Augmenting the Population of Electroactive Sulfur in Crystalline Silicon

Nurullo Zikrillaev[1], Kanatbay Ismailov[2], Bayrambay Ismaylov[2,3], Parakhat Dlimbetov[2] and Alloberdi Saparov[2]
[1]Tashkent State Technical University named after Islam Karimov, Universitetskaya Str. 2, 100095 Tashkent, Uzbekistan
[2]Karakalpak State University named after Berdakh, Ch. Abdirov Str. 1, 230100 Nukus, Uzbekistan
[3]University of Business and Science, Gavhar Str. 1, Yakkabog MFY, Uzbekistan
kanatbay.ismailov@gmail.com, ismaylovb81@gmail.com, dlimbetov8326@gmail.com, alloberdisaparov@gmail.com

Keywords: Sulfur Doping, Two-Stage Diffusion, Crystalline Silicon, Electroactive Impurity Atoms, Deep-Level States, Fermi Level, Hall Effect Measurements, Surface Erosion Suppression, High-Concentration Doping, Infrared Photodetectors, Thermal Sensors, Optoelectronic Applications.

Abstract: A novel two-stage sulfur diffusion technique for doping crystalline silicon has been developed and experimentally validated. The main advantage of the proposed method is the almost complete suppression of surface erosion, which is one of the most critical drawbacks of conventional high-temperature diffusion processes. Systematic studies were carried out on Czochralski-grown p-type silicon samples with different initial boron concentrations, under controlled sulfur vapor pressures ranging from 1.16 atm to 7.32 atm. Electrical parameters were investigated using the Hall effect method, and the total concentration of electroactive sulfur atoms was determined from charge neutrality equations, taking into account the Fermi level position.The results demonstrate that the initial boron concentration has virtually no effect on the incorporation of electroactive sulfur atoms at constant sulfur vapor pressure. In contrast, a strong dependence on sulfur vapor pressure was established: an increase from 1.16 atm to 7.32 atm resulted in nearly a two-order-of-magnitude rise in the concentration of electroactive sulfur atoms, exceeding the maximum values previously reported in the literature by approximately 1.4 orders of magnitude. Complementary studies using SIMS/ToF-SIMS, Raman, and TEM analyses confirmed the distribution of sulfur atoms, the formation of defect-related states, and the microstructural modifications induced by diffusion. These findings highlight the efficiency of the two-stage diffusion approach and its potential for achieving ultrahigh impurity concentrations. From a practical perspective, the method significantly broadens the functionality of sulfur-doped silicon, particularly for the development of infrared photodetectors and highly stable thermal sensors.

1 INTRODUCTION

Atoms of group VI elements such as sulfur, selenium and tellurium in the silicon lattice are of significant scientific and practical interest. This is primarily due to the relatively high density of electroactive sulfur atoms, and secondly, as noted by the authors of [1], [2], at elevated concentrations sulfur atoms can exist in various configurations (S_2, S_4) [3], [4]. Consequently, additional energy levels may arise, which are shallower compared to those introduced by isolated sulfur atoms in silicon ($E_1 = E_C - 0.25$ eV and $E_2 = E_C - 0.46$ eV). Such features significantly broaden the functional capabilities of sulfur-doped silicon, particularly for the design of photodetectors operating in the spectral range $\lambda = 2.1 \div 10$ µm.

A stable and efficient technological route enabling a considerable increase in the concentration of electroactive sulfur atoms in crystalline silicon has not yet been achieved. Furthermore, it should be stressed that traditional methods of sulfur doping are commonly associated with substantial surface deterioration, which complicates their practical implementation in the development of functional semiconductor devices [5]. The integral concentration of electrically active sulfur atoms in the examined silicon specimens was quantitatively determined by solving the charge neutrality condition, with explicit consideration of the Hall effect measurement data (ECOPIA HALL HMS-7000). However, a reproducible and technologically reliable methodology that would enable a controlled increase in the concentration of such impurity atoms has not yet been established. Moreover, conventional approaches to sulfur doping are commonly accompanied by pronounced surface degradation, which substantially restricts the applicability of the resulting materials in semiconductor device fabrication. In this regard, the present investigation introduces an innovative doping strategy that effectively suppresses surface deterioration of silicon and simultaneously provides a significant enhancement in the concentration of electroactive sulfur atoms within the crystal lattice.

