**Electrical and Photovoltaic Properties of Silicon Incorporating Binary Band-Gap Compounds**

Giyosiddin Kushiev1, a), Nurullo Zikrillaev1, Kutub Ayupov1, Bahrom Abdurakhmanov, Bobir Isakov1, Stansilav Tachilin1, Ernazar Kosbergenov2, Feruza Urakova1,

1 Tashkent state technical university named after Islam Karimov, Tashkent, Uzbekistan

2National University of Uzbekistan named after Mirzo Ulugbek, Tashkent, Uzbekistan

a) Corresponding author: [giyosiddinabdivaxobogli@gmail.com](mailto:giyosiddinabdivaxobogli@gmail.com)

**Abstract.** The fabrication of binary compounds such as AIIBVI and AIIIBV for solar cell applications requires high energy consumption and costly technological infrastructure, significantly increasing the overall production cost of photovoltaic devices. Therefore, the development of alternative materials with superior electrophysical and photoelectric properties is essential for creating highly efficient single-junction solar cells. Studies on silicon samples co-diffused with gallium and phosphorus have demonstrated the in-situ formation of GaP binary compounds, which markedly modify the intrinsic properties of the silicon matrix. This phenomenon highlights promising opportunities for designing new classes of optoelectronic and photovoltaic devices. By employing a two-stage, low-temperature diffusion technique, the optimal thermodynamic parameters necessary for synthesizing gallium–phosphorus binary compounds within silicon were established. This innovative approach enabled the formation of a heterojunction structure directly inside the silicon substrate, opening new pathways for material engineering and improving the performance of silicon-based solar cells enriched with Ga–P compounds. Additionally, technological protocols were developed for producing silicon samples containing binary com-pounds on the surface and within the near-surface region. This strategy enhanced the samples’ sensitivity to short-wavelength solar radiation. Determining the optimal parameters for silicon modified with GaP compounds has laid a scientific foundation for the development of high-efficiency photovoltaic devices. Moreover, the research confirms the potential of GaP-containing silicon synthesized through gas-phase diffusion for creating photodetectors with a broad spectral response and high operational efficiency.

**INTRODUCTION**

Generating electricity from renewable energy sources (RES) has gained significant traction globally in the 21st century. The rationale and feasibility of transitioning to renewable energy sources are primarily supported by several factors: the gradual depletion of hydrocarbon fuel reserves, the rapid growth of the global population leading to an increased demand for electricity, and the concerning rise in the "greenhouse effect" due to the accumulation of carbon dioxide (CO2) in the atmosphere

According to the UN classification, RES encompass the following categories:

Biomass energy.

Energy derived from the seas and oceans (tides and currents).

Energy harnessed from terrestrial water flows (micro-hydropower plants <1 MW).

Geothermal energy.

Natural energy derived from plantations (biomass of plants and trees for combustion).

Secondary thermal energy released from various installations.

Peat energy.

Wind energy.

Solar energy.

Of these renewable sources, solar energy, recognized as the most environmentally friendly, is poised to become the predominant energy source for humanity, both in the near and distant future. Despite the higher cost of energy derived from renewable sources compared to hydrocarbon-based electricity, the utilization of solar energy for electricity generation is experiencing rapid growth. Scientists and experts from around the world are actively exploring new technologies to procure materials for developing highly efficient solar cells and to reduce the associated electricity generation costs [1-6].

Currently, over 90% of ground-based photovoltaic plants operate utilizing silicon photovoltaic cells. However, the widespread adoption of silicon photovoltaic cells in photovoltaics is hindered by their relatively modest efficiency, which has reached approximately ~20% at the industrial level and around ~25% under laboratory conditions [7-16].

**EXPERIMENTAL RESEARCH**

Nevertheless, silicon remains the primary material among the potential semiconductor materials for solar cell production. A comprehensive analysis of literature data reveals that the limited efficiency of silicon solar cells is predominantly attributed to the fundamental parameters of this material (refer to Table 1), characterized by a narrow band gap, an indirect band gap structure, and low carrier mobility (in comparison to AIIIBV semiconductor compounds). Consequently, it can be argued that without altering the fundamental parameters of silicon, achieving higher efficiency in solar cells based on it is exceedingly challenging [17-25].

