

Metastable and bistable defects in silicon

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Abstract. Existing data on the properties and structure of metastable and bistable defects in silicon are analyzed. Primary radiation-induced defects (vacancies, self-interstitial atoms, and Frenkel pairs), complexes of oxygen, carbon, hydrogen and other impurity atoms, and defects with negative correlation energy are considered.

*Dedicated to the memory
of Victor Sergeevich Vavilov*

1. Introduction

Thirty five years ago Viktor Sergeevich Vavilov, one of the founders of the physics of semiconductors, published his review [1] in *Usp. Fiz. Nauk* reporting that under the action of irradiation defect complexes are formed in semiconductors, which are more involved than merely vacancies and interstitial atoms (Frenkel pairs) separated by different interatomic distances. The migration of Frenkel pair components and their interaction with one another and with impurities yield secondary radiation defects (complicated intrinsic complexes, interstitial impurities, complexes of primary defects and impurities, etc. [2–4]) which ultimately determine many properties of crystals in the equilibrium state. The problem of defects in the crystalline structure later became of paramount importance owing to the development of microelectronics whose advances are largely due to the deep insight into the fundamental properties of defects and impurities in silicon which is the main material in modern microelectronics.

The behavior of defects in semiconductors appeared to be much more sophisticated and interesting than the previously

suggested simple succession of reactions between point defects. For example, new fundamental properties of defects, such as metastability and bistability, were discovered in covalent and complex semiconductors. These physical phenomena are now being thoroughly investigated [5–7]. For practical application they are of interest as providing the possibility of creating a new generation of memory cells using bistability. Now that a microvolume of a substance with a prescribed succession of impurity and defect distributions can be created, the engineering has closely approached the construction (at a submicron level) of devices executing various functions and operating on the basis of one-electron transport. Hence, the active element of such units is now an urgent problem. This may be a molecular object with a bistable center as a basis. From the scientific point of view it is attractive to find various mechanisms of metastability and bistability at the microscopic level. One of these mechanisms is the electron–phonon interaction which is the most general physical basis of bistability. It also plays an important part in the explanation of many physical properties of the solid state, such as the appearance of superconductivity in metals [8] or the ‘pinning’ of the Fermi level in amorphous chalcogenide semiconductors [9].

Analogs of the ground and excited states of atomic systems in defect crystals are respectively stable and metastable (bistable) defects. Such a division is rather arbitrary in some cases and cannot be rigorously adopted, but it is nevertheless very useful. We note here that all the radiation-induced defects are thermodynamically metastable, but many of them remain stable indefinitely at room temperature. Therefore, by metastable defects one typically understands either defects unstable under normal conditions or defects with a concentration exceeding equilibrium. The configuration diagram of defects in a crystal, i.e., the dependence of the defect energy on some generalized lattice coordinate characterizing the mutual position of the defect components, always has a set of local minima near the stable ground state (Fig. 1a); the energy difference of the main and side minima can be large, $\Delta E \gg kT$. If the energy barrier for the transition to the ground state in the course of defect formation is also sufficiently large, $E_{\text{barrier}} \geq kT$, the metastable states can be pinned, that is, metastable defects can be formed. The instability of these defects leads to either their irreversible

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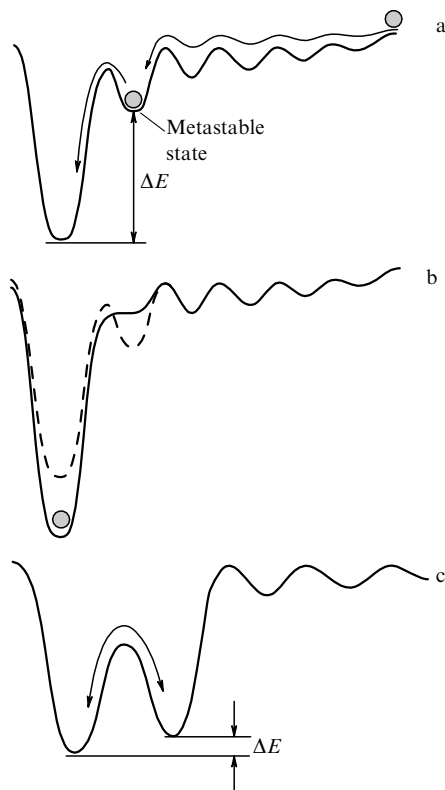


Figure 1. Configuration diagrams of (a) a metastable defect, (b) a metastable defect after transition to the ground state, and (c) a bistable defect.

modification into more stable configurations or complete disappearance. The transition from a metastable to a stable state may proceed either by migration of defect components through one or several interatomic spacings or by way of a local rearrangement of the defect structure. The metastable defects that are of practical interest are characterized by a narrow stability region at nearly room temperatures. A transition to the ground state may also cause an irreversible defect rearrangement under which nonground (metastable) states disappear (Fig. 1b).

As distinct from metastable defects, bistable defects are normally those which have more than one stable state and under certain conditions may reversibly pass over from one state to another, i.e., may reversibly change their spatial and electronic structures. A necessary condition for the existence of bistable states is the presence of a multiwell adiabatic potential for a defect or an impurity atom. However, not all the systems with a multiwell potential exhibit bistability. For example, a defect whose symmetry is lower than cubic will be orientationally degenerate, and although at high enough temperatures transitions among its different states will occur, bistability will not be observed. (Close examples are Yahn–Teller defects, off-center impurities in cubic crystals, etc.) Hence, a necessary condition for the occurrence of bistability is the existence of several states of the center, possessing different energies. Accordingly, the configuration diagram of bistable defects (Fig. 1c) has the main and at least one additional energy minimum and can be obtained from the diagram of metastable defects by making the energies of the ground and metastable states separated by an energy barrier closer, so that the energy difference would become insignificant, $\Delta E \sim kT$; such a barrier can be overcome by thermal