2 MATERIALS AND METHODS

As opposed to standard diffusion doping techniques [6], the experimental procedure involved the application of a two-stage diffusion process. For this purpose, silicon samples exhibiting different p-type resistivities were encapsulated in evacuated quartz ampoules along with 5 mg of elemental sulfur, a quantity sufficient to generate a vapor pressure on the order of one atmosphere at the chosen diffusion temperature. The ampoules were initially heated in a furnace from room temperature (t=27 °C) to 580 °C at a rate of 7 °C/min to ensure gradual evaporation of sulfur. Upon completion of the preliminary stage, the quartz ampoules were temporarily removed from the furnace, and the temperature was further raised to T=1200 °C. Thereafter, the ampoules were reintroduced into the high-temperature zone, where diffusion was conducted over a period of 15 hours. To provide a comparative basis, a control series of silicon samples was subjected to diffusion annealing under equivalent thermal and ambient conditions, except that the initial low-temperature stage was omitted.

Experimental results demonstrated that, in all specimens treated with the two-stage diffusion method, virtually no signs of surface degradation of the silicon crystal were observed. In contrast, samples obtained by skipping the preliminary stage typically exhibited pronounced surface erosion.

The electrical parameters of the doped silicon specimens were systematically investigated employing the Hall effect methodology, with all measurements carried out under uniform and controlled conditions. It was revealed that, irrespective of the initial resistivity of the silicon substrate, the concentration of electroactive sulfur atoms in samples processed by the two-stage diffusion technique was nearly 2.4÷3.1 times higher compared with those subjected to direct diffusion at T=1200 °C. These findings suggest that surface erosion may act as a limiting factor, trapping a considerable fraction of sulfur atoms at the surface and thereby reducing their incorporation into the bulk crystal.

For the purpose of verifying the proposed assumption and enriching the dataset with supplementary results, additional experimental studies were undertaken.

3 EXPERIMENTAL RESULTS AND THEIR DISCUSSIONS

For the experimental procedure, three independent series of quartz ampoules were fabricated, each accommodating an identical ensemble of silicon specimens: KDB-0.5 ($N_B=4\cdot10^{16}$ cm^{-3}), KDB-3 ($N_B=7\cdot10^{15}$ cm^{-3}), and KDB-10 ($N_B=2\cdot10^{15}$ cm^{-3}). All investigated specimens were monocrystalline silicon substrates produced by the Czochralski method, exhibiting an oxygen concentration of $N_{O_2}=7\cdot10^{17}$ cm^{-3} and a uniform dislocation density [7]. The ampoules were charged with varying amounts of sulfur, thereby establishing vapor pressures of P=1.16 atm, 3.75 atm, and 7.32 atm. The diffusion process was implemented in a two-stage regime, with the terminal stage performed at a temperature of T=1200 °C for a duration of 15 hours. The ampoules were placed into the furnace simultaneously, ensuring strictly identical diffusion conditions.

This approach allowed us to investigate not only the influence of sulfur vapor pressure on the extent of surface erosion of silicon crystals, but also the effect of sulfur vapor pressure (i.e., concentration of sulfur atoms in the ampoule atmosphere) on the incorporation of electroactive sulfur atoms into silicon samples with identical initial parameters. In addition, the dependence of sulfur atom concentration in the lattice on the initial boron concentration in the substrate was examined under otherwise identical experimental conditions.

The results of the electrical characterization of the samples, obtained using the Hall effect method, are summarized in Table 1, where F denotes the Fermi level position at t = 23 °C and NAS is the total concentration of electroactive sulfur atoms in silicon.

