

Infrared photoconductivity of chalcogen-doped silicon

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Abstract. Hyperdoping is the incorporation of impurities into semiconductors with concentrations exceeding the equilibrium solubility by orders of magnitude ($\sim 10^{20} \text{ cm}^{-3}$). It opens the way to the formation of impurity bands in the silicon band gap. The chalcogens' (S, Se, Te) incorporation allows to achieve enhanced absorption coefficient ($10^2 - 10^4 \text{ cm}^{-1}$) in the infrared range (1–6 μm) due to subband transitions. The review covers the mechanisms of formation of impurity states, synthesis methods (ion implantation, laser processing), as well as structural, electrical, and optical properties. A special focus is on the application in infrared photodetectors operating at room temperature and solving instability problems (segregation, defects) through annealing optimization, selective doping, and heterostructures.

Keywords: silicon, chalcogens, doping, ion implantation, pulsed laser annealing, melting, crystallization, deep levels, impurity band, photodetector

1. Introduction

Single-crystal silicon (Si), possessing a diamond-like cubic lattice (space group $Fd\bar{3}m$), remains a key structural and functional material for micro- and optoelectronics owing to its unique combination of physical properties. The high electron mobility ($\mu_e \approx 1400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and hole mobility ($\mu_h \approx 450 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) at room temperature in Si results from weak carrier scattering by acoustic phonons, which

makes it an efficient charge conductor. The availability of the thermodynamically stable chemical compound SiO_2 , which is based on silicon and possesses dielectric properties and is technologically compatible with thin-film deposition processes, ensures high device reliability and reproducibility. The wide optical transparency range (1.1–20.0 μm) opens up opportunities for applications in integrated photonics [1], and the ability to precisely control electronic characteristics through doping enables the fabrication of heterostructures with tailored parameters [2, 3].

However, the rapid development of quantum technologies, next-generation optoelectronics, and hybrid materials requires substantial modification of the electronic structure of semiconductor systems, including basic elements such as silicon [4]. One of the fundamental limitations of its application in photonic devices is the indirect nature of the band gap ($E_g = 1.12 \text{ eV}$ at 300 K), in which the absolute conduction band minimum is located at the Δ -point, while the valence band maximum is at the Γ -point. This arrangement of the energy band extrema implies the mandatory participation of phonons with a wave vector of $\sim 0.85(2\pi/a)$ to satisfy the law of quasi-momentum conservation during optical transitions. Such a band structure character limits optical absorption to wavelengths below 1.1 μm , and also drastically reduces the radiative recombination probability — by approximately five orders of magnitude — compared to direct-bandgap semiconductors such as GaAs or InP.

To overcome these limitations, methods for the deliberate creation of localized states within the band gap through the formation of deep impurity levels have been actively developed [5]. According to effective mass theory, impurity atoms with a large atomic radius in silicon ($R_B \approx 10 \text{ \AA}$) create deep discrete donor and acceptor levels (E_d, E_a). At concentrations exceeding $\sim 10^{19} \text{ cm}^{-3}$ these levels overlap and form impurity bands with a width of $\Delta E_{IB} \approx e^2 N_d^{1/3} / (4\pi\epsilon_0\epsilon)$ (e — electron charge; N_d — impurity concentration) [6]. In this context promising method is doping with transition metals (Au, Ti, V) [7, 8] and chalcogens (S, Se, Te) [9, 10], which form deep levels with high ionization energies ($E_i \gg k_B T$). Using the density functional theory [11] quantum-chemical calculations confirm the formation of chalcogen donor states ($E_d =$

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$E_c - (0.1-0.6)$ eV) and transition metal acceptor levels ($E_a = E_v + (0.2-0.8)$ eV), accompanied by significant hybridization of d-orbitals with the valence band and conduction band.

Modern approaches to the electronic structure of silicon engineering are based on understanding of the physical mechanisms emerging under extreme synthesis conditions. The technological implementation of such synthesis methods comprises three key stages [12]: preliminary ion implantation, laser or rapid thermal treatment, and subsequent liquid-phase epitaxial recrystallization (LPER), each having a rigorous physical justification. In particular, the LPER process requires the transition of the material's surface layer into the liquid state ($T > T_m \approx 1687$ K for Si) on time scales of the order of 10^6-10^9 s [13]. From the perspective of condensed matter physics [14], this leads to: (1) breaking of chemical bonds and dissolution of impurity atoms in the liquid phase; (2) epitaxial restoration of the crystal lattice at a velocity of $V \approx 1-10$ m s⁻¹, described by the Frank–Read model [15]; (3) efficient incorporation of impurity atoms into regular lattice sites due to rapid solidification. Here, the cooling rate must exceed 10^{10} K s⁻¹ in order to suppress precipitation processes and the formation of secondary phases.

The combination of these physical mechanisms opens up the possibility of creating metastable solid solutions with impurity concentrations exceeding the equilibrium solubility limits by 2–3 orders of magnitude ($> 10^{18}$ cm⁻³). These systems are characterized by extended phase diagrams, the emergence of new metastable phases and the modification of thermodynamic potentials. Thus, modern silicon modification technologies represent a synthesis of fundamental physical principles and precision technological methods. Such an approach makes it possible to overcome the intrinsic limitations of equilibrium systems and also to create new classes of functional materials with unique electro-optical properties that provide significant absorption via impurity-to-band transitions, which opens up broad prospects for the development of quantum computing, integrated photonics and next-generation hybrid semiconductor systems.

This review presents an analysis of the physical mechanisms governing the formation of deep impurity states of chalcogens (S, Se, Te) in single-crystal silicon under hyperdoping regimes. The main approaches to creating nonequilibrium impurity concentrations exceeding the equilibrium solubility limits by several orders of magnitude ($> 10^{18}$ cm⁻³) are considered, which leads to the formation of impurity bands within the semiconductor band gap. Optical transitions between impurity levels and conduction bands that give rise to efficient absorption in the infrared wavelength range of 1–6 μ m are analyzed. The structural and electronic characteristics of hyperdoped layers formed by ion implantation and laser processing techniques are investigated. Fundamental issues associated with the thermodynamic instability of these systems, including impurity precipitation and secondary phase formation, are discussed, along with possible ways to address them. The potential of hyperdoped silicon for practical application in infrared photodetectors operating at room temperature is demonstrated.

1.1 Electronic structure and properties of silicon

Silicon, which is a Group IV element of the periodic table, has a diamond-type crystal lattice in the solid phase, which is

formed through sp³ hybridization of the outer electron orbitals and tetrahedral coordination of the atoms. Modern experimental investigation techniques, such as angle-resolved photoemission spectroscopy, as well as theoretical approaches based on density functional theory, have enabled a high degree of detail in the band structure of this material to be achieved. The electronic structure of silicon is characterized by a complex multilevel configuration of the valence band, the maximum of which is located at the central point of the Brillouin zone, Γ . The conduction band has a minimum near the Δ -point, corresponding to the direction between the zone center (Γ) and the X point, at a distance of $\sim 0.85 (2\pi/a)$ from the Γ -point to X.

A more detailed understanding of the mechanisms of light interaction with the electronic states of the material has been obtained through modern studies of the optical properties of silicon, such as variable-angle spectroscopic ellipsometry, Fourier-transform infrared (IR) spectroscopy and spectrophotometry. Fundamental absorption in silicon is associated with two main types of electronic transitions. Direct optical transitions between the valence band and the conduction band at the Γ point of the Brillouin zone ($\Gamma'_{25V} \rightarrow \Gamma_{15C}$) occur at an energy of 3.4 eV, corresponding to the ultraviolet spectral region [16]. Indirect optical transitions ($\Gamma'_{25V} \rightarrow \Delta_C$), which are characteristic of photons with energy of 1.12 eV and higher, and which dominate in the visible and near-infrared range, exhibit a pronounced temperature dependence of the band gap, which can be described by the empirical formula $E_g(T) = 1.17 - (4.9 \times 10^{-4} T^2)/(T + 655)$ [17], where the temperature T is expressed in Kelvin. This relationship accounts for the influence of thermal lattice expansion and electron-phonon interaction on the band structure.

