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PHYSICAL AND MAGNETIC PROPERTIES OF SILICON DOPED WITH IMPURITY GERMANIUM ATOMS

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This paper presents the results of a study of silicon diffusion-doped with germanium impurity atoms. For the diffusion of germanium impurity atoms, the original single-crystal silicon of the KEF-100 brand was used, in which the phosphorus concentration was equal to $N_p \approx 5 \cdot 10^{13}$cm^{-3}. The selection of such a concentration of phosphorus impurity atoms was justified by the fact that this concentration of phosphorus atoms has practically no effect on the electrophysical properties of the obtained samples of silicon doped with germanium impurity atoms (Si<Ge>) due to the high solubility of germanium impurity atoms in silicon. As shown by the conducted experimental studies in silicon samples doped by the developed new technology, there are a number of important practical features as well as, the time of the diffusion process of impurity atoms of germanium in silicon according to the developed new technology is reduced by 2-2.5 times, the power consumption during diffusion is reduced by 2 times, the formation of various impurities, silicides, both on the surface and at the surface region of silicon and surface erosion are almost completely eliminated. The study of the electrophysical and magnetic properties of silicon doped with impurity atoms of germanium showed that on the surface and in the near-surface, in addition to the formation of saturated layers of impurity atoms of germanium, binary compounds Ge_xSi_{1-x} are also formed. Based on the X-ray energy dispersive microanalysis, it was determined that the concentration of silicon atoms on the surface is ~44.32%, germanium atoms ~38.11%, oxygen atoms ~15.58% and carbon atoms ~1.98%. These data showed that the number of germanium atoms on the surface is almost half the number of the main silicon atoms. The presence of impurity germanium atoms leads to a strong change in the fundamental parameters of the original silicon. The results of the study showed that in the samples of silicon doped with impurity germanium atoms, ferromagnetic properties are observed at relatively high temperatures ($T = 300$ K). For the first time in the samples of silicon doped with impurity germanium atoms, galvanomagnetic parameters such as M_s-saturation magnetization, M_r-residual magnetization and H_c-coercive force were determined. It was shown that in samples of silicon doped with impurity atoms of germanium, the fundamental parameters (the value of the width of the forbidden zone, mobility and band structure) of the original silicon change in a wide range, which leads to an expansion of the spectral range of photosensitivity, as well as magnetic properties, i.e. ferromagnetism is observed at relatively high temperatures ($T=300$ K).

Keywords: *Silicon; Compounds; Diffusion; Germanium; Concentration; Impurity; Physical Mechanism*
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INTRODUCTION

The measurement and control of magnetic fields have always been and remain an urgent challenge, attracting significant interest from scientists and specialists. From literary analysis it has been established that the measurement and conversion of the magnetic field value to an electrical signal requires the creation of modern magnetic resistors based on semiconductor materials and structures. To date, semiconductor materials and multilayer structures based on binary compounds have been primarily used for this purpose, often necessitating modern and costly equipment [1-4].

In compensated silicon doped with impurity atoms that create deep electronic levels within the forbidden band, a range of intriguing physical phenomena have been observed. These include high photosensitivity, temperature and infrared quenching of photoconductivity, tensile and magnetic properties, current auto-oscillations, and more [5-8]. Studies on the magnetic properties of silicon doped with isovalent and rare-earth impurity atoms have revealed high magnetosensitivity, both negative and positive magnetoresistance, and transitions to a ferromagnetic state at relatively low temperatures in certain samples [9-10]. This paper presents the results of the study of physical properties of silicon samples doped with impurity germanium atoms.

METHODS

To obtain silicon samples doped with germanium impurity atoms, a two-stage diffusion technique was developed, which enabled a significant increase in the diffusion coefficient of germanium atoms into silicon.

It is well-known that diffusion in semiconductors occurs primarily through the interaction of diffusing impurity atoms with the host atoms and point defects within the crystal lattice of the initial material. The gas-phase diffusion of impurity atoms in semiconductors typically follows Fick's law. However, this approach often fails to fully capture the physical mechanisms of diffusion in semiconductors [11,12].