Compositional and morphological analyses of sulfur-doped silicon were performed in order to substantiate the experimental evidence indicating the successful incorporation of sulfur atoms into the silicon lattice. The elemental composition of sulfur-doped silicon, confirming the presence of sulfur, is shown in Figure 1. The surface morphology and distribution of sulfur on the silicon surface are presented in Figure 2.

A comprehensive evaluation of the concentration of electroactive sulfur atoms in the studied specimens was carried out by solving the charge neutrality condition, wherein the results of Hall effect measurements were incorporated as fundamental input. In particular, the calculation was performed using the experimentally determined position of the Fermi level in the samples.

$$N_{Si}=p_0+n+f(E_1)+f(E_2),$$

where:

- p_0 – initial hole concentration in the samples;
- n – electron concentration after diffusion in overcompensated samples;
- $f(E_1)$ – occupancy of the first sulfur energy level in the silicon band gap ($E_1=E_C-0.24$ eV);
- $f(E_2)$ – occupancy of the second sulfur energy level $E_2=E_C$-0.45 eV).

In the case of uncompensated samples, i.e., those in which the conductivity type did not change after diffusion, the concentration of electroactive sulfur atoms (N_{AS}) was determined by the relation:

$$N_{AS} = p,$$

where p is the hole concentration in the samples after sulfur diffusion.

Table 1: Electrical characteristics of silicon samples after two-stage sulfur diffusion.

Doping conditions	ρ, Ω·cm	ρ, Ω·cm	μ, cm²/V·s	Type	F, eV	N_{AS}, cm^{-3}
1200° C 1,16 atm	0,5	2,5	290	p	0,192	5,2×10^{16}
	3	0,9	1210	n	0,205	1,5×10^{17}
	10	0,45	1210	n	0,195	2×10^{17}
1200°C 3,75 atm	0,5	0,75	1220	n	0,205	4,5×10^{17}
	3	0,50	1110	n	0,193	2,9×10^{17}
	10	0,35	1170	n	0,185	3,8×10^{17}
1200°C 7,21 atm	0,5	0,60	1180	n	0,195	5,6×10^{17}
	3	0,45	1190	n	0,190	2,8×10^{17}
	10	0,35	1250	n	0,185	4,9×10^{17}
1200°C 7,32 atm	0,5	0,41	1210	n	0,185	10^{18}

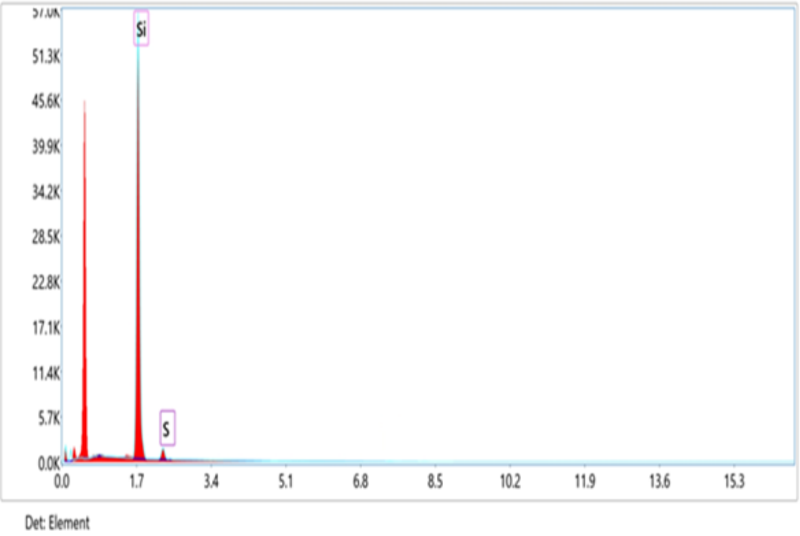
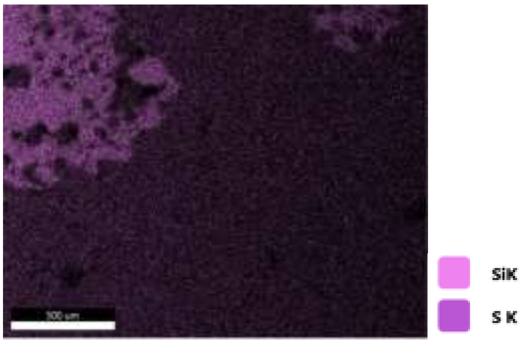


Figure 1: Full spectrum of elemental composition of impurity sulfur atoms in silicon (Zeiss EVO MA10).