excitation. For certain values of external parameters (sample temperature, intensity of the external light, injection current, etc.), an equilibrium or quasi-equilibrium occupation of the ground and metastable states sets in. If the external conditions are changed in a jump, the barrier will be an obstacle for the system to pass over to a new equilibrium distribution, and therefore its state in the new conditions will be metastable. Such a sharp change of conditions is particularly easy to achieve by way of electric recharging of the center which has several charge states. Four types of configuration diagrams for bistable defects are presented in Ref. [5]. The overwhelming majority of bistable centers observed in semiconductors have deep levels in the forbidden gap, and therefore the electronic state is strongly localized, which causes a considerable lattice distortion. Recharging switches on the driving forces of the bistability mechanism which may be the Coulomb interaction between the components of the defect, a dissimilar variation of the chemical bonds for different defect configurations upon a change of the charge state, the electron–electron interaction, an intense lattice relaxation (the electron–phonon interaction). The explanation of each case of bistability is hampered by a close interweaving of these factors that control bistability.

For different charge states of a defect, the minimum energy may correspond to different configuration states and the defect configuration may almost completely be transformed into another one by changing the charge state. So, the system is a microscopic switcher to several positions. Such a possibility is the most intriguing point in the bistability problem. As was justly noticed by Barraff [7], when examining a typical defect, one has to give an answer to the question of ‘what it is’ and in the case of a bistable defect also to the question of ‘how it works.’ Hence, the study of the structure of a bistable defect is inseparable from the understanding of the switching mechanism, i.e., the bistability mechanism.

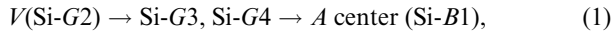
An appreciable advance in the understanding of the bistability mechanism of some defects in semiconductors has recently been made owing to intense studies using electron paramagnetic resonance (EPR), infrared spectroscopy, DLTS, and a number of other spectroscopic methods. In this paper we make a review of the experimental data on metastable and bistable defects mainly in silicon, because, since the appearance of the previous reviews [5–7] published rather long ago, the range of investigated phenomena has become much wider. To begin, we will analyze metastable centers, including primary defects, i.e., Frenkel pairs, and then bistable defects. Special consideration will be given to centers with a negative correlation energy as an important case of bistable defects. We will discuss both the data available in the literature and those obtained by us and will also present some original results of our recent studies.

2. Metastable defects in silicon

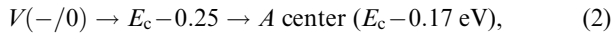
There exist a whole number of defects that, when arising, have an unstable structure which is then irreversibly modified into a more stable one. Thus, a metastable structure can only be observed at the initial stages of formation of these defects.

Predecessors of the V –O defect in silicon. These were the first metastable radiation-induced defects revealed in semiconductors. After low-temperature (~ 20 K) irradiation by electrons of silicon grown by the Czochralski method (later on denoted as Cz-Si), Watkins [10] observed individual vacancies V^+ (EPR center Si-G1) and V^- (Si-G2) which in

n-type silicon, at a temperature of $\sim 50\text{--}70\text{ K}$, migrated about the lattice and were captured by interstitial oxygen atoms thus forming a $V\text{--O}$ center (the so-called A center). However, the A center was not formed immediately during the vacancy annealing, but appeared in the reaction



i.e., through the intermediate states (the EPR centers $G3$ and $G4$) which are close in structure to a single vacancy but are disturbed by a closely located defect. This was very clearly pronounced in p-type Si, where the mobility of vacancies is lower. The observed 'one-to-one' transition of $G4$ ($G3$) to A centers shows that this defect is an oxygen atom located in the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions from the vacancy for $G3$ and $G4$ centers, respectively. Recently, in an n-Cz-Si-based Schottky diode irradiated at 77 K under a back bias, the DLTS method was used to observe a level $E_c - 0.25\text{ eV}$ (E_c is the bottom of the conduction band) and to register the transitions



which enabled the level $E_c - 0.25\text{ eV}$ to be identified as belonging to the metastable predecessor of the A center [11]. The existence of the defect-predecessor is rather typical of radiation-induced defects and demonstrates the general property of crystal defects to possess a discrete set of metastable configurations which at high temperatures have a low population, but in the case of low-temperature defect formation their nonequilibrium population may be high, which provides the possibility of observing metastable states.

Metastable complex $(\text{C-O})_i$. The interstitial impurity carbon atoms C_i in silicon, which are due to irradiation and the substitution reaction [4] (the indices s and i denote the positions of atoms in lattice sites and interstices, respectively),



move at room temperature and in Cz-Si are captured mostly by the oxygen atoms to form $(\text{C-O})_i$ complexes (so-called K

centers) [12–15]. In Ref. [16], the formation of K centers has been shown to proceed through an intermediate state. However, the studies [17] using a DLTS spectrometer with an improved resolution have shown that annealing of C_i centers ($E_v + 0.29\text{ eV}$, where E_v is the top of the valence band) is accompanied by the formation of almost equal concentrations of K centers in their stable, $E_v + 0.38\text{ eV}$, and metastable (M), $E_v + 0.35\text{ eV}$, configurations (Fig. 2a). This makes it possible to propose a model for a metastable M center, which differs from the stable configuration of a K center only by the exchange of places of Si_i and C_i atoms (Fig. 2b). The concentrations of K and M centers formed during the migration of a C_i atom to an oxygen atom will be almost equal statistically, which agrees with experiment. The energy of the deep level of K and M centers is mainly determined by the p orbital of the carbon atom, and therefore the defect levels will be nearly equally deep inside the forbidden gap, the M -center level lying between the donor levels of the C_i atom [18, 19] and the K center [16, 18], which also agrees with experiment.