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For the diffusion of impurity atoms of germanium, the initial single-crystal silicon of the KEF-100 brand was used, in which the phosphorus concentration was equal to $N_p \approx 5 \cdot 10^{13} cm^{-3}$. Such a concentration of impurity atoms of phosphorus has practically no effect on the physical properties of the obtained samples of silicon doped with impurity atoms of germanium (Si<Ge>) due to the high solubility of impurity atoms of germanium in silicon. Powdered germanium with a purity of ~99.999% was used for the diffusion of impurity atoms of germanium. The essence of the developed low-temperature diffusion is as follows. The studied samples of the initial silicon and a diffusant of a certain mass (this is determined by the volume of the ampoule) are in evacuated quartz ampoules (the pressure in the ampoule is $P = 10^{-6}$ mm Hg) and placed in a diffusion furnace at a temperature of T = 300 K. The temperature of the furnace from the quartz ampoule is gradually raised at a rate of 5ºC/min. Then the temperature rises to T = (823 ÷ 973) K and is maintained at this temperature for t = (10 ÷ 20) min, then the furnace temperature rises fairly quickly (T = 423÷ 473 K/min) to a certain temperature (T = 960 ÷ 1050 K) and the samples are maintained at this temperature for t = 3 ÷ 5 hours, after which the ampoules are removed from the furnace and cooled at a rate of 200 ºC/sec. The developed new diffusion technology was carried out dozens of times of diffusion of impurity atoms of germanium from the gas phase. After each diffusion, 5 to 7 samples of silicon were obtained, the surface of which was examined by an electron microscope of the MIM-8 brand. Diffusion was also carried out by the usual high-temperature diffusion method. As the analysis of the obtained results of the study showed, in contrast to the samples obtained by the usual method, in the samples obtained by the developed low-temperature technology no surface erosion was detected, impurities and silicides were not formed, both on the surface and in the surface area. To determine the penetration depth of impurity atoms in the diffusion process, a study of the specific resistance of silicon samples doped with impurity atoms of germanium was carried out by the 4-probe method on the Van der Pauw installation of the Hall Measurements system 7000 brand with the removal of the thickness of the obtained samples, and the concentration of mobility and charge carriers were determined.

EXPERIMENTAL PART

Ferrimagnetic properties were first discovered in silicon doped with germanium impurity atoms at relatively low temperatures (T ≈ 30 K). Studies on the properties of silicon diffusively doped with germanium were conducted at a temperature of T = 300 K, where ferrimagnetic behavior was observed in these samples under specific conditions – a phenomenon not previously documented.

The magnetic properties of the obtained Si<Ge> samples were examined using a magnetic force microscope, the FM-Nanoview 1000. "Magnetic" images of the topography of germanium-doped silicon were obtained at the submicron level, providing detailed visualization of the sample structure (Fig. 1).

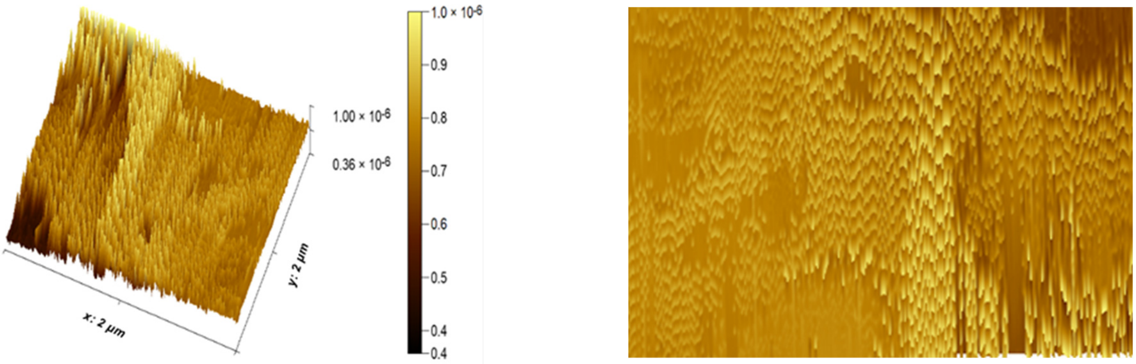


Figure 1. 3D-representation of magnetic domain topography and magnetic topography images in Si<Ge> samples, at T=300 K