Element	*Weight %*	*MDL*	*Atomic %*	*Net Int.*	*R*	*A*	*F*
Si K	91.2	0.10	92.5	545.3	0.9094	0.7426	1.0031
S K	8.1	0.28	7.2	16.1	0.9166	0.3279	1.0037

(a)



(b)

Figure 2: Composition and morphology of surface sulfur in silicon: a) elemental composition map; b) surface morphology image.

As shown in Table 1, at a fixed sulfur vapor pressure the initial boron concentration in the samples has practically no effect on the final concentration of electroactive sulfur atoms in silicon, although the boron content varied by a factor of 20. In contrast, the concentration of electroactive sulfur atoms exhibits a pronounced dependence on the sulfur vapor pressure in the ampoules, even for samples with identical initial parameters.

The performed experiments revealed a strong dependence of the concentration of electroactive sulfur atoms in silicon on the sulfur vapor pressure in the ampoules. When the vapor pressure was increased from 1.16 atm to 7.32 atm, i.e., by almost a factor of six, the concentration of electroactive sulfur atoms rose by nearly two orders of magnitude. Notably, this value is approximately 1.42 orders of magnitude higher than the maximum concentrations reported in earlier works [8]-[11].

Such a significant enhancement can be explained by the suppression of surface erosion during the two-stage diffusion process. In conventional high-temperature sulfur diffusion, erosion of the silicon surface leads to partial retention of sulfur atoms at the boundary, thereby limiting their incorporation into the bulk lattice. In contrast, the applied method minimizes surface degradation, which promotes deeper diffusion of sulfur atoms and a higher degree of their electrical activation. This indicates that optimization of vapor pressure, together with two-stage thermal treatment, represents a key factor for achieving high concentrations of electroactive sulfur atoms in crystalline silicon.

4 CONCLUSIONS

The results of the present investigation provide a comprehensive understanding of the influence of diffusion conditions on the incorporation of sulfur atoms into the crystalline lattice of silicon. The application of a specially developed two-stage diffusion procedure has demonstrated its high efficiency in almost completely eliminating surface erosion of silicon, which traditionally constitutes one of the most critical technological challenges during the introduction of group VI elements. The practical significance of this approach lies in its universality: the methodology can be extended to other deep-level impurities such as selenium and tellurium, for which diffusion processes are typically accompanied by intense surface degradation, thereby considerably limiting their applicability. Thus, the developed method opens new opportunities for expanding the technological base of controlled doping of silicon with deep-level impurities.

A detailed analysis of the electrical characteristics of the obtained samples has shown that the concentration of initial boron atoms in the substrate exerts an almost negligible effect on the resulting concentration of electroactive sulfur atoms at a fixed vapor pressure. This observation is particularly important, since it confirms that the efficiency of sulfur activation in silicon is determined predominantly by external diffusion parameters rather than the background level of shallow acceptor doping. At the same time, it was clearly established that the concentration of electroactive sulfur atoms exhibits a strong and non-linear dependence on the vapor pressure of sulfur in the diffusion ampoules. An increase in sulfur vapor pressure by nearly six times leads to a rise in the concentration of electroactive atoms by almost two orders of magnitude, which significantly exceeds the maximum values previously reported in the literature [8]–[11]. This finding convincingly demonstrates that the sulfur vapor pressure is the decisive technological parameter controlling the degree of impurity activation.