The indirect band-gap structure of silicon has a significant influence on both its optical and transport properties. The effective masses of charge carriers, calculated based on the analysis of energy-level dispersion, amount to $m_e = (0.36 \pm 0.02)m_0$ for electrons, where m_0 is the free electron mass, and $m_h = (0.49 \pm 0.01)m_0$ for heavy holes [18]. These values play a key role in determining the transport characteristics of silicon devices.

Considering the mechanisms of optical absorption in crystalline silicon, two characteristic energy regions should be distinguished. For photons with energies from 1.12 eV (≤ 1.1 μ m), corresponding to the indirect transition ($\Gamma'_{25V} \rightarrow \Delta_C$), the intrinsic absorption of the semiconductor dominates (from 10^3 cm⁻¹), formed by the injection of valence electrons across the band gap into the conduction band. For the energy region below 1.12 eV, the level of optical absorption decreases significantly and, for crystalline c-Si, amounts to less than 10^0 cm⁻¹. The residual absorption in the near- and mid-IR spectral range consists of absorption by charge carriers, localized states, and the crystal lattice [19]. Moreover, the highest level is exhibited specifically by absorption on localized states, which can be formed by the presence of defects or impurities in the silicon crystal lattice [20].

Thus, the introduction of impurity centers, i.e., doping, is one of the most effective ways to control not only the electrical but also the optical properties of silicon. Therefore, for a qualitative review of chalcogen-doped silicon structures, a classification of impurity elements according to their characteristics and influence on the properties of silicon is necessary.

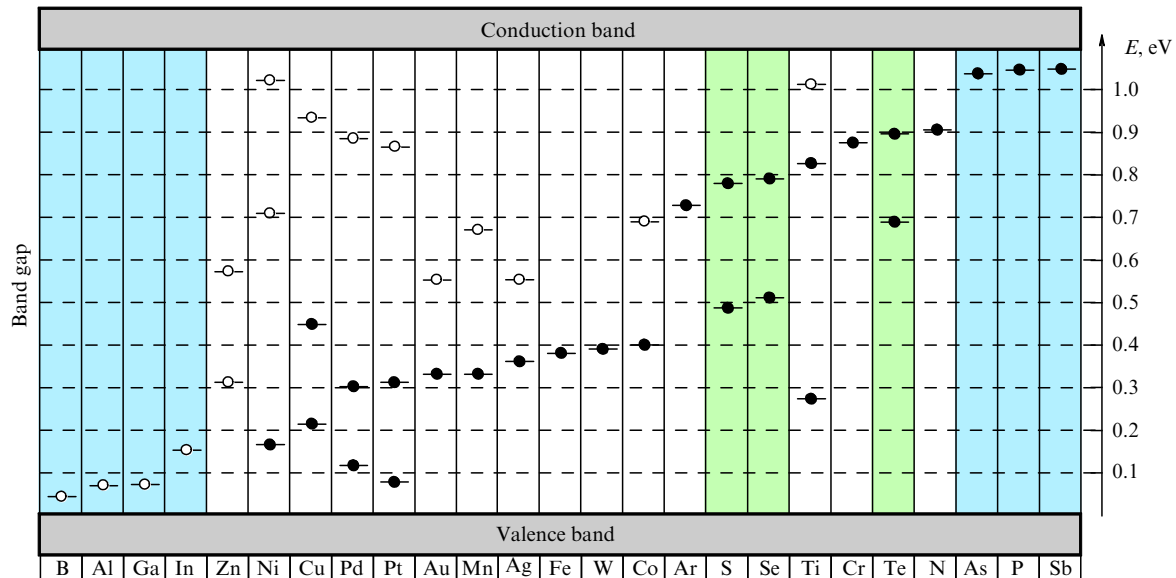


Figure 1. Main energy levels of impurity atoms in silicon. Blue region — shallow impurity region; white region — deep-level region. Filled circles — donor levels; empty circles — acceptor levels. Chalcogens are highlighted in green. (Adapted from [22].)

1.2 Classification of impurities and their influence on the properties of silicon

Systematization of impurity centers in silicon plays a key role in understanding and controlling its electronic and optical properties, especially in the development of new functional materials for optoelectronics. Within the framework of this review, the analysis is focused on chalcogen donor impurities: sulfur (S), selenium (Se), and tellurium (Te). A classification is proposed based on three key characteristics: the ionization energy of the impurity level, the type of conductivity created, and the diffusion kinetics of impurity atoms. Such an approach enables more accurate prediction of the behavior of hyperdoped material and optimization of the technological processes for its fabrication.

1.2.1 Energy characteristics of impurity levels. The impurity ionization energy (ΔE ; Fig. 1) is a key parameter determining its electronic properties. According to this criterion, impurity levels in silicon are typically divided into shallow ($\Delta E < 0.1$ eV) and deep ($\Delta E > 0.1$ eV). The introduction of Group V elements (P, As, Sb) into the silicon crystal lattice leads to the formation of shallow donor levels located near the bottom of the conduction band. The ionization energies of these levels, which determine the depth of their occurrence in the band gap, are 45 meV (P), 54 meV (As), and 43 meV (Sb), respectively. When silicon atoms are substituted by Group III elements (B, Al, Ga), shallow acceptor levels are formed, located near the top of the valence band. The corresponding ionization energies are: 45 meV (B), 72 meV (Al), 74 meV (Ga).

Chalcogens belong to the category of deep double donors with ionization energies in the range of 0.2–0.6 eV relative to the conduction band bottom (E_c). Sulfur, for example, forms two donor levels at ~ 0.32 eV and ~ 0.61 eV below E_c , which makes it weakly ionizable at room temperature. Theoretical models based on density functional theory (DFT) confirm the localized nature of chalcogen donor levels and their weak dependence on the environment [21]. These data are consistent with experimental measurements, including photoconductivity spectroscopy and the Hall effect, and enable more accurate prediction of the electronic properties of doped silicon.

1.2.2 Type of conductivity created. In doped semiconductors, the type and magnitude of conductivity depend directly on the ionization of the corresponding impurity centers. All chalcogens in silicon exhibit a donor nature upon ionization, providing n-type conductivity. The ionization of chalcogen levels at room temperature is described in terms of the distribution of electrons at donor levels, which depends on the product of their concentration and the Fermi–Dirac distribution function [23]:

$$n_d \approx N_d \left[1 + \frac{1}{2} \exp \left(\frac{E_d - E_F}{kT} \right) \right]^{-1}.$$

In experiments at high chalcogen concentrations (above 10^{20} cm^{-3}), semiconductor degeneracy occurs and an impurity band is formed. This leads to metallic degeneracy of the electron gas and changes in transport properties, including a sharp decrease in mobility due to enhanced scattering on ionized impurities.

1.2.3 Diffusion of impurities in silicon. Diffusion of impurities in the silicon crystal lattice is a thermally activated process that plays a key role in shaping the electrophysical and optical properties of the material. Compared with the diffusion of traditional doping elements, the diffusion pattern of chalcogens—sulfur, selenium, and tellurium—differs due to their unique electronic structure and the nature of their interaction with the silicon lattice.

In single-crystal silicon, two main solid-phase diffusion mechanisms are realized: interstitial and substitutional. Chalcogens predominantly occupy substitutional positions, similar to Group V atoms (e.g., phosphorus), but diffuse mainly as an interstitial impurity [24]. The kinetics of this process are described by the Arrhenius equation:

$$D = D_0 \exp \left(-\frac{E_a}{kT} \right),$$

where D is the diffusion coefficient; D_0 is a pre-exponential frequency factor; E_a is the diffusion activation energy.