Metastable complex $\text{C}_i\text{--C}_s$. In silicon samples grown by zone melting (further on referred to as FZ-Si) and having a low oxygen concentration, the main traps for C_i atoms are carbon atoms themselves; the $\text{C}_i\text{--C}_s$ pairs thus produced contain EPR centers Si-G11 [20], Si-G17, Si-L7 [21], the G photoluminescence line [22, 23], and IR absorption bands at 969 meV [24]. However, upon room-temperature migration of C_i atoms and their trapping by C_s atoms, $\text{C}_i\text{--C}_s$ centers, which are stable below $T \sim 200^\circ\text{C}$, are not immediately formed but through a metastable phase responsible for the appearance of IR absorption lines at 860 and 966 cm^{-1} [25]. The formation of a final structure from the metastable state proceeds in a single jump near room temperature, which is seen from the high transition frequency factor ($\sim 10^{-13}\text{ s}^{-1}$).

Deep hydrogen-carbon donor in silicon. This center can also be considered metastable (at room temperature) defects. As shown in Refs [26, 27], in the space-charge region of Schottky diodes or in the region of $p^+ - n$ transitions containing impurity hydrogen and carbon atoms, after annealing at

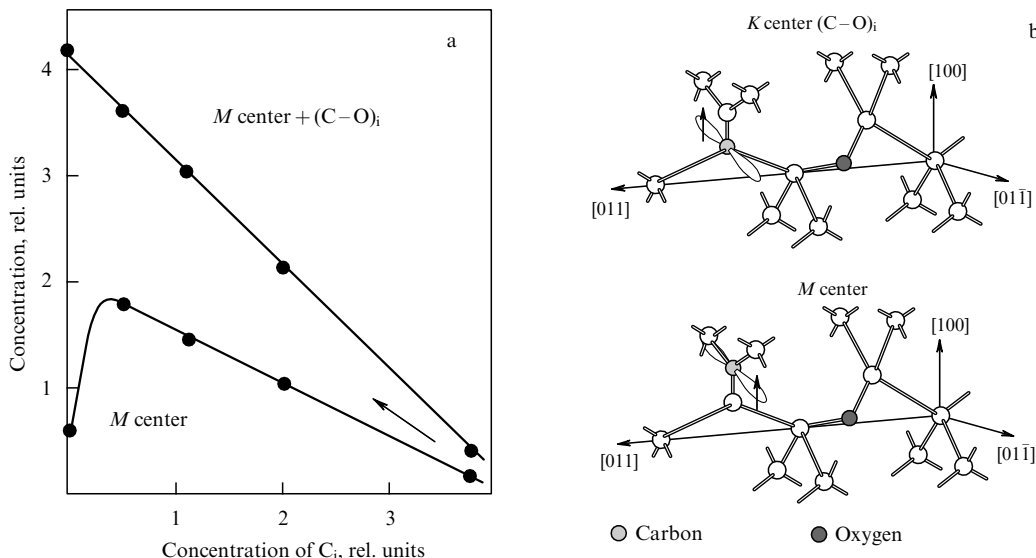


Figure 2. (a) Dependence of the concentration of M centers ($E_v + 0.35\text{ eV}$) and the sum of concentrations of M and K centers on the concentration of C_i defects in an irradiated p-Cz-Si sample on thermal annealing at $20\text{--}50^\circ\text{C}$. (b) Models of K center [14] and M center.

$T \sim 320$ K for 17 h under a back bias of -4 V, C_s-H_i donors with a level $E_c - 0.16$ eV are formed. The donors appear as a result of emission of atomic hydrogen H^0 previously trapped by phosphorus atoms, trapping a hole H^+ , migration about the crystal, and trapping by carbon atoms which acquire a small negative charge in the lattice because they are more electronegative than silicon atoms. The centers are unstable at room temperature in n-Si, i.e., in the neutral charge state $(C_s-H_i)^0$. However, a repeated sample annealing under a back bias again leads to the formation of $(C_s-H_i)^+$ centers, although with a lower concentration.

The H atoms also interact with impurity oxygen atoms [28] to form a metastable donor. The level of this donor is close to the levels of the defect C_s-H_i and the state $H_{BC}(+/0)$ [29], which may testify to a weak disturbance of a hydrogen atom level in the BC position upon trapping on a C or O impurity.

Metastable Frenkel pairs. It is a well-known fact that the rate of introduction of low-temperature radiation-induced defects in silicon is much smaller than calculated [30–32]. The cause is the appearance of metastable Frenkel Si_i-V pairs, the majority of which then annihilate. In n-Si, Frenkel pairs were observed after low-temperature (~ 10 K) electron irradiation [33]; these pairs appear to be stable to approximately 70 K and are apparently annealed at the expense of the motion of vacancies, because self-interstitial atoms begin moving in n-Si at $T \sim 140$ K [34] (in a high-resistivity silicon, Si_i atoms begin migrating at $T \sim 190$ K [35] and in p-Si at 260 K [36]). In p-Si, vacancies remain stable up to temperatures of ~ 160 K [37], and therefore Frenkel pairs were expected to be easily produced and examined. But no Frenkel pairs were observed in p-Si after irradiation with electrons. The cause of this is the high concentration of nonequilibrium carriers during irradiation, which results in an athermal migration [38, 39] of Si_i atoms involved in the pairs; this migration entails either annihilation of the Frenkel

pairs or Si_i liberation and the formation of interstitial complexes by substitutional impurity atoms and vacancies. However, upon irradiation by protons or α -particles, each introduced defect yields much fewer electron–hole pairs. That is why the greater part of the Frenkel pairs avoid recombination-accelerated annihilation, and after irradiation at 80 K by small doses of protons and α -particles, the pairs are the main defects in p-Si [36]. In DLTS spectra, it is the DLTS level $E_v + 0.20$ eV that belongs to the Frenkel pairs. This level was observed in Refs [40, 41] and was preliminarily identified as belonging to a nonreorientable divacancy [34]. However, an extensive study of the properties of the $E_v + 0.20$ eV band shows that it belongs to both single Frenkel pairs Si_i-V and multiple Frenkel pairs $n(Si_i-V)$. This is confirmed by the following facts:

- annihilation of the greater part of $E_v + 0.20$ eV defects upon annealing;
- the appearance of vacancies, divacancies, and self-interstitial complexes upon annealing of $E_v + 0.20$ eV defects;
- dependence of the annealing rate of the $E_v + 0.20$ eV level on the Fermi level (as in the case of vacancy [37]);
- the annealing kinetics of the $E_v + 0.20$ eV band; observation of annealing stages of order two and three testifying to pairwise annihilation, and the presence of components with correlated positions;
- the capability of $E_v + 0.20$ eV defects to be annealed upon low-temperature (77 K) injection and the appearance, owing to such annealing, of vacancies and interstitial carbon atoms (C_i atoms appear as a result of simultaneous injection annealing of Si_i centers) (Fig. 3a);
- the smeared spectrum of the $E_v + 0.20$ eV band; the nonexponential decay of the relaxation DLTS signal, which proves that the $E_v + 0.20$ eV band includes a group of defects with similar energies;
- the appearance of additional bands $H5 = E_v + 0.21$ eV and $H6 = E_v + 0.28$ eV owing to a decrease in the concentra-

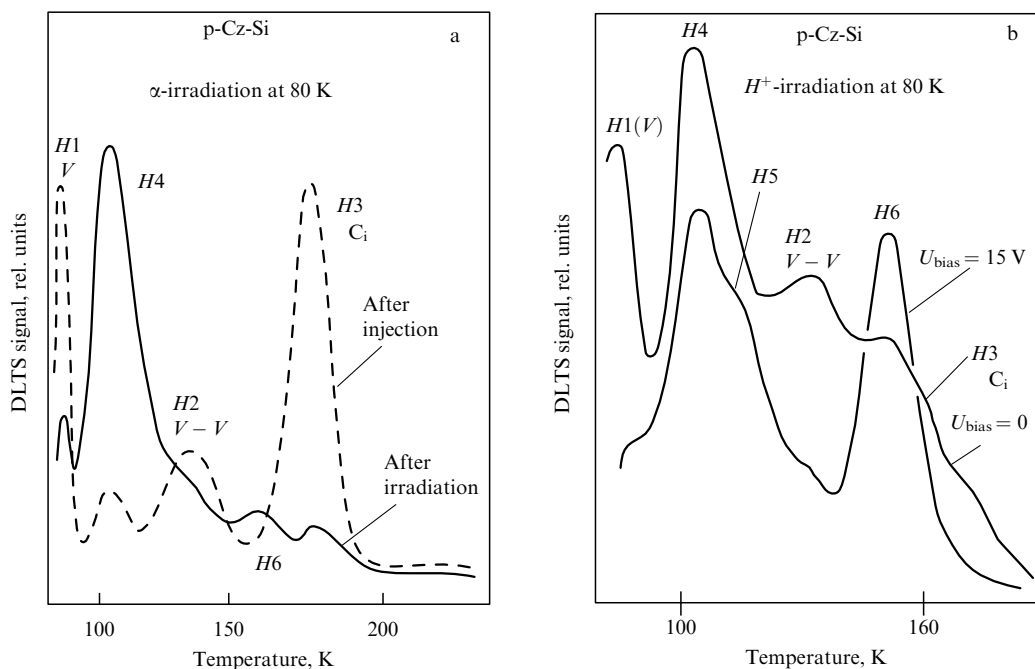


Figure 3. DLTS spectra of p-Cz-Si samples irradiated at $T = 77$ K by α -particles (to a dose of $\sim 5 \times 10^9$ cm $^{-2}$) (a) immediately after irradiation and after injection annealing at 77 K (for 10 min with a current of ~ 0.5 A cm $^{-2}$); and (b) after irradiation by protons (to a dose of $\sim 5 \times 10^{12}$ cm $^{-2}$), with a zero bias voltage and a back bias of 15 V on the sample during irradiation.

tion of nonequilibrium carriers upon irradiation under a back bias.

The appearance, along with the $E_v + 0.20$ eV complexes, of related DLTS defects $H5$ and $H6$ formed upon back-bias irradiation (Fig. 3b) is indicative of the presence of several types of stable configurations of pairs that differ in the structure of dangling bonds that form a complex electron spectrum of defects belonging to metastable Frenkel pairs. This is also in agreement with the existence of a set of metastable states of a defect which in this case differ in the distance between V and Si_i . A change in the conditions of irradiation and formation of these defects at a low temperature, such that normally induces no thermal diffusion of components, leads to occupation of some metastable states of Frenkel pairs in silicon.

Defect including an aluminum atom and mobile at 200 K. As is well known, under nonequilibrium conditions, i.e., upon injection of carriers, the barrier for interstitial aluminum atom migration in silicon falls from 1.2 eV to nearly 0.3 eV, and so the migration may proceed at room temperature [42]. In Ref. [43] we reported the phenomenon of low-temperature (< 200 K) hydrogen-accelerated diffusion of aluminum atoms in both FZ-Si(Al) samples implanted with protons at 80 K and FZ-Si(Al) : H samples irradiated at 80 K. The long-path migration of aluminum atoms is indicated by the formation of an EPR center (denoted as Si-AA15) including two almost equivalent aluminum atoms (Fig. 4). An analysis of the hyperfine structure of ^{27}Al nuclei allowed AA15 to be identified as two Al atoms located in the interstice split along $\langle 011 \rangle$. AA15 centers appeared as a result of annealing at $T \sim 180\text{--}200$ K, and simultaneously an EPR center (denoted as Si-AA16) including one aluminum atom was observed in the same narrow temperature range (see Fig. 4). The hyperfine structure of AA16 testifies to the fact that the center is an Al atom located in the interstice and shifted in the $\langle 111 \rangle$ direction from the T_d position. Since $(\text{Al}-\text{Al})_i$ pairs (the EPR center AA15) were only observed in hydrogen-containing samples and the known Al_i centers (the EPR center Si-G18) were absent, it was concluded [44] that the substitution reaction