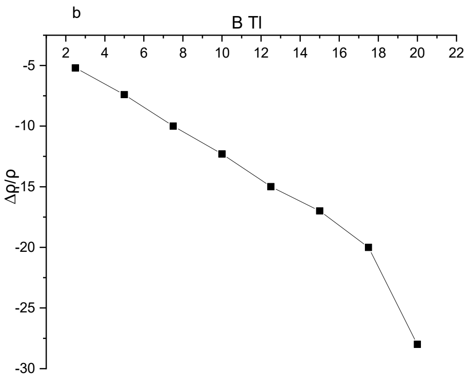


Figure 2. Dependence of negative magneto-resistance on the magnitude of magnetic field in samples p-Si<Ge>, at E =100 V/cm, a) T = 80K, b) T = 300K

These results confirm that silicon samples doped with germanium impurity atoms exhibit ferrimagnetic properties not only at low temperatures ($T_{Ge} \approx 30$ K) but also at relatively high temperatures (T = 300 K). The study of the magnetic properties of Si<Ge> samples demonstrate a significant negative magnetosensitivity in silicon doped with germanium impurity atoms (Fig. 2).

A Scanning Electron Microscope (SEM) provides high-quality imaging and analysis of material surfaces. This technique enhances image quality and resolution by using a stream of high-energy electrons to scan the surface, producing highly detailed images [13,14]. Figures 3a and 3b show the surface topology of a silicon sample doped with germanium impurity atoms, obtained using a JSM-IT 200 SEM. The elemental composition of the silicon surface is presented in Figure 3c.

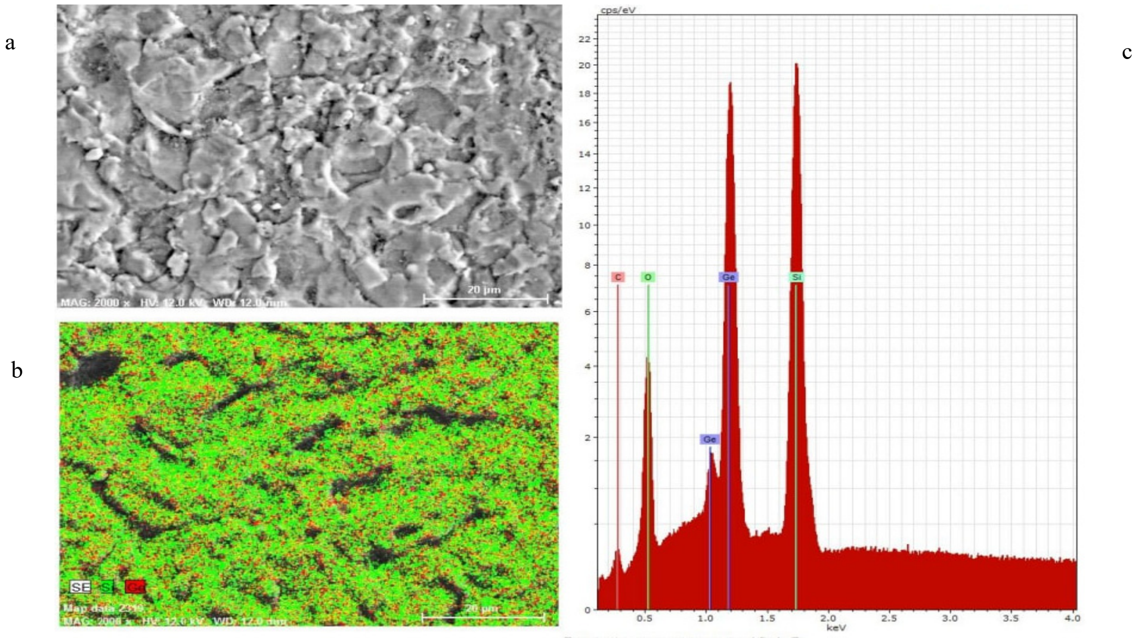


Figure 3. a) and b) surface topology of silicon diffusion-doped with germanium impurity atoms, c) results of micro-X-ray energy-dispersive analysis (scale 20 µm).