For sulfur in silicon, the experimentally determined values are $D_0 = 4.7 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ and $E_a = 1.8 \text{ eV}$, which indicates a significant activation energy characteristic of substitutional diffusion [25]. At a temperature of $\sim 1100^\circ\text{C}$, the diffusion coefficient of sulfur is of the order of $\sim 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, which is several orders of magnitude larger than that of conventional donors, e.g., phosphorus ($\sim 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) [23]. This testifies to the complex nature of the diffusion mechanism, involving interaction with vacancies and the formation of temporarily stabilized complexes. Meanwhile, at temperatures above 1414°C in liquid silicon, the diffusion coefficient for most impurities increases by several orders of magnitude to values of $10^{-4} \text{ cm}^2 \text{ s}^{-1}$.

Moreover, the solubility of chalcogens in silicon also exhibits a strong temperature dependence, described by the equation:

$$C_{\max} = C_0 \exp\left(-\frac{\Delta H_{\text{sol}}}{kT}\right),$$

where ΔH_{sol} is the heat of dissolution.

For sulfur in solid silicon, the maximum equilibrium solubility is $\sim 10^{16} \text{ cm}^{-3}$ at a temperature of $\sim 1300^\circ\text{C}$ [24]. Attempts to exceed this limit give rise to the problem of segregation and formation of secondary phases, such as silicon sulfides (SiS_2), which reduce the optical and electrical homogeneity of the material. Therefore, promising synthesis technologies are nonequilibrium doping methods (e.g., ion implantation or laser processing), which enable concentrations of up to 10^{20} cm^{-3} and above to be achieved, as required to provide significant impurity absorption.

1.3 Methods of nonequilibrium silicon doping

The challenge of creating localized states in the form of deep impurity levels requires the controlled incorporation of chalcogen atoms into crystalline silicon at concentrations above the equilibrium solid solubility limit, while preventing their precipitation. Moreover, conventional gas-phase doping by diffusion of impurity elements into the bulk of the semiconductor does not allow such concentration levels to be achieved [26]. A breakthrough in this area has become possible owing to the development of nonequilibrium doping methods, in particular the combination of ion implantation and pulsed laser annealing (PLA) [27, 28]. This approach enables the formation of layers with impurity concentrations of up to $\sim 10^{21} \text{ cm}^{-3}$, unattainable under thermodynamic equilibrium, as well as the restoration of the crystal lattice with minimal defect density. As a result, excitation of IR photoconductivity and a significant increase in the absorption coefficient in the $1.1\text{--}20 \mu\text{m}$ range are observed. Although several mechanisms for incorporating impurities into the crystal lattice are known today: growth of crystals with a predetermined composition [29], irradiation with charged particles [30], ion implantation and laser processing [31, 32], the most versatile and controllable method remains ion implantation, which allows precise dosing of the impurity and adjustment of its depth profile. However, high-dose implantation processes are often accompanied by amorphization of the crystal structure and accumulation of defects, which require subsequent recrystallization [33]. For this purpose, various annealing regimes are used: from conventional thermal annealing ($10^1\text{--}10^4 \text{ s}$) to pulsed annealing ($10^{-6}\text{--}10^{-1} \text{ s}$), including flash lamp annealing (FLA) and laser processing. Particularly promising is nanosecond pulsed laser annealing, which realizes LPER, making it possible to achieve minimal defect density and maximum concentration of electrically active impurity [34]. Figure 2 presents the time scale of the processes associated with

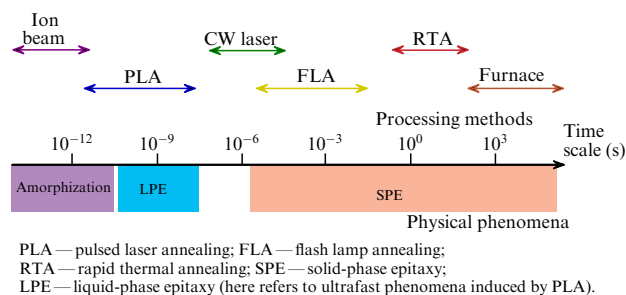


Figure 2. Approximate time scales characterizing various Si processing techniques. (Adapted from [12].)

the penetration and stopping of ions in a solid, as well as the subsequent recrystallization of the implanted layers under liquid-phase and solid-phase epitaxy conditions. This scheme makes it possible to determine the optimal doping and annealing parameters for obtaining silicon structures with predetermined electronic and optical properties.

2. Review of early research on silicon doping with chalcogens (1950s–1990s)

Investigations of the impurity photoconductivity effect in silicon were initiated in the mid-20th century, during the 1950s–1960s. During this period, a number of fundamental works were carried out devoted to the analysis of incorporated impurities impact on the optical and electrophysical semiconductor materials properties. The key results of the research of this period are systematized in the Robert Bube's monograph (1960) [35] and presented in Table 1, which gives the ionization energies of the main donor and acceptor levels, as well as the calculated and experimentally determined long-wavelength photoconductivity cutoffs (λ^*) for various impurity centers in silicon.

Group III and V impurities of the Periodic Table of Elements, such as boron, aluminum, phosphorus, arsenic, and antimony, form shallow donor or acceptor levels with low ionization energies (less than 0.1 eV). This results in the corresponding transitions under IR radiation excitation occurring in the far-IR range ($> 20 \mu\text{m}$). However, since significant thermal ionization of these levels takes place at room temperature, experimental investigations of the photoconductivity of such systems were performed at cryogenic temperatures (typically down to liquid nitrogen temperature, $\sim 77 \text{ K}$), in order to minimize the background current. In contrast, impurities that form several energy levels, for example, transition metals (Cu, Au, Fe, Mn) and chalcogens (Se, S, Te), are characterized by large ionization energy values exceeding 0.1 eV . Accordingly, their long-wavelength photoconductivity cutoff shifts into the mid-IR spectral range ($\sim 1\text{--}5 \mu\text{m}$), which opens up the potential possibility of creating IR detectors based on doped silicon.

In the 1970s–1990s, the attention of researchers was focused on the incorporation of chalcogen atoms, in particular selenium, sulfur, and tellurium, into the silicon crystal lattice [36]. These impurities exhibit a double donor nature, creating two deep levels in the silicon band gap, which makes them promising for realizing photoconductivity in the IR spectral region. In the earliest works, impurity atoms of selenium, sulfur, and tellurium were incorporated into silicon wafers under equilibrium conditions by means of diffusion at temperatures up to 1300°C , which was dictated by the

Table 1. Ionization energies and long-wavelength photoconductivity cutoffs of some impurities in Si [35].

Impurity	Periodic table group	Donor (D) or acceptor (A)	$E_c - E_I$, meV	$E_I - E_v$, meV	Calculated long-wavelength cutoff λ^* , μm	Observed long-wavelength cutoff λ^* , μm
Li	I	D	33	—	38.0	—
Cu	I	A	—	490	2.5	2.5
		D	—	240	5.2	5.2
Au	I	D	—	330	3.8	3.8
		A	540	—	2.3	2.1
Zn	II	A	550	—	2.3	2.3
		A	—	300	4.1	4.1
B	III	A	—	45	28.0	30.0
Al	III	A	—	57	22.0	—
Ga	III	A	—	65	19.0	—
In	III	A	—	160	7.7	9.0
P	V	D	44	—	28.0	—
As	V	D	49	—	25.0	—
Sb	V	D	39	—	32.0	—
Mn	VII	D	530	—	2.3	2.1
		D	530	—	2.3	2.3
Fe	VIII	D	—	400	3.1	3.1
		D	—	400	3.1	3.1

feasibility of diffusional doping from gas media. However, this limited the concentration of impurities to the equilibrium solubility level of $\sim 5 \times 10^{16} \text{ cm}^{-3}$. Later, ion implantation began to be applied to increase the impurity concentration, but the subsequent thermal annealing still resulted in equilibrium concentrations. Below, we consider the main scientific research conducted before 2000, aimed at investigating both the electronic properties of silicon doped with selenium, sulfur, and tellurium (Si:Se, Si:S, Si:Te, respectively) and the IR photoconductivity of the obtained structures.