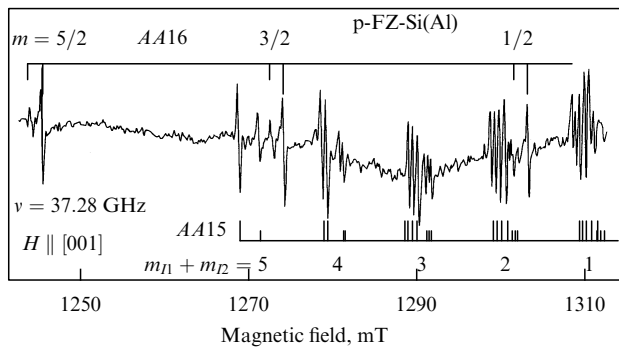
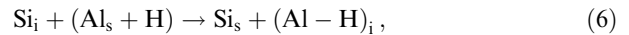
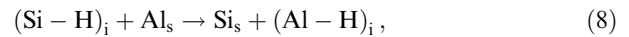


Figure 4. Part of the EPR spectra of Si-AA15 and Si-AA16 on the side of a weak magnetic field in a p-FZ-Si(Al) sample implanted by 30-MeV protons (to a dose of $\sim 3 \times 10^{15} \text{ cm}^{-2}$) at 80 K and then annealed at ~ 190 K. The values of the nuclear spin projections are given in the assumption that the hyperfine interaction constant is positive. The measurements were taken at 77 K.

is not dominant and, instead, during irradiation of FZ-Si(Al) : H samples, the reactions



or



proceed to form a mobile interstitial defect $(\text{Al}-\text{H})_i$ at a temperature $T \leq 180\text{--}200$ K. Upon defect migration and trapping by the second Al atom:



$(\text{Al}-\text{Al})_i$ pairs, i.e., Si-AA15 defects are formed. Note that the EPR center AA16 is a quite probable candidate for the role of a mobile $(\text{Al}-\text{H})_i$ defect.

As is well-known, the injection of carriers induces accelerated Al_i atom diffusion [42]; the diffusion mechanism was theoretically considered in Ref. [45]. In the case of hydrogen-accelerated diffusion, the mechanism of aluminum diffusion acceleration can be represented as follows. A migrating $(\text{Al}-\text{H})_i$ defect may consist of Al and H atoms located at neighboring T_d interstices. The presence of an H atom may, owing to the electron-phonon interaction and Coulomb attraction between Al_i^{++} and $\text{H}_{T_d}^-$, lower the barrier for Al atom migration through the hexagonal interstice located between the atoms. However, the position of the H atom may appear to be unstable when both the atoms find themselves in the same T_d interstice. The simultaneous effect of both these factors may lead to an appreciable lowering of the barrier for $(\text{Al}-\text{H})_i$ complex diffusion even if nonequilibrium carriers are not injected. A model of such a defect is given in Fig. 5a, and Fig. 5b presents a model of an $\langle 011 \rangle$ -aligned Al-Al pair, which agrees in the best possible way with the hyperfine structure of the Si-AA15 spectrum.

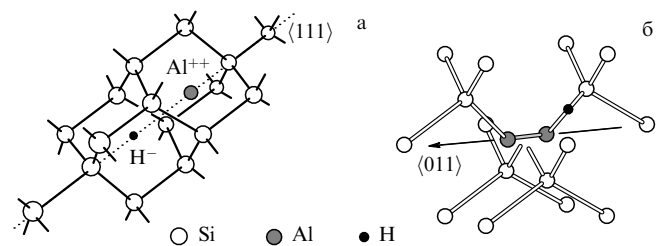


Figure 5. Tentative models for (a) the EPR centers Si-AA16 and (b) Si-AA15.

Note that a low- and room-temperature solution of impurity Al in silicon is in a supersaturated metastable state, but its decomposition is limited by the limited Al atomic diffusion. With the possibility of diffusion acceleration, Al atoms precipitate as they should and a phase enriched with impurity atoms sets in. Al-Al pairs (the AA15 center) are nucleation centers of the new phase, and the complexes may then increase owing to the additional Al atoms. Indeed, in a repeated hydrogen-accelerated diffusion in samples in which the AA15 spectrum was observed, the latter either is not formed at all or has a very low intensity. Instead, a complex

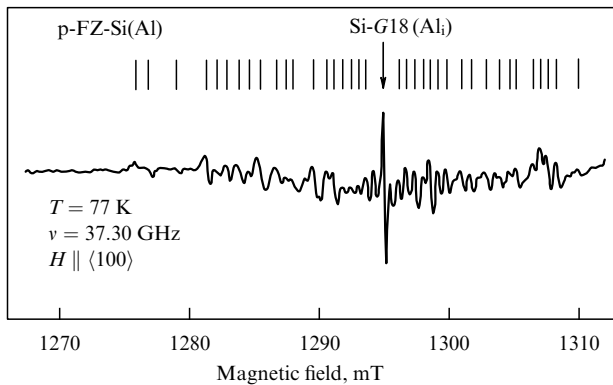


Figure 6. EPR spectrum of a p-FZ-Si(Al) sample in which Si-*A15* and Si-*A16* spectra were observed and which, after room temperature annealing was again implanted by protons at 80 K to a dose of $3 \times 10^{15} \text{ cm}^{-2}$ and then annealed at 200 K. One of the six Si-G18 spectrum lines is shown, which corresponds to a transition with projection $m_l = 1/2$.

spectrum is observed (Fig. 6), which may belong to defects involving several aluminum atoms. Unfortunately, the spectrum appeared only for the magnetic field $H \parallel \langle 001 \rangle$, and therefore its angular dependence was not determined. The spectrum may belong to microscopic conglomerates of the aluminum-enriched phase and may testify to further aluminum aggregation and second-phase precipitation from the supersaturated aluminum solution in silicon.