From a broader scientific and practical perspective, these results contribute to the understanding of fundamental mechanisms of impurity incorporation in semiconductors and simultaneously highlight promising directions for applied research. The possibility of achieving ultrahigh concentrations of electroactive sulfur atoms in silicon not only deepens our knowledge of defect-impurity interactions but also provides a technological pathway for creating new classes of semiconductor materials with tailored electronic properties. In particular, sulfur-doped silicon obtained under optimized diffusion conditions may serve as a promising material for the fabrication of infrared photodetectors operating in the 2.1÷10 μm spectral range, with performance metrics: $NEP = 7\times10^{-14}$ W/√Hz, responsivity $R = 71$ A/W, and detectivity $D^* = 2\times10^{10}$ cm·√Hz/W These findings confirm the suitability of the material for optoelectronic and thermal sensing applications. The ability to control the concentration of deep-level impurities in a predictable manner significantly broadens the functionality of silicon and opens up prospects for its use in advanced optoelectronic and sensor applications.

In summary, the work carried out demonstrates that careful optimization of diffusion parameters, especially the sulfur vapor pressure, makes it possible to obtain fundamentally new regimes of deep-level impurity doping in silicon. The proposed two-stage diffusion technique ensures the technological reliability of the process, minimizes surface degradation, and enables a controllable increase in the concentration of electroactive sulfur atoms to unprecedented levels. These results are expected to stimulate further research on the diffusion of chalcogen atoms in semiconductors and promote the development of new functional devices based on modified silicon structures.

REFERENCES

[1] A. A. Taskin, “Deep boron levels in silicon,” Semiconductors, vol. 36, no. 10, pp. 1083–1087, Oct. 2002, doi: 10.1134/1.1518016.

[2] A. A. Taskin and Ye. G. Tishkovskiy, “Formation of complexes associated with selenium atoms in silicon,” Semiconductors, vol. 36, no. 6, pp. 620–624, Jun. 2002, doi: 10.1134/1.1484697.

[3] Yu. A. Astrov et al., “Broadband IR photoconductivity of silicon p–n junctions with hyperdoped layers,” Semiconductors, vol. 47, no. 2, pp. 211–215, Feb. 2013, doi: 10.1134/S1063782613020120.

[4] A. Milnes, Deep-Level Impurities in Semiconductors. Moscow, Russia: Mir Publishers, 1976 (translated from Wiley, 1973).

[5] M. G. Milvidskiy, “Giredmet’s contribution to semiconductor technology development,” Semiconductors, vol. 32, no. 1, pp. 3–18, Jan. 1998, doi: 10.1134/1.5013313.

[6] B. I. Boltaks, Diffusion and Point Defects in Semiconductors. Leningrad, USSR: Nauka, 1972 (in Russian).

[7] G. Wang et al., “Hyperdoped silicon for infrared photonics,” Nature Photonics, vol. 13, pp. 770–775, Nov. 2019, doi: 10.1038/s41566-019-0530-4.

[8] Y. Yang et al., “Sulfur-hyperdoped silicon: mechanisms, properties and applications,” Advanced Optical Materials, vol. 9, no. 7, Art. no. 2001782, Apr. 2021, doi: 10.1002/adom.202001782.

[9] T. E. Murphy, “Recent advances in hyperdoped silicon for optoelectronics,” Applied Physics Reviews, vol. 9, no. 4, Art. no. 041315, Oct. 2022, doi: 10.1063/5.0097375.

[10] B. K. Ismaylov, N. F. Zikrillayev, K. A. Ismailov, and Z. T. Kenzhaev, “Physical mechanism of gettering of impurity Ni atom clusters in Si lattice,” Semiconductor Physics, Quantum Electronics & Optoelectronics, vol. 27, no. 3, pp. 294–297, 2024, doi: 10.15407/spqeo27.03.294.

[11] E. B. Saitov and U. M. Akhmedov, “Tracking maximum power point of photovoltaic modules,” in AIP Conference Proceedings, vol. 2789, Art. no. 060005, 2023, doi: 10.1063/5.0145470.