Table 1 shows the elemental composition of silicon samples doped with germanium impurity atoms, determined from micro X-ray energy dispersive analysis obtained using a scanning electron microscope.

Table 1. Elemental composition of silicon samples doped with impurity germanium atoms

Element	AN	Series	unn. C {wt}	norm. C {wt.%}	Error {wt}.
Si	14	K	44.45	44.32	1.8
O	8	K	15.63	15.58	1.9
Ge	32	K	38.23	38.11	2.1
C	6	K	1.99	1.98	0.4
Total:			100.29	100.00	

THEORETICAL CALCULATIONS AND RESEARCH RESULTS

Analysis of the study results revealed that after the diffusion of germanium impurity atoms onto the silicon surface, a thin layer forms where germanium-silicon compounds (GeSi) are present. The elemental composition of the silicon surface is shown in Table 1. X-ray energy-dispersive microanalysis indicated that the surface concentrations are approximately 44.32% silicon atoms, 38.11% germanium atoms, 15.58% oxygen atoms, and 1.98% carbon atoms. This data demonstrates that the quantity of germanium atoms on the surface and near-surface layer of silicon is nearly half that of the primary silicon atoms.

Microscopic analysis revealed that a compound layer with an approximate composition of $Ge_{0.38}Si_{0.62}$ and a thickness of 0.5–2 microns formed on the surface and near-surface region of the silicon. Beyond this layer, the concentration of germanium atoms decreases sharply; at a depth of 5–6 microns, the compound composition reaches $Ge_{0.05}Si_{0.95}$. These findings confirm the formation of binary $GeSi_{1-x}$ compounds and heterostructures of the Ge_xSi_{1-x}-Si type on the silicon surface and near-surface region through the diffusion of germanium impurity atoms.

Fig. 4a shows the surface topography of a silicon sample doped with germanium impurity atoms, obtained using a JSM-IT 200 scanning electron microscope (SEM) in secondary electron mode. The X-ray spectrum at point 3 (Fig. 4) indicates a composition of 86% silicon and 14% germanium atoms, corresponding to the binary compound ratio $Ge_{0.14}Si_{0.86}$.

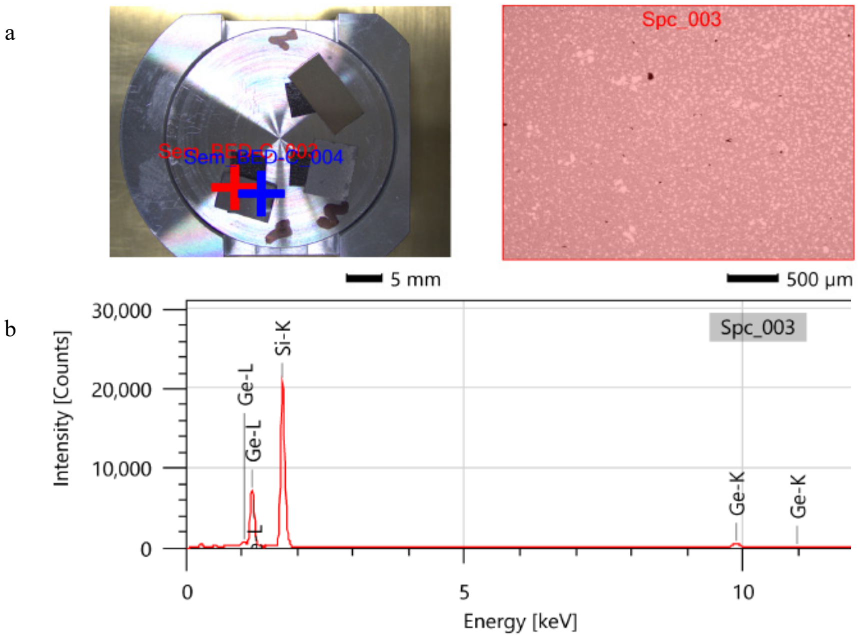


Figure 4. a) Surface topography of silicon sample doped with impurity germanium atoms. b) X-ray energy dispersive microanalysis of silicon samples doped with impurity germanium atoms.