The first observations of IR photoconductivity in Si:Se were reported by Sultanov (1975) [37] and Kozlov with Zhdanovich (1976) [38]. Later, the research group of Vydyanath et al. (1978–1979) [39, 40] investigated in detail the diffusion processes of selenium in p-Si doped with boron, gallium, aluminum, and indium. The maximum Se concentration reached $\sim 7 \times 10^{16} \text{ cm}^{-3}$, and the process itself was accompanied by conductivity type inversion, which confirms the donor nature of the impurity. The presence of two donor levels was established: $E_c - 0.3 \text{ eV}$ and $E_c - 0.2 \text{ eV}$, the latter of which is associated with a Se-acceptor complex. Based on the obtained structures, the first n–p junctions were created, demonstrating a detectivity of $1.5 \times 10^{11} \text{ cm Hz}^{1/2} \text{ W}^{-1}$ at a wavelength of $3.8 \text{ }\mu\text{m}$ at a temperature of 90 K .

In the early 1980s, the investigations were expanded by the research of N. Sclar [41–43], who studied the low-temperature photoconductivity of Si:S and Si:Se doped by diffusion at 1200°C under various pressures of the impurity-containing gas. To increase the concentration of electrically active centers, quenching after annealing was employed. The experiments demonstrated a photoconductivity peak at wavelengths of $5.5 \text{ }\mu\text{m}$ (Si:S) and $3.5 \text{ }\mu\text{m}$ (Si:Se) at a temperature of 78 K .

For a more precise understanding of the electronic structure of chalcogen impurity levels in silicon, in 1980–

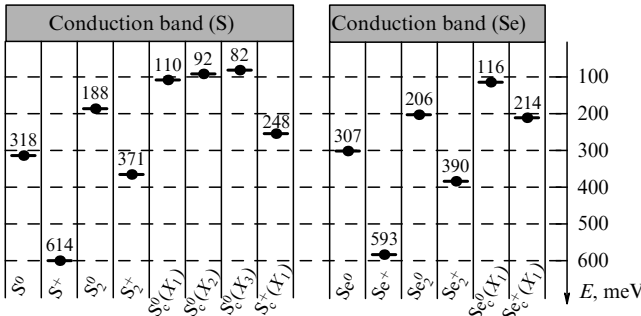


Figure 3. Ionization energy values of donor levels of sulfur and selenium depending on their localization in the silicon crystal lattice (ionization energies are given in meV as absolute values measured from the silicon conduction band bottom). (Adapted from [46].)

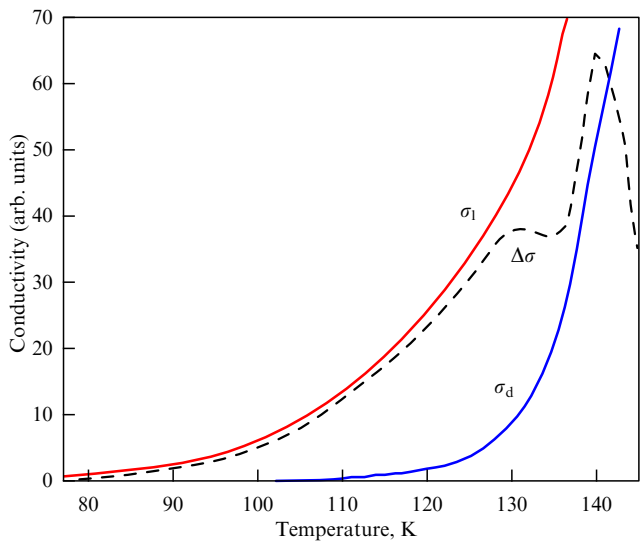


Figure 4. Temperature dependence of conductivity for a Si:Se sample (σ_d — dark conductivity, σ_1 — photoconductivity under illumination with photon energy of 0.35 eV , $\Delta\sigma = \sigma_1 - \sigma_d$). (Adapted from [49].)

1984 the Swedish research group of Grimmeiss et al. carried out investigations using the diffusion method at 960°C with equilibrium concentrations of $(0.2\text{--}2.0) \times 10^{15} \text{ cm}^{-3}$ [44–46]. As a result, the ionization energies of Se and S levels were refined depending on their localization in the lattice (Fig. 3) — isolated and dimer states, substitutional positions. It was also established that chalcogens behave as double donors, forming two deep levels in the band gap (the first two states in Fig. 3: neutral and ionized).

Research on Si:Te was initiated in 1981 by the same research group [47]. Tellurium, similarly to Se and S, formed two donor levels with energies of $E_c - 0.199 \text{ eV}$ and $E_c - 0.411 \text{ eV}$ for the isolated states of tellurium Te^0 and Te^+ , respectively, which is confirmed by DLTS (deep-level transient spectroscopy) analysis data.

An important step was the application of the ion implantation method to achieve higher impurity concentrations. In 1985, a group of scientists from the Ioffe Physical-Technical Institute [48, 49] reported results on doping silicon with selenium at an ion energy of 100 keV and a dose of 10^{15} cm^{-2} . After annealing at 1000°C , an increase in photoconductivity was observed at temperatures below $130\text{--}140 \text{ K}$, whereas at higher temperatures the signal disappeared owing to thermal emission of electrons from the $E_c - 0.2 \text{ eV}$ level (Fig. 4). The authors also noted that a similar effect had

Table 2. Photodetector structures based on silicon doped with chalcogens. Characteristics of an InGaAs p–i–n photodiode are presented as a comparison.

Impurity	Layer structure	Detectivity, $\text{cm Hz}^{1/2} \text{ W}^{-1}$ (wavelength)	Temperature, K	Reference
Si:Se	n–p	1.5×10^{11} (3.8 μm)	90	[40]
Si:Se	n–p	2.2×10^{11} (3.5 μm)	120	[41]
Si:S	n–p	0.5×10^{11} (5.5 μm)	80	
InGaAs (as a comparison)	p–i–n	$10^{11}–10^{14}$ (1.5 μm)	300	[50]

most likely been detected in one of the aforementioned studies by N. Sclar [41]. This effect was attributed to the dominance of dark current caused by low-energy states, such as Se_2^0 dimers and clusters.

Thus, despite the promising results of early investigations, all silicon samples doped with chalcogens known at that time exhibited pronounced photoresponse only at cryogenic temperatures (Table 2). This is explained by the fact that equilibrium doping and subsequent steady-state thermal annealing led to the formation of predominantly neutral dimers and clusters (Se_2^0 and S_2^0 , etc.), which create shallow levels with ionization energies of < 0.2 eV. Deep levels associated with isolated chalcogen atoms in substitutional positions (Se^0 , S^0 , Se^+ , S^+) had a low concentration, which limited the efficiency of IR photoconductivity at room temperature. Consequently, achieving photoconductivity at room temperature required the development of new doping approaches capable of increasing the concentration of deep impurity levels and preventing the formation of impurity dimers and clusters. Such tasks became the subject of further research in the late 20th and early 21st centuries.