Thus, radiation-induced and hydrogen-accelerated diffusion may initiate micro- and nanoclusters of a new, aluminum-enriched phase in the silicon matrix. As is well known, the decomposition of a supersaturated solid solution is one of the ways to form nanoclusters [46]. For example, impurity oxygen in Cz-Si is also in a supersaturated state and annealing at $T \sim 450\text{--}500^\circ\text{C}$ leads to oxygen precipitation. These microscopic precipitates may later on getter (i.e., capture) impurities and defects, which results in a purification of bulk material [47]. It is not excluded that clusters enriched with aluminum atoms may also interact with defects and impurities and may possess other interesting and unexpected properties, and hence further studies in this direction should be carried out. It is also of interest to check the existence of hydrogen-accelerated migration of impurity boron and gallium whose chemical properties are similar to aluminum in many respects.

3. Bistable defects

3.1 Bistable impurity pairs in silicon

The large number of bistable defects in silicon is due to impurity pairs. The dependence of the microscopic structure on the charge state and the complete reproducible reversibility of the properties under the action of certain factors (temperature, light, and injection of nonequilibrium carriers) have been revealed for some impurity pairs.

Bistable $C_i\text{--}C_s$ defect. The behavior of the bistable carbon–silicon–carbon center in irradiated silicon has been studied most thoroughly [21]. For this center, three EPR spectra have been revealed: two with C_{1h} symmetry (Si-G17 and Si-G11) and one with C_{3v} symmetry (Si-L7), which belong to bistable configurations of the $C_s\text{--}Si_i\text{--}C_s$ complex with two nonequivalent and equivalent carbon atoms, respectively.

Moreover, the DLTS method helped to detect the electronic levels of the defect in samples of both n- and p-type conductivity. A combination of EPR and DLTS results allowed the determination of the total spectrum of the complex and the microstructure of its states. Structure bistability is provided in this case by bond ‘switching’ upon which one of the carbon atoms leaves the site and occupies a position close to a $\langle 100 \rangle$ -split interstice. The bistability is due to a dissimilar change of the strength of the chemical bonds in different microscopic defect configurations upon a change in the charge state, the closeness of the energies of these different defect configurations, and the low barrier height between them. As a result, the coordination number of one of the carbon atoms and a Si_i atom located between two carbon atoms changes upon defect recharging, i.e., there occurs a switching of the chemical bond. Since the energy minimum of different charge states is reached in different microscopic configurations, a change in the charge state may provide a full transfer between metastable states of the defect.

Bistable $Fe_i\text{--}A_s$ pairs (with *A* as a Group III acceptor). Well investigated bistable pairs are centers such as $Fe_i\text{--}B_s$, $Fe_i\text{--}Al_s$, $Fe_i\text{--}Ga_s$, and $Fe_i\text{--}In_s$ [48–51]. The bistability of the Fe_i -atom position is due to competition between the elastic repulsion from and the Coulomb attraction to the acceptor. For the $Fe_i\text{--}Al_s$ case examined using the DLTS and EPR methods, two types of pairs were revealed: a close pair ($r = 2.35 \text{ \AA}$) with $\langle 111 \rangle$ as the symmetry axis and a Fe_i atom located in the T_d interstice on the first coordination shell of the atom and a more remote pair ($r = 2.72 \text{ \AA}$) with symmetry C_{2v} [52].

Bistable $C_i\text{--}D_s$ pairs (with *D* as a Group V donor). These pairs also exhibit structure bistability [53, 54]. The defect $C_i\text{--}P_s$ corresponds to three EPR centers (*L8*, *L9*, *L10*) and four DLTS levels. Bistability in this case is due to a weak bond between C_i and P_s atoms and to the ability of the C_i atom to migrate upon carrier injection. As a result, under injection at $\sim 240 \text{ K}$ the C_i atom moves away from P_s , and an impurity pair is created having the largest distance between the components. Subsequent annealing leads to a steplike nearing of the atoms and the formation of a number of metastable configurations until the most compact and stable pair, a $\langle 100 \rangle$ -split interstitial $C_i\text{--}P_i$, is produced.

Bistable copper–chalcogen pairs. These pairs were revealed quite recently and are therefore not so well examined. The bistability of the properties of $Cu\text{--}S$ and $Cu\text{--}Se$ centers in silicon was disclosed in Refs [55–57]. Under a long-term exposure to light at a low temperature of 4.2 K, the stable configuration, observed by photoluminescence and optically detected magnetic resonance, passed over to a metastable one which disappeared on heating to 40 K. The center is characterized by a low symmetry C_1 ; its exact structure has not been identified.

The $(Si\text{--}O)_i$ complex in irradiated Cz-Si. The $(Si\text{--}O)_i$ defect [33, 58–60] can be regarded as a quasi-impurity pair. It is formed upon low-temperature irradiation of Cz-Si samples during which mobile self-interstitials are captured by oxygen atoms. The center is stable up to $T \sim 250 \text{ K}$, after which the Si_i atoms again leave the traps. Thus, the oxygen atoms, unlike C, Al, B, and Ga impurities, are ‘traps’ for Si_i . The trapping and emission of Si_i atoms on impurity oxygen atoms are considered in more detail in the sequel. It is, however, of great interest that the $(Si\text{--}O)_i$ defect itself is bistable and may find itself in two different configurations *A* and *B*. As is shown in Refs [59, 60], configuration *A* corresponds to the EPR

spectrum Si-A18 (A^+ state of C_{1h} symmetry) and configuration B to the Si-AA13 center (C_{3v} symmetry) and Si-AA14 (C_1 symmetry). This means that the center possesses three structures with different symmetries. Furthermore, the defect may appear in at least two different EPR-inactive configurations, A^0 and B^0 . Possible structures of states A and B are presented in Fig. 7.