Table 2. Elemental composition of silicon samples doped with impurity germanium atoms

Element	Line	Weight %	Atom %
Si	K	70.34±0.24	85.97±0.3
Ge	K	29.66±0.44	14.03±0.21
Total:		100.00	100.00

Literature data [15] indicate that it is impossible to achieve a uniform distribution of germanium impurity atoms in silicon at concentrations around 80%. In our study, the results can be explained by the fact that, during the additional heat treatment of silicon samples doped with germanium impurity atoms, binary compounds such as Ge_xSi_{1-x} with high concentrations were formed in addition to individual impurity atoms.

To confirm the formation of binary compounds Ge_xSi_{1-x}, silicon samples doped with germanium impurity atoms were examined using an atomic force microscope (FM-Nanoview 1000) (Fig. 5).

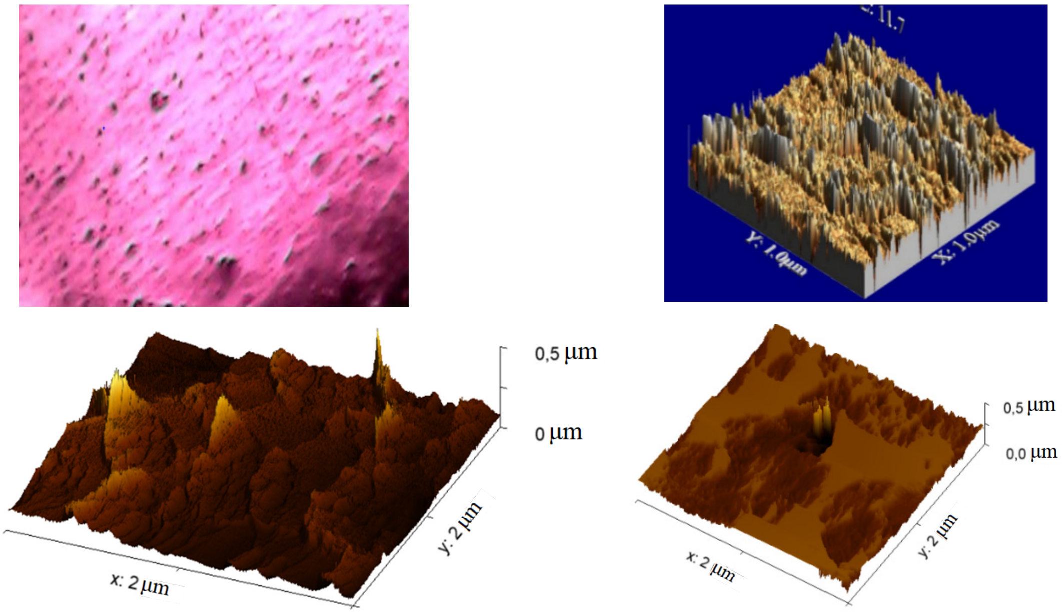


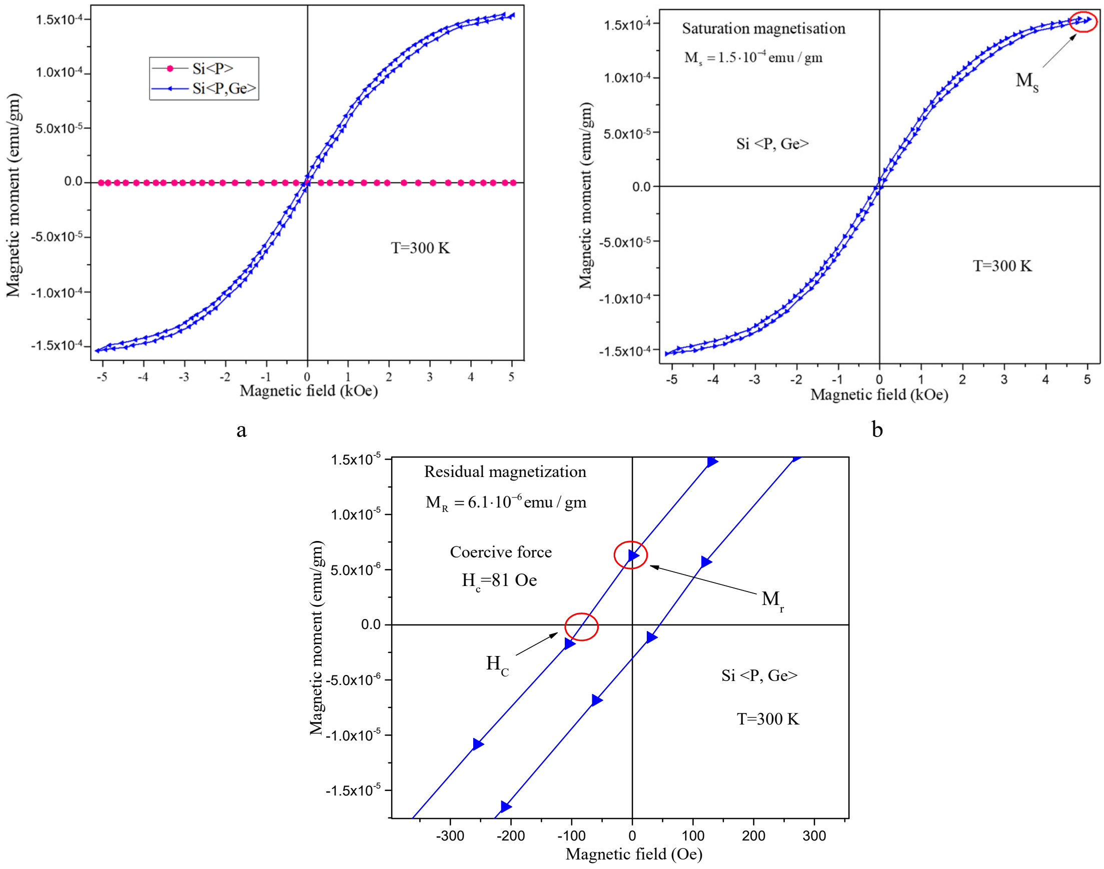
Figure 5. AFM images of the surface of silicon doped with impurity germanium atoms

The results showed the formation of islands on the surface and near-surface regions of the silicon samples, which are key to the formation of Ge_xSi_{1-x} compounds. Further analysis of the silicon samples doped with germanium was conducted using an IR microscope. The results revealed that the size of the formed silicon-germanium binary compounds reaches up to 1–2 µm, and these compounds were found in large quantities on both the surface and near-surface layer of the silicon.