3. Review of modern research on silicon doping with chalcogens (2000–present)

In the early 2000s, interest in chalcogen doping of silicon was revived with the research by Professor Eric Mazur's group at Harvard University [51]. In a paper published in 1998, a method was proposed for microstructuring the surface of single-crystal silicon using femtosecond laser radiation (wavelength $\lambda = 800$ nm, pulse duration $\tau = 100$ fs, fluence on the order of 10 kJ m^{-2}) in a sulfur hexafluoride (SF_6) atmosphere. It is assumed that SF_6 promotes active plasma-chemical etching of the surface under the action of laser radiation, which enhances the formation of conical microstructures on the silicon surface. It should be noted that research into laser microstructuring of silicon surfaces was conducted in the context of improving the efficiency of photovoltaic modules by increasing light absorption. The formation of regular microstructures leads to significant scattering of incident radiation, thereby increasing the optical path and overall absorption in the silicon wafer (Fig. 5a and 5b). In contrast to traditional chemical texturing methods, which provide increased absorption only in the spectral region of intrinsic absorption of silicon ($\sim 300–1100$ nm), laser treatment makes it possible to

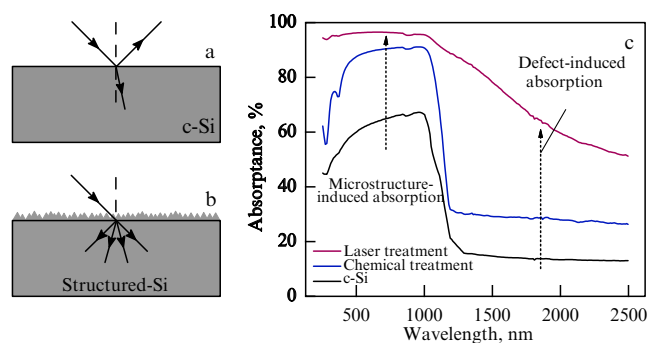


Figure 5. (a) Schematic representation of the ray path upon incidence on a polished surface of a silicon wafer. (b) Schematic representation of the ray path upon incidence on a microstructured surface of a silicon wafer. (c) Contribution of various absorption mechanisms to the absorbance spectra of silicon wafers.

extend the spectral absorption range into the near-infrared (NIR) region, as shown in Fig. 5c. Such ultra-broadband absorption is associated with the formation of crystal lattice defects and localized states in the band gap. However, despite the increase in the absorption coefficient, this effect is accompanied by a substantial increase in the charge carrier recombination rate, which limits the practical application of such structures in solar cells.

Later, in 2001 [52], it was experimentally established that microstructured silicon exhibits enhanced absorption not only in the region of intrinsic absorption of silicon (up to a wavelength of $\sim 1.1 \mu\text{m}$), but also beyond it—in the infrared spectral range ($> 1.1 \mu\text{m}$). The discovered phenomenon of impurity absorption does not fit within the classical theory of optical transitions for intrinsic semiconductors, according to which photons with energy below the band gap are incapable of inducing interband transitions. Nevertheless, the generation of photocarriers was experimentally observed upon irradiation of the samples with laser radiation at a wavelength of $\lambda = 1.31 \mu\text{m}$, which indicates the presence of additional levels within the band gap created both by impurities and by defects induced by laser processing. Secondary ion mass spectrometry (SIMS) revealed high concentrations of sulfur (~ 0.1 at.%, corresponding to $\sim 5 \times 10^{19} \text{ cm}^{-3}$) and fluorine ($\sim 10^{-3}$ at.%, $\sim 5 \times 10^{17} \text{ cm}^{-3}$) in the near-surface layer of silicon after laser microstructuring. After thermal annealing at a temperature of 1200 K for 3 hours, the concentration of these elements decreased by more than a factor of two, which correlated with a reduction in the sub-bandgap absorption intensity. Based on these data, the authors suggested that sulfur diffuses into the silicon crystal lattice, forming deep localized impurity levels that may partially degenerate to form an impurity band. This opens up the possibility of optical transitions between the impurity band and the conduction band at photon energies below the band gap of silicon, which explains the observed absorption in the NIR spectral region.

In 2005, an optimized design of a photodetector based on microstructured silicon was proposed [53]. The doped layer was formed by scanning a femtosecond laser beam over the surface of a silicon substrate. After thermal annealing at 825 K for 30 minutes and subsequent deposition of Cr–Au contacts, the current-voltage and spectral characteristics of the device were investigated. At a bias voltage of -0.5 V, the responsivity at a wavelength of 1000 nm was 120 A W^{-1} , which indicates the realization of an avalanche photodiode effect.

One of the most important results of the work was the demonstration of current responsivity at wavelengths of 1330 nm and 1550 nm at room temperature, which amounted to 50 mA W^{-1} and 35 mA W^{-1} , respectively. However, these values remain relatively low for photodiodes, which is probably associated with a high recombination rate of charge carriers at surface defects and structural imperfections arising from laser microstructuring. Subsequent investigations [54] did not allow the level of spectral responsivity in the near-infrared range to be significantly increased: at a wavelength of 1330 nm it was 90 mA W^{-1} , and at 1550 nm only 20 mA W^{-1} . This points to the limited efficiency of microstructured silicon as an active material for NIR detectors without additional surface passivation and optimization of transport properties.

Further, in order to achieve more controllable doping and to minimize the negative influence of defects on the transport properties of silicon, a method of high-dose ion implantation of chalcogens followed by pulsed laser annealing was proposed [55]. Within the framework of this approach, singly charged sulfur ions (S^+) were implanted into n-type silicon substrates with an energy of 200 keV and a dose of $1 \times 10^{16} \text{ cm}^{-2}$. After implantation, annealing was carried out using a short optical pulse from an excimer laser (wavelength $\lambda = 308 \text{ nm}$, duration $\tau = 25 \text{ ns}$), which enabled the restoration of the crystal structure and activation of the introduced impurities. It was experimentally established that after laser annealing, the absorbance of the material in the NIR range increases to 40–50%. SIMS analysis showed minimal redistribution of the sulfur concentration profile, which indicates its retention in the silicon crystal lattice and points to effective activation of impurity atoms without significant migration into the substrate. Moreover, it was shown that conventional thermal annealing leads to a decrease in the intensity of impurity-to-band absorption. This phenomenon is attributed to the diffusion of sulfur atoms from optically active positions, as well as their possible deactivation due to the formation of electrically inactive complexes or surface segregation.

Investigations carried out in 2007 [56] demonstrated a significant improvement in the crystalline quality of sulfur-implanted silicon after pulsed laser annealing. Rutherford backscattering spectrometry with channeling (RBS/C) analysis showed a reduction in point defect density, especially with an additional thermal anneal at a temperature of 550°C . Electrical measurements performed using the Hall effect method revealed a threefold increase in charge carrier mobility, which indicates effective restoration of the crystal lattice and reduced carrier scattering on structural defects. However, the question regarding the mechanisms behind the decrease in NIR absorption during thermal annealing remained open. In a 2013 study [57], the deactivation processes of hyperdoped silicon metastable state were investigated in detail. It was established that subsequent thermal annealing leads to the diffusion of sulfur atoms from substitutional positions into configurations characterized by the formation of dimers or clusters. Such structures possess lower optical activity, which explains the observed reduction in absorption. Here, the increase in charge carrier mobility by an order of magnitude is associated with decreased scattering on structural defects and impurities. Thus, it was shown that the optical activity of hyperdoped silicon depends directly on the spatial position of sulfur atoms in the crystal lattice. Laser annealing, in contrast to thermal

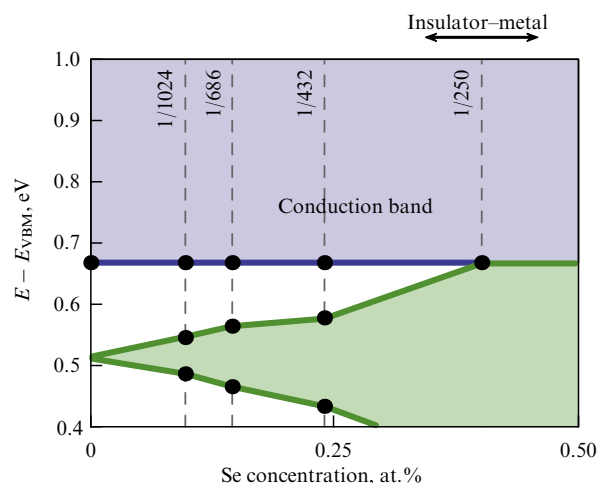


Figure 6. Schematic representation of the silicon band gap near the conduction band edge as a function of selenium concentration. (Adapted from [58].)

annealing, makes it possible to ‘freeze’ the impurity in substitutional lattice sites, preserving its high electrical and optical activity. This makes it the preferred method for forming optoelectronic structures with specified properties. Today, the advantages of laser annealing over conventional thermal annealing are becoming increasingly evident. This fact also provides an explanation for the results of early studies, such as [41] or [49], in which the use of thermal annealing restricted the observation of photoconductivity to only cryogenic temperatures. This is due to the fact that, under thermal heating, only a small fraction of sulfur atoms remain in the deep localized states necessary for the realization of impurity-to-band optical transitions.