**Table 1.** Main fundamental parameters of semiconductor material

|  |  |  |  |
| --- | --- | --- | --- |
| Semiconductor material | Forbidden gap width Eg, eV | Electron mobility, µn, cm2/Vꞏs | Zone  structure |
| Si | 1.12 | 1300 | Indirect zone |
| GaP | 2.26 | 110 | Direct zone |
| GaAs | 1.42 | 8500 | Direct zone |
| GaSb | 0.87 | 5000 | Direct zone |
| InP | 1.35 | 4600 | Direct zone |
| InSb | 0.17 | 80000 | Direct zone |
| InAs | 0.36 | 3300 | Direct zone |

In our quest to produce silicon with binary compounds of elements from the AIII and BV groups, we conducted an assessment of the fundamental conditions required for their formation within the silicon lattice [26-28].

Theoretical calculations and scrutiny of existing experimental findings have highlighted several prerequisites for obtaining binary compounds of elements from groups III and V within silicon:

1. The combined covalent radii of the atoms from groups III and V should closely approximate the sum of two silicon atoms' covalent radii, expressed as:

(RIII+RV) ≈ 2RSi.

2. The electronegativity of atoms from groups III and V should not markedly deviate from that of silicon atoms.

3. The solubility and diffusion coefficients of atoms from groups III and V within silicon, along with their solubility, should closely align.

4. Higher concentrations of atoms from groups III and V are preferable, as lower concentrations diminish the likelihood of binary compound formation during diffusion doping.

5. The stability of formed binary compounds should escalate with increasing bond energy between impurity atoms while decreasing with the rise of impurity-silicon bond energy.

Drawing from these criteria, we evaluated the potential for forming binary compounds composed of elements from groups III and V within a silicon lattice:

• Optimal pairs include BBi, AlP, and GaP.

• Viable pairs encompass BSb, AlAs, and GaAs.

• Feasible pairs consist of BAs, GaSb, and InP.

• Unfavorable pairs involve the remaining elements from groups III and V in various combinations.

The binding energy of atoms involved in binary compounds can significantly differ from those of original silicon atoms, thereby enabling the attainment of distinct energy band gaps based on the chemical bonding energy of impurity atoms within the tetrahedral unit cell of silicon (see Fig.1).



Eg1 – Si = Si = 1,12 eV

Eg2 – Si = АIII

Eg3 – Si = BV

Eg3 – АIIIBV = 2,26 eV

**Figure.1.** a-binary compounds of type AIIIBV in a silicon lattice, b-tetrahedral silicon cell with binary compounds AIIIBV

Samples of silicon doped with phosphorus and gallium impurity atoms were acquired through diffusion from the gas phase within evacuated quartz ampoules. The residual gas pressure in the ampoules did not exceed P = 10-5–10-6 mm Hg. It is recognized that the maximum concentration of impurity atoms in semiconductors is constrained by their solubility limit, contingent on the diffusion temperature and the characteristics of the impurity atoms. At a certain diffusion temperature, the concentration of soluble impurity atoms reaches a peak, beyond which any further temperature increase leads to a decline in their concentration [29-31].

Before diffusing phosphorus and gallium atoms into silicon, the theoretical distribution of the concentration of these impurities in silicon was calculated using the Mathcad program. Figure 2 illustrates typical results of theoretical calculations depicting the distribution of concentrations of phosphorus and gallium impurity atoms after sequential diffusion into the original KEF-100 grade silicon. The diffusion temperature for phosphorus impurity atoms was set at T = 1000 ºC, with a diffusion duration of t = 2 hours, followed by calculations for the subsequent stage of gallium impurity atom diffusion at T =1250 ºC for t = 4 hours [32-36].

However, the sequential method of diffusing phosphorus and gallium impurity atoms is technologically complex and unsuitable for achieving high and uniform concentrations of these impurities, which are necessary to obtain the maximum concentration of the formed binary compounds. Therefore, in further experiments, the method of simultaneous diffusion of both impurities was employed. The diffusant utilized was the chemical compound GaP deposited onto the surface of the original silicon sample.