As shown in Fig. 5, the formation of islands consisting of binary Ge_xSi_{1-x} compounds on the silicon surface leads to an increase in the average roughness size [16]. This indicates that the binary Ge_xSi_{1-x} compounds are forming on the silicon surface due to the impurity germanium atoms, whose electric potential is higher than that of the original silicon.

The experimental results revealed that silicon samples doped with impurity germanium atoms exhibit a ferromagnetic state at a temperature of T = 300 K (Fig. 6).

Studies of the dependence of the magnetic moment of silicon samples doped with impurity atoms of germanium on the specific resistance of the material showed that in high-resistance samples (where the specific resistance is close to the intrinsic conductivity $\rho \geq 10^5\ \Omega\cdot$cm) and in samples less than with $\rho < 4\times10^4\ \Omega\cdot$cm, a decrease in the magnetic moment is observed. According to the results of studying the negative magnetoresistance in samples obtained in similar modes, a similar picture of a noticeable decrease in the NMR is observed in silicon samples doped with impurity atoms of germanium at the same specific resistances. On this basis, it can be considered that the NMR phenomena that are observed can be directly related to the presence of magnetic ordering in these samples.



a b

c

Figure 6. Magnetization dependence on magnetic field of silicon samples doped with impurity germanium atoms at T= 300 K, a) in samples of silicon Si <B, Ge>, $\rho = 4\times10^4\ \Omega\cdot$cm, *p*-type (blue color) and original silicon (red color), b), v) finding the parameters M_s-saturation of magnetization, M_r-residual magnetization and H_c-coercive force.