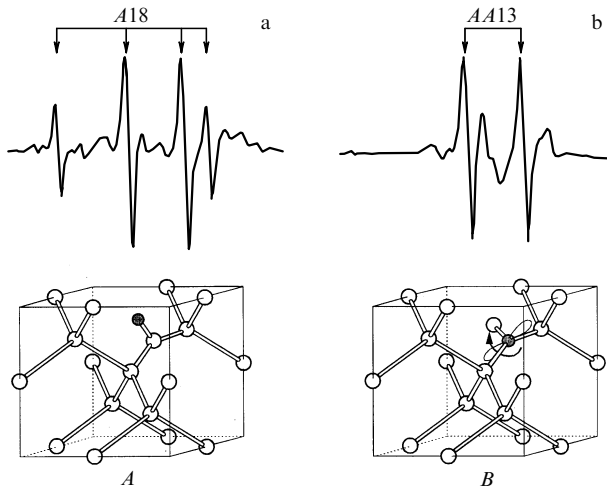


Figure 7. Possible models of the bistable complex $(\text{Si}-\text{O})_i$ in Cz-Si irradiated at 80 K: A configuration of symmetry C_{1h} (A^+ corresponds to the EPR spectrum Si-A18) and B configuration of symmetry C_{3v} (the spectrum Si-AA13).

A simultaneous analysis of EPR and DLTS data shows that the $(\text{Si}-\text{O})_i$ complex is the result of trapping of the Si_i atom by the impurity oxygen O_i (for instance, upon binding with an unshared electron pair of oxygen) accompanied by the appearance of the B configuration of the complex, which corresponds to the AA13 (see Fig. 7) and AA14 [60] spectra. The configuration B is stable in the charge state B^0 , but in the positive charge state the energy of the system is lower in the state A^+ , and therefore the injection of carriers or illumination at 77 K bring the complex into configuration A (spectrum A18). Heating up to ~ 160 – 180 K leads to the ionization $A^+ \rightarrow A^0 + h$ and to the reverse transition $A^0 \rightarrow B^0$ into a stable neutral state. Such a transfer between the configurations A and B can be carried out repeatedly without loss of the general number of defects $(\text{Si}-\text{O})_i$.

The $(\text{Si}-\text{O})_i$ defect also possesses properties that may be indicative of a negative correlation energy. This is testified by the observed instability of the EPR-inactive state B^{2+} and by theoretical calculations of the structure of the $(\text{Si}-\text{O})_i$ defect. In the theoretical paper [61] the defect IO (where I is a self-interstitial atom), which is quite analogous to the B configuration (see Fig. 7), was considered as the simplest thermal donor, and its bistable behavior was predicted. It was assumed that such a defect, as well as the IO_2 complex, may play the role of the precipitation center of O_i atoms in the formation of oxygen thermodonors.

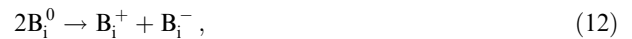
3.2 Centers with negative correlation energy

A negative correlation energy of a center possessing several charge states E_n, E_{n+1}, E_{n+2} implies that the following relation holds

$$E_n + E_{n+2} < 2E_{n+1}, \quad (10)$$

where n is the number of electrons at the center, i.e., the state with $n+1$ electrons is unstable and falls into the states E_n and E_{n+2} . This is possible in the case of a strong electron–phonon interaction, which lowers the energy of the defect E_{n+2} and compensates for the Coulomb repulsion of electrons (the correlation energy U), thus leading to a negative effective energy. The concept of negative- U states was initially developed to account for the Fermi level stabilization in amorphous chalcogenide semiconductors [9], but shortly after that, defects with $U < 0$ were revealed in silicon and other semiconductors. Although the E_{n+1} state is unstable, it can be separated by an energy barrier, and at low temperatures centers with $U < 0$ will be bistable defects.

V and B_i centers. As has been shown in Refs [62, 63], a vacancy and an interstitial boron atom in silicon are centers with $U < 0$. This results in the instability of the states V^+ and B_i^0 and their decomposition by way of the reactions



but the EPR-active metastable states V^+ and B_i^0 can be observed upon excitation by light or injection of carriers and can be frozen in this metastable state at low temperatures. This shows that the decay of a metastable state proceeds through an energy barrier. The energy barrier is due to the electron–phonon interaction, which occurs in the center with two electrons and causes a substantial lattice relaxation [64]. As a result of relaxation, which may be accompanied by a change in the symmetry and a rearrangement of the chemical bonds, the energy of the center E_{n+2} lowers, and in spite of the Coulomb repulsion of electrons (holes in the case of V^{2+}) relation (10) holds. This situation is typical of all systems with $U < 0$.

Self-interstitial atoms. Primary defects Si_i, too, may be centers with a negative correlation energy. This is confirmed by both theoretical and experimental data. As is well known, under low-temperature electron excitation of p-Si the Si_i atoms are mobile and migrate under irradiation even at 4.2 K [20]. Migration proceeds by one of the recombination accelerated mechanisms, most probably athermally, and as a result all the Si_i atoms are trapped by impurity atoms. In n-Si, Si_i atom mobility is much lower, which is confirmed by the absence of interstitial impurity defects after low-temperature irradiation. Impurity C_i atoms appear only after annealing at $T \sim 140$ K [34], which is indicative of either migration or emission of Si_i atoms from traps at these temperatures. However, irradiation by protons or α -particles, which gives a much lower concentration of nonequilibrium carriers per created defect, does not entail significant athermal diffusion of Si_i atoms in p-Si, as is clear from the low concentration of interstitial impurity atoms. Under these conditions, Si_i atoms were registered by capacity methods and EPR [17, 36, 60]. In DLTS spectra, Si_i atoms correspond to the level $E1 = E_c - 0.39$ eV (Fig. 8a), which was observed in many p-Si samples having different concentrations of impurity C, O, B, Al, and Ga under irradiation at 77 K by optically stimulated and thermally stimulated DLTS. In all the cases, injection annealing of $E1$ defects at 77 K induced synchronous appearance of the known interstitial impurity complexes of C_i and Al_i. The large cross section of the electron trapping into the $E_c - 0.39$ eV level (comparable with the cross section of the trapping of, e.g., an impurity sulfur into $(+/+)$ levels in silicon) suggests that the transition corresponds to electron