**Figure 2.** Concentration distributions of impurity atoms after diffusion into silicon, obtained by calculation: 1 – for phosphorus atoms (T = 1000 ºC, t = 2 hours), 2 – distribution of phosphorus atoms after additional thermal annealing (T = 1250 ºC, t = 4 hours) , 3 – for gallium atoms (T = 1250 ºC, t = 4 hours), 4 – gallium atoms in silicon, pre-diffusion doped with phosphorus atoms, 5 – original silicon (KEF-100).

To apply onto the surface of the original silicon, gallium phosphide (GaP) was utilized, which was prepared as a powder with grains ranging from 200 to 300 microns in size, obtained by crushing pure single-crystalline gallium phosphide of the FGEC-1-17 grade. A GaP layer approximately 1 μm thick was deposited onto the surface of the original silicon through vacuum-thermal evaporation of the powder using a VUP-5 vacuum setup equipped with a quartz boat and a tungsten heater. During the heating process, the GaP powder evaporates from the surface of the silicon substrate and also settles on the cooler parts of the inner surface of the quartz boat. As the heating progresses, the surface temperature of the quartz boat rises, causing GaP to evaporate from the boat's surface. During the re-sputtering process, partial decomposition of GaP binary compounds into individual atoms occurs on the boat's surface, resulting in noticeable darkening of the resulting film. In such instances, the GaP deposition process on silicon was halted using a shutter as soon as noticeable darkening commenced. In our scenario, the deposited film exhibits a yellow hue, characteristic of pure single-crystal gallium phosphide.

The simultaneous diffusion of phosphorus and gallium impurity atoms was conducted within the temperature range of T = 1000 – 1250ºC and for a duration of t = 1–10 hours. Subsequent to diffusion, the surface of the silicon samples was cleansed of potential residual contaminants using a chemical solution comprising 30% HCl and 70% HNO3, followed by a rinse in a 10% aqueous solution of HF acid.

Analysis of numerous experimental datasets has revealed that the formation of electrically neutral GaP binary compounds necessitates additional thermal annealing at relatively lower temperatures than the diffusion temperature. This annealing temperature for impurity atoms of phosphorus and gallium falls within the range of T = 850 – 900°C. It has been established that thermal annealing at higher temperatures (T˃1000°C) results in the decomposition of the formed binary compounds.

The results of measuring the absorption spectra of the obtained samples on a Shimadzu 1900i spectrometer revealed that the absorption spectrum of silicon with binary GaP compounds indeed differs from the absorption spectrum of the original silicon (Fig. 3). Using the Taus method (Formula 1), the band gap of the original silicon, pure single-crystal gallium phosphide, and silicon doped with impurity atoms of phosphorus and gallium, obtained through the simultaneous diffusion method, was calculated from the acquired absorption spectra.

Equations for the dependence of the absorption spectrum on the band gap (Taus method)

(1)

(2)

where α is the coefficient of the absorption spectrum, hν represents the photon energy, n denotes the index of the band structure of semiconductors (where n = 2 signifies a direct-gap semiconductor, and n = 1/2 indicates an indirect-gap semiconductor), K is the proportionality coefficient, and Eg represents the band gap of the semiconductor. The resulting calculated values of the band gap were as follows: for initial silicon – 1.126 eV, for single-crystal pure gallium phosphide – 2.255 eV, and for silicon doped with impurity phosphorus and gallium atoms – 1.173 eV.



**Figure 3.** Absorption spectrum of a pure crystal of gallium phosphide (curve 1), initial single-crystalline silicon (curve 2) and silicon with binary compounds of atoms doped with impurity atoms of phosphorus and gallium (curve 3).

Based on calculations of the absorption spectrum of silicon doped with gallium and phosphorus impurity atoms, it was established that the energy value of the band gap is equal to Eg = 1.173 eV, which is 10.7% greater than that of the original silicon. These research results indicate that the formed GaP binaries in silicon have different binding energies between gallium and phosphorus atoms depending on the concentration of the formed binaries.