However, achieving the maximum concentration of optically active chalcogen centers in the silicon crystal lattice does not guarantee efficient impurity photoconductivity. In Ref. [58], based on DFT calculations, it was shown that the donor levels associated with chalcogen atoms are located only 0.1–0.3 eV below the conduction band bottom. An increase in the impurity concentration to $\sim 0.37 \text{ at.}\%$ leads to broadening of the impurity band due to inter-impurity interactions and its overlap with the conduction band (Fig. 6). The donor nature of these levels promotes their strong occupation by electrons, as a result of which the Fermi level is located within the merged band, providing a metallic type of conductivity. This is consistent with experimental data, where a weak temperature dependence of conductivity was observed for a sample of $\text{Se}_{0.1}\text{Si}_{0.9}$ composition—a characteristic sign of degenerate semiconductors or metals. In addition, Hall effect measurements for highly doped samples confirmed an extremely high electron concentration in the conduction band ($\sim 10^{21} \text{ cm}^{-3}$) [59].

In Ref. [60], an attempt was made to control the Fermi level position in hyperdoped silicon by compensating the donor levels of sulfur with an acceptor impurity—boron. The implantation profiles were chosen such that the concentrations of both impurities overlapped in the same surface layer after annealing. With an increase in the boron-to-sulfur concentration ratio ($N_{\text{B}}/N_{\text{S}}$), the Fermi level gradually shifted deeper into the impurity band, and at $N_{\text{B}}/N_{\text{S}} > 1$, conductivity type inversion was observed, which was confirmed by Hall effect measurements.

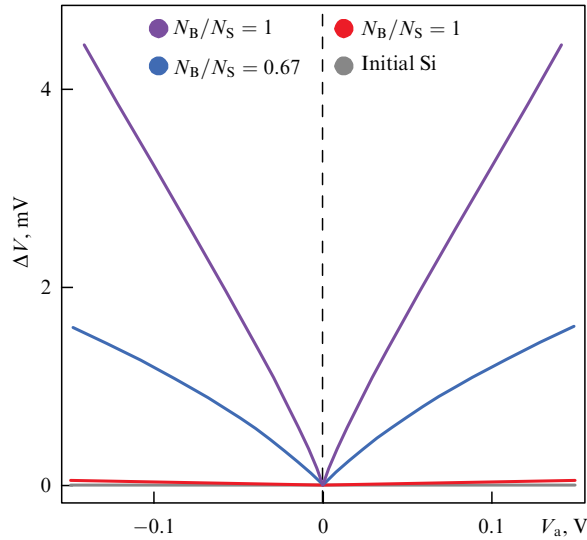


Figure 7. Relative increase in the photoconductivity signal as a function of the impurity concentration ratio. (Adapted from [60].)

Spectral measurements showed a decrease in optical absorption intensity in the photon energy range from 0.2 to 1.0 eV. This phenomenon is explained by the change in the available number of states for optical transitions between the impurity band and the conduction band (IB → CB) as the Fermi level shifts. At the same time, the number of available states for transitions from the valence band to the impurity band (VB → IB) increases. Thus, depending on the relative contribution of these two types of transitions, infrared absorption may either decrease or increase with rising compensation degree. Despite the decrease in absorption, as expected, compensation led to a significant increase in infrared impurity photoconductivity (Fig. 7). The measurements were carried out in the photoresistive mode; therefore, high absolute values of spectral responsivity were not anticipated. Nevertheless, the authors observed a pronounced relative increase in photocurrent at room temperature under illumination at a wavelength of 1550 nm. The current-voltage characteristics of the samples exhibited a linear behavior, consistent with the photoresistive mode of operation. At the same time, no signal could be detected from the control silicon sample and the sample without compensa-

tion. Owing to the introduction of the compensating impurity, the dark carrier concentration in the conduction band was reduced by two orders of magnitude, which is associated with a decrease in the contribution of thermal ionization of impurity levels. This, in turn, led to an increase in the infrared photoresponse by approximately three orders of magnitude at a wavelength of 1550 nm. Thus, in this work, the key physical mechanisms contributing to the enhancement of impurity photoconductivity were experimentally demonstrated. At the same time, achieving high absolute values of spectral responsivity (A W^{-1}) represents a separate task related to the design and optimization of the device, including photodiode architecture, surface passivation, contact geometry, and other technological parameters.

4. Prospects

Over the past two decades, research on hyperdoping of silicon with chalcogens (S, Se, Te) has demonstrated significant progress, opening up fundamentally new possibilities for extending the functional properties of one of the most studied and technologically advanced semiconductors. For the first time, it has become possible to go beyond the traditional understanding of the optical and electronic properties of silicon—by incorporating chalcogen atoms directly into the substitutional sites of its crystal lattice. This leads to the formation of deep donor levels, which, at concentrations of $\sim 10^{19} - 10^{20} \text{ cm}^{-3}$, can degenerate into an impurity band and even partially overlap with the conduction band. Such degeneracy gives rise to a unique phenomenon—direct impurity absorption, whereby photons with energies below the band gap are capable of generating free charge carriers. This effect does not fit within the standard rules of optical transitions for semiconductors and demonstrates that silicon can be adapted for NIR detection tasks and other promising applications. For example, Table 3 presents the achieved characteristics of fabricated NIR photodetector devices based on hyperdoped silicon.

One of the most effective methods for implementing this approach has been the microstructuring of the silicon surface using femtosecond laser radiation in an SF_6 atmosphere. This approach provides both physical enhancement of light trapping and active doping with sulfur impurity, which occupies substitutional positions in the lattice. At concentrations on the order of 10^{19} cm^{-3} , these atoms form a dense

Table 3. Characteristics of photodetector structures based on silicon doped with chalcogens by nonequilibrium methods. Characteristics of an InGaAs photodiode are presented as a comparison.

Impurity (formation features)	Sample structure	Detectivity, $\text{cm Hz}^{1/2} \text{ W}^{-1}$ (wavelength)	Reference, year of publication
Si:S (structured)	$n^+ - n$	5.64×10^9 (1.55 μm) 8.06×10^9 (1.31 μm)	[53], 2005
Si:S (structured)	$n^+ - n$	4.13×10^8 (1.55 μm) 1.86×10^9 (1.31 μm)	[54], 2006
Si:Se (implantation + annealing)	$n^+ - p$	3.76×10^6 (1.55 μm)	[61], 2017
Si:Te (implantation + annealing)	$n^+ - p$	1.07×10^7 (1.55 μm)	[62], 2018
Si:S (structured + passivation)	$n^+ - n$	1.96×10^{11} (1.55 μm) 1.42×10^{11} (1.31 μm)	[63], 2020
Si:Te (distributed waveguide detector)	$p - i - n$	1.76×10^7 (1.55 μm)	[64], 2025
InGaAs (as a comparison)	heterostructure	6.3×10^{12} (1.55 μm)	Hamamatsu, G12180-010A

system of donor levels, creating an impurity band that can interact with both the valence band and the conduction band. The possibility of photocurrent generation at room temperature under irradiation with a wavelength of $\lambda = 1.31 \mu\text{m}$ ($h\nu \approx 0.95 \text{ eV}$) has been experimentally demonstrated, indicating the successful realization of impurity absorption in real devices.