DISCUSSIONS

Based on experimental studies, it has been shown that by controlling the parameters of the low-temperature diffusion process, binary compounds of the Ge_xSi_{1-x} type can be obtained with a thickness of up to 5–6 µm, and with germanium atom concentrations on the surface reaching up to 27%.

The formation of Ge_xSi_{1-x} binary compounds in silicon doped with germanium impurity atoms leads to a change in one of silicon's fundamental parameters: the bond dissociation energy. The bond dissociation energy between germanium and silicon atoms is higher than that of the germanium-germanium bond but lower than that of the silicon-silicon bond.

It has been established that, in addition to various combinations of Ge_xSi_{1-x} forming in the silicon crystal lattice, neutral molecular compounds, such as Si_2-Ge_xBrSi_{1-x}, may also form. These compounds consist of tetrahedral clusters of three silicon atoms surrounded by germanium atoms. The formation of such compounds contributes to the creation of heterostructures of the type $GeSi_{1-x}$ -Si on the surface and near-surface regions of silicon.

The results of the study also revealed that silicon samples doped with germanium impurity atoms exhibit ferromagnetic properties at a temperature of T = 300 K.

CONCLUSIONS

Analysis of the study results revealed that in silicon samples doped with germanium impurity atoms, there is a wide range of changes in the fundamental parameters of silicon, such as the width of the bandgap, mobility, and electronic structure. These changes lead to an expansion of the spectral range of photosensitivity and the emergence of magnetic properties, including ferromagnetism at relatively high temperatures (T = 300 K). This makes the doped silicon suitable for the development of sensitive photodetectors, solar cells, and magnetic sensors.

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ФІЗИЧНІ ТА МАГНІТНІ ВЛАСТИВОСТІ КРЕМНІЮ, ЛЕГОВАНОГО ДОМІШКОВИМИ АТОМАМИ ГЕРМАНІЮ

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У даній роботі представлені результати дослідження дифузійно легованого домішками атомів германію кремнію. Для дифузії домішкових атомів германію використовувався вихідний монокристалічний кремній марки КЕФ-100, в якому концентрація фосфору дорівнювала $N_p \approx 5 \cdot 10^{13}$ см$^{-3}$. Вибір такої концентрації домішкових атомів фосфору був обґрунтований концентрацією атомів фосфору, яка практично не впливає на фізичні властивості отриманих зразків кремнію, легованого домішковими атомами германію (Si<Ge>) через високу розчинність домішки. атомів германію в кремнії. Дослідженням електрофізичних і магнітних властивостей кремнію, легованого домішковими атомами германію, встановлено, що на поверхні і в приповерхневій зоні крім утворення насичених шарів домішкові атоми германію утворюють також бінарні сполуки Ge_xSi_{1-x}. На основі рентгенівського енергодисперсійного мікроаналізу встановлено, що концентрація атомів кремнію на поверхні становить ~44,32 %, атомів германію ~38,11 %, атомів кисню ~15,58 % і атомів вуглецю ~1,98 %. Ці дані показали, що кількість атомів германію на поверхні становить майже половину кількості основних атомів кремнію. Наявність домішкових атомів германію призводить до сильної зміни фундаментальних параметрів вихідного кремнію. За результатами дослідження встановлено, що в зразках кремнію, легованого домішковими атомами германію, феромагнітні властивості спостерігаються відносно високих температур (T=300 K). Вперше гальваномагнітні параметри, такі як M_s-намагніченість насичення, M_r-залишкова намагніченість і H_c-коерцитивність, були визначені в зразках кремнію, легованих домішковими атомами германію.

Ключові слова: *силікон; компаунд; дифузія; германій; концентрація; домішка; фізичний механізм*