allows you to control the electrical, photoelectric and optical parameters of silicon, which makes it possible to obtain a new material with unique photoelectric and optical properties.

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REFERENCES

ПОТОЧНИЙ СТАН ДОСЛІДЖЕНЬ КРЕМНІЮ З БІНАРНИМИ СПОЛУКАМИ $\text{Ge}_x\text{Si}_{1-x}$ТА МОЖЛИВОСТІ ЇХ ЗАСТОСУВАННЯ В ЕЛЕКТРОНІЦІ

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Визначено технологічні режими отримання сплавів $\text{Ge}_x\text{Si}_{1-x}$ шляхом введення атомів германію в монокристалічний кремній дифузійним методом. За результатами дослідження встановлено, що фундаментальні параметри сформованих сплавів $\text{Ge}_x\text{Si}_{1-x}$ відрізняються від фундаментальних параметрів вихідного кремнію, зокрема змінюються енергетичні значення ширини забороненої зони кремнію. Елементний аналіз поверхні зразків показав, що концентрація кремнію (в атомних відсотках) становила ~70,66%, германію ~29,36%. Передбачалося, що на поверхні кремнію і в лицевій частині утворюється тонкий шар сплаву сполуки складу приблизно $\text{Ge}_0.3\text{Si}_0.7$ (0,5–2 мкм). Аналіз спектрів (p) показує, що спектр містить піки ~303 cm$^{-1}$ and ~406 cm$^{-1}$, що відповідають зв'язкам $\text{Ge-Ge}$ і $\text{Si-Ge}$ відповідно. Також було показано, що бінарні сполуки $\text{Ge}_x\text{Si}_{1-x}$ є нових матеріалів для сучасної електроніки, показано можливість створення на їх основі властивостей в електроніці, на їх основі запропоновано створювати прилади з новою функціональністю та високоефективними сонячними елементами.

Ключові слова: дифузія; германій; кремній; розчинність; концентрація; бінарні комплекси