The key factor in obtaining stable optically active states is control over the recrystallization processes and the pinning of impurity atoms at substitutional sites. Here, a decisive role is played by pulsed laser annealing, which makes it possible, within short times ($\sim \text{ns-ps}$ range) of laser exposure, to restore the crystal lattice and ‘freeze’ sulfur atoms in optically active positions. This sharply reduces the probability of their thermally activated diffusion and allows a high density of states in the impurity band to be preserved. In contrast, steady-state thermal annealing, especially at temperatures above 550°C , causes solid-phase diffusion of sulfur into less active states, such as dimeric or cluster formations. This substantially reduces the optical activity of the material; however, it has a positive effect on the structural quality of the crystal lattice, and transport characteristics improve as well—the charge carrier mobility increases (up to a three-fold increase—according to Hall effect data) owing to a reduction in the scattering rate on defects and grain boundaries [65], and the carrier lifetime increases due to a reduction in the Shockley–Read–Hall recombination rate at more sparse impurity–atom traps, as well as grain-boundary and surface recombination [66]. Thus, thermal annealing is advisable to use for defect passivation, but not for increasing optical activity.

Another powerful tool for controlling the properties of hyperdoped silicon is Fermi level engineering. Through compensation doping with boron, the Fermi level can be controllably shifted within the impurity band, modifying the ratio of transition probabilities between the valence band, the impurity band, and the conduction band. Such control makes it possible to minimize thermal ionization of impurity levels, reduce the dark carrier concentration, and enhance the signal-to-noise ratio. Despite a certain reduction in overall IR absorption, this leads to a significant increase in photoconductivity at room temperature—especially under excitation at a wavelength of 1550 nm ($h\nu \approx 0.8 \text{ eV}$). Thus, Fermi level engineering becomes an important element in optimizing the performance of silicon detectors in the near-IR range.

However, in order to achieve high spectral responsivity values (A W^{-1}), a number of technological barriers must be overcome. The key limitations include:

- the presence of surface defects that enhance carrier recombination [66], and their insufficient passivation;
- difficulties in forming contacts to heavily doped silicon layers;
- uncontrolled formation of clusters and chemical compounds (or even phases thereof) of the impurity.

Consequently, further progress in this field is associated with the development of reproducible fabrication technologies for hyperdoped silicon structures, including combined approaches employing ion implantation, laser annealing, and subsequent compensation doping. At the same time, optimization of photodiode device architectures is required, aimed at improving contact geometry, minimizing recombination losses, and enhancing the collection efficiency of photogenerated carriers. Only an integrated approach will make it possible to realize the full potential of hyperdoped silicon as a

material for high-efficiency radiation detectors in the near- and mid-infrared ranges.

At the same time, despite the considerable volume of experimental and theoretical research, the task of objectively comparing the efficiency of various hyperdoping methods remains methodologically challenging. The main difficulty is caused by the significant heterogeneity of the initial conditions, namely, differences in the thickness of the substrates, the initial type of conductivity, the crystallographic orientation, as well as the technological parameters of doping, including the energy and dose of ion implantation. To ensure comparability and an objective assessment of the prospects of hyperdoped structures, it is advisable to use integral criteria that take into account not only the optical activity of the material but also its key transport characteristics of the charge carriers. Thus, in Ref. [67], a complex figure of merit is proposed, defined as the product of three fundamental parameters: absorption coefficient (α), drift mobility of charge carriers (μ), and their lifetime (τ). This approach enables quantitative comparison of different hyperdoping technologies and identification of optimal processing regimes, with the dopant concentration serving as the central control parameter that determines the magnitude of the optoelectronic response of hyperdoped silicon. It should be noted that it was previously assumed that the high carrier recombination rate through intermediate band states could be suppressed by delocalization of these states arising from a concentration-induced metal–insulator transition [68]. The nature of this transition can theoretically be either abrupt (according to the Mott model [68]) or continuous (percolation-type—within the frameworks of the Anderson and Lifshitz models [69, 70]).

In a review paper [71], the authors analyzed the parameters of hyperdoped material for various impurity elements as a function of implantation doses. However, no conclusions were drawn in that study regarding the optimal choice of impurity element and/or implantation dose. Moreover, the analysis relative to implantation doses, rather than bulk impurity concentrations, does not account for the redistribution of the impurity during the annealing procedure. Therefore, the analysis of the hyperdoped material efficiency presented below is carried out as a function of bulk concentration. Furthermore, sulfur was chosen as the impurity, since the greatest number of studies have been conducted compared to other chalcogens: selenium and tellurium.

Figure 8a presents the results of absorption coefficient measurements for silicon doped with sulfur by ion implantation followed by laser annealing, as a function of impurity concentration [72]. Similarly, Figs 8b and 8c show the results of carrier mobility and carrier lifetime measurements obtained by Hall effect analysis and by the femtosecond optical laser pump/picosecond THz probing technique, respectively. In addition to the results presented in the cited works, the graphs include the results of our own measurements of samples fabricated within the framework of work [59]. The graphs also indicate the threshold sulfur concentration at which the insulator–metal transition occurs [73].

Based on the presented values of α , μ and τ from various works, an approximation of the values with an exponential function as a function of sulfur concentration was performed. Subsequently, similarly to work [71], a calculation of the complex figure of merit FOM (figure-of-merit) for silicon heavily doped with sulfur was carried out using the formula:

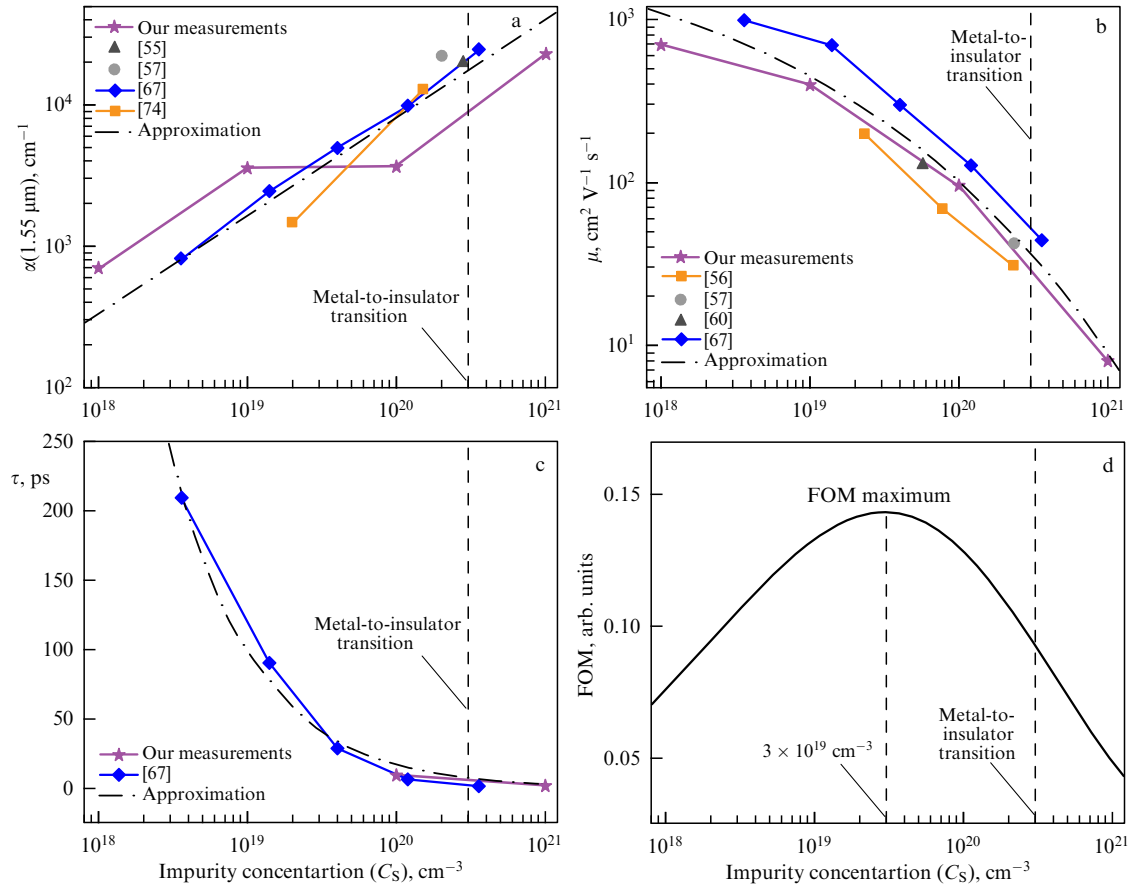


Figure 8. (a) Absorption coefficient at a wavelength of 1.55 μm , (b) charge carrier mobility, (c) charge carrier lifetime, and (d) figure of merit as a function of sulfur atom concentration.