From the analysis of the research results obtained, it can be assumed that in silicon samples doped with impurity gallium and phosphorus atoms, the band gap width varies from Eg1 = 2.26 eV for the pure GaP binary compound on the silicon surface to the band gap width of pure silicon in the depth of the sample. This indicates the possibility of obtaining a graded-gap structure with a surface layer of silicon and, accordingly, the appearance of an electric field, which increases the coefficient of collection of current carriers in a silicon-based solar cell with GaP binary compounds (see Fig. 4).



**Figure 4.** Distribution of formed GaP binary compounds on the surface and in the near-surface layer of silicon.

With further penetration into the silicon volume, the concentration of binary GaP compounds decreases exponentially. From the analysis of the obtained experimental research results, the distribution of the concentration of atoms of the GaP binary compound in silicon can be divided into four sections:

On the surface, where the concentration of GaP binary compounds is equal to or greater than the concentration of individual silicon atoms in the source material.

The concentration of binary compounds decreases, and neutral molecular compounds of the Si2GaP type appear.

The number of neutral molecular compounds increases, and GaP binary compounds actually disappear.

A region mainly consisting of silicon atoms. This region may contain binary GaP compounds and neutral molecular Si2GaP compounds, but their concentration is much lower than the concentration of the original silicon atoms.

These research results show that on the silicon surface, the concentration of GaP binary compounds will be quite large, and the chemical bond energy between gallium (Ga) and phosphorus (P) atoms has a different value than the chemical bond energy between silicon-silicon atoms, which is equal to the width band gap of silicon (EgSi =1.12 eV). From the analysis of literature data, it was established that the energy value of the band gap of pure binary compounds of gallium phosphide (GaP) is equal to Eg = 2.26 eV.

These research results are in good agreement with the results of theoretical calculations, which showed an increase in the band gap of silicon samples with binary compounds of gallium and phosphorus atoms.

An analysis of these research results shows that silicon samples doped with phosphorus and gallium impurity atoms make it possible to change the fundamental parameter(the energy value of the band gap) of silicon over a wide range, which leads to an expansion of the spectral range of photosensitivity to solar radiation. Additionally, using planar diffusion technology, it is possible to obtain heterovariz-gap structures in the near-surface layer of silicon doped with phosphorus and gallium impurity atoms.

Manufactured silicon-based solar cells with heterovariz-gap structures of GaP binary compounds increase their efficiency by increasing the spectral range of absorption of solar radiation. From the analysis of the results obtained, it was established that the formation of binary compounds of elements of groups III and V in silicon changes the fundamental parameters of the original silicon, enabling the replacement of existing materials based on binary semiconductor compounds in photoenergetics and the creation of photocells with high efficiency in converting solar radiation into electricity.

From the results of studies using a JSM-IT200 scanning electron microscope, the elemental composition of the surface and near-surface layers of silicon doped with phosphorus and gallium impurity atoms showed the formation of GaP binary compounds. These results also confirm that a region enriched with impurity atoms of phosphorus and gallium appears on the surface and in the near-surface layer of silicon, which changes the fundamental parameters (band gap, band structure, and carrier mobility) in the original silicon. From the results of studies of the morphology of the silicon surface using an FM-Nanoview 1000 atomic force microscope, it was established that the sizes of the formed binary compounds depend on the concentration of impurity atoms and modes of diffusion doping technology and can range from several nanometers to several hundred nanometers.

**CONCLUSIONS**

The results of studies of silicon doped with gallium and phosphorus impurity atoms showed that a high concentration (N ~ 1020 – 1021 cm-3) of the formed binary compounds leads to a change in the fundamental parameters of the original silicon. These research results make it possible in the future to create photodetectors with a wide range of photosensitivity and efficient solar cells based on silicon with GaP-Si heterovariant-gap structures obtained by the diffusion of impurity gallium and phosphorus atoms.

Experimental results based on our calculations and our proposed technological solution for producing silicon with new fundamental parameters allow us to open the following directions:

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