$\text{FOM} = (E_g/q) \alpha^2 \mu \tau$. The result of the theoretical calculation is presented in Fig. 8d, where the FOM maximum occurs at a sulfur concentration of $3 \times 10^{19} \text{ cm}^{-3}$ and amounts to ~ 0.15 .

From the standpoint of photovoltaics, for efficient conversion, the FOM value must be $\gg 1$ [75, 76], which considerably exceeds the FOM maximum in the case of heavily doped silicon (Fig. 8d). In this case, the strongest limiting factor is specifically the charge carrier lifetime, which drops sharply at high doping levels down to units of picoseconds. In a hyperdoped layer, charge carrier recombination mainly occurs at the same deep levels (Shockley–Read–Hall recombination) that provide the enhanced impurity-to-band absorption. Therefore, improving the operating efficiency of devices based on heavily doped silicon can be achieved through rapid injection of photogenerated charge carriers from the doped layer into pure silicon. This can be accomplished by the formation of high internal electric fields within photodetector structures, for example, by means of p–n junctions or Schottky barriers. An alternative approach to increasing the lifetime and, consequently, the figure of merit, is a sharp reduction in the doping concentration down to threshold values at which an impurity band just begins to form. Despite the fact that this will inevitably lead to a sharp drop in the absorption coefficient of silicon in the NIR region, this limitation can be overcome through a manifold increase in the optical path length [64]. For instance, in waveguide schemes, the absorbing layer can be formed with a length of up to units of millimeters, in contrast to classical photo-

detector structures on heavily doped silicon, in which the absorbing layer is limited by the doped layer thickness of up to 500 nm.

Recent non-contact terahertz studies of dynamic conductivity in hyperdoped silicon with widely varying donor sulfur impurity concentration ($C_S = 10^{18} - 10^{21} \text{ cm}^{-3}$) have revealed [72] that the process of charge carrier capture at ionized impurity centers followed by recombination via the Shockley–Read–Hall mechanism is accompanied by the emission of ~ 250 zone-edge transverse acoustic (TA) phonons, where the total capture time is the carrier lifetime, and the TA phonon emission time characterizes the carrier scattering time on the lattice, which determines its mobility. This observation points to the existence of a concentration-invariant relationship between the carrier lifetime τ and the characteristic time of a single scattering event at an ionized impurity center τ_{sc} [77], which testifies to a fundamental link between elementary scattering events and macroscopic recombination dynamics. The observed effects of strong electron–electron and electron–ion interactions within the impurity band and conduction band are not yet fully understood and require further investigation.

It was also experimentally established [72] that at impurity concentrations below the metal–insulator transition point, the carrier scattering rate ν , as well as their lifetime τ , remain virtually independent of C_S —up to the attainment of a certain sulfur concentration $C_S^* \approx (2-3) \times 10^{19} \text{ cm}^{-3}$. At $C_S > C_S^*$, a power-law dependence of the form $\nu \propto 1/R_S^2$ is observed, where $R_S = \sqrt[3]{1/C_S}$ is the mean inter-ion distance,

and πR_S^2 is the effective transport scattering cross section. Thus, the concentration C_S^* , identified for the first time, serves as a boundary separating two qualitatively different regimes of electron interaction with the impurity subsystem:

- at $C_S < C_S^*$, uncorrelated (random) scattering dominates, caused by grain-boundary recombination [65];
- at $C_S > C_S^*$, correlated interaction is realized, the spatial scale of which is limited by the value $R_S^* \approx 3$ nm, which corresponds to the mean distance between ions at C_S^* and is considerably smaller than the crystallite size [65].

Taking into account the established experimental dependences of the drift mobility $\mu_d(C_S)$ and carrier lifetime $\tau_d(C_S)$ [78], as well as the weak concentration dependence of the absorption coefficient $\alpha_d(C_S)$ (see Fig. 8), the optimal impurity concentration that provides the maximum of the integral figure of merit FOM practically coincides with C_S^* and turns out to be almost an order of magnitude lower than the metal–insulator transition concentration in silicon doped with sulfur impurity ($\sim 10^{20}–10^{21}$ cm $^{-3}$ [59]). It is noteworthy that a significant decrease in both carrier mobility and lifetime is observed already after reaching the transition point. The obtained data indicate that the maximum photoconversion efficiency is achieved near the threshold of the formation of a correlated impurity environment—at $C_S \approx C_S^*$, where a balance between high mobility, long lifetime, and sufficient optical absorption is maintained.

5. Conclusion

The presented review of the fundamental mechanisms and technological approaches to hyperdoping of single-crystal silicon with chalcogens demonstrates that this method represents a powerful tool for the targeted modification of the electronic structure of one of the key semiconductor materials. Exceeding the equilibrium solubility limit of impurities (up to concentrations of $\sim 10^{20}–10^{21}$ cm $^{-3}$) makes it possible to form deep donor levels in the silicon band gap, which, upon critical overlap of wave functions, degenerate into an impurity band. This, in turn, opens up the possibility of realizing impurity optical transitions that provide efficient absorption of infrared radiation in the 1–6 μ m range—a region inaccessible to undoped silicon due to its indirect band-gap structure.

The key technological breakthrough that enabled the realization of metastable states with a high concentration of electrically active impurity centers was the combination of ion implantation with PLA, which implements the liquid-phase epitaxial recrystallization regime. This method ensures the ‘freezing’ of chalcogen atoms at substitutional lattice sites on time scales that preclude diffusion and segregation, which is critically important for preserving optical activity. In contrast to conventional thermal annealing, PLA minimizes the formation of electrically inactive clusters and dimers, which dominated in early works and limited photoconductivity to cryogenic temperatures.

Experimental and theoretical investigations of the past two decades have confirmed that the optical and transport properties of hyperdoped silicon are governed by a complex interplay between the impurity concentration, its spatial distribution, the structural perfection of the material, and the position of the Fermi level. It has been established that controlling the latter through compensation doping (e.g., with boron) enables a substantial improvement in the signal-to-noise ratio by suppressing dark conductivity, even at the

expense of a certain reduction in the absorption coefficient. This makes compensation an important tool for optimizing the performance of photodetector devices operating at room temperature.

The fundamental limitation on the efficiency of hyperdoped structures is associated with charge carrier recombination via the Shockley–Read–Hall mechanism at the same deep impurity levels that provide impurity-to-band absorption. Pulsed terahertz studies of dynamic conductivity have revealed the universal nature of electron-ion interaction and discovered a new critical impurity concentration $C_S^* \approx (2–3) \times 10^{19}$ cm $^{-3}$. This value separates the concentration regimes of low-frequency random grain-boundary scattering and high-frequency correlated impurity scattering of carriers, and, remarkably, coincides with the optimal concentration for achieving the maximum complex figure of merit FOM. At higher concentrations, the FOM drops sharply due to a drastic reduction in carrier lifetime ($\tau \sim$ ps), which renders classical photovoltaic schemes with bulk absorption inefficient.

Thus, the prospects for the practical application of hyperdoped silicon in infrared photonics are associated not with the creation of standalone high-efficiency solar cells, but with the development of specialized photodetector devices, in which minimization of recombination losses is achieved through the rapid extraction of photogenerated carriers from the hyperdoped layer. This can be realized by forming strong internal electric fields (for example, in p–n or p–i–n heterostructures) or by using a waveguide geometry, which allows the effective optical path to be increased manifold while maintaining a small active layer thickness. An integrated approach combining precision control over the impurity concentration and distribution, optimization of the structural quality of the material, and energy band engineering opens the way to the creation of new classes of integrated photonic devices based on silicon that are compatible with existing CMOS technology and capable of operating in the near- and mid-infrared ranges at room temperature.

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