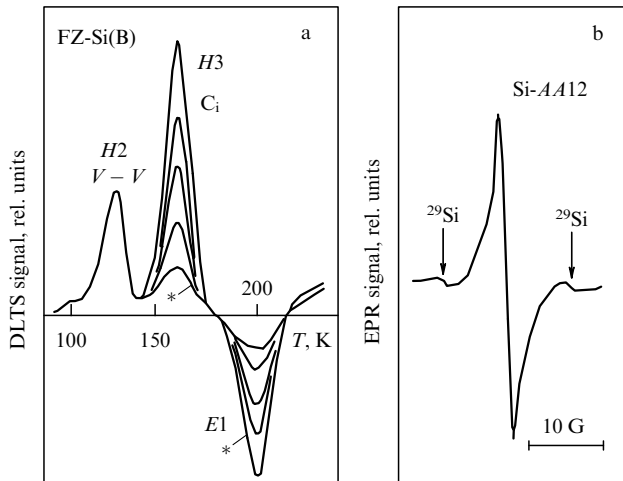


Figure 8. (a) DLTS spectrum of a p-FZ-Si(B) sample irradiated by α -particles at 250 K (to a dose of $\sim 5 \times 10^9 \alpha \text{ cm}^{-2}$). The spectra were recorded at a low injection level, which allowed registration of the line $E1$ but did not induce its rapid annealing. The curve marked with an asterisk (*) was recorded immediately after the irradiation. Before each subsequent recording of the spectra, a short-term (~ 1 s) injection was made at 77 K. (b) EPR spectrum of Si-AA12 in a p-FZ-Si sample irradiated by protons at 80 K and annealed at 250 K. The spectrum was recorded at 77 K, $H \parallel (001)$, $\nu = 37.15$ GHz.

trapping on a positive doubly charged center. The absence of the $E_c - 0.39$ eV band in n-Si testifies to the inverse position of $(0/+)$ and $(+/++)$ levels, which fully agrees with the theoretical conclusions about the negative correlation energy on the Si_i center [4, 65, 66]: according to the calculations, the $(+/++)$ level is located at $E_c - 0.40$ eV (which perfectly coincides with our experimental data [36, 60]), and the $(0/+)$ level either lies near the valence band or coincides with its boundary.

In the EPR spectra, the $E_c - 0.39$ eV defect corresponds to the EPR center Si-AA12 (Fig. 8b), which can be seen from the full coincidence of the properties of $E1$ and AA12 defects:

- $E1$ and AA12 defects are observed in very different silicon samples, and their formation does not depend on the impurity composition of samples.

- The electronic levels of both defects (0.39 eV) are coincident within the error.

- Both defects are subject to low-temperature (77 K) injection annealing.

- The temperature region of stability and the character of annealing (the absence of a clearly pronounced annealing stage below $T \sim 350$ K and the more rapid annealing in Cz-Si than in FZ-Si) coincide.

- Annealing (either thermal or injection) of $E1$ and AA12 defects induces the known, previously identified impurity defects (C_i , Al_i).

As noted above, partially reversible reactions of $E1$ and AA12 defect trapping by interstitial O_i atoms are observed. Figure 9a presents the DLTS results. It can be seen that injection annealing at 77 K leads to the transformation of $E1$ defects into C_i and $(\text{Si}-\text{O})_i$ centers and subsequent thermal annealing leads to the disappearance of $(\text{Si}-\text{O})_i$ (the $E_v + 0.13$ eV level) and a partial reconstruction of $E1$ centers. Similarly, in the EPR measurements the $(\text{Si}-\text{O})_i$ complex (A18 and AA13 spectra in Fig. 9b) is annealed at $T \sim 225$ K with the formation of the AA12 spectrum which,

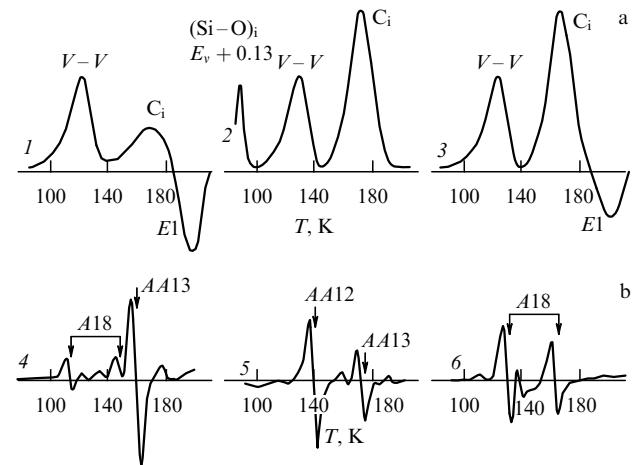


Figure 9. (a) DLTS spectra of a p-Cz-Si sample irradiated by α -particles at 265 K. Curve 1 was recorded immediately after irradiation; the concentration of C_i centers is low and the line $E1$ dominates. The amplitude of $E1$ increases significantly with increasing injecting-pulse amplitude, but the line becomes rapidly annealed. Therefore, the injection level was made low for recording the DLTS spectrum. Curve 2: rapid growth of the concentration of $E_v + 0.13$ and C_i defects upon injection annealing of $E1$ at 77 K. Curve 3: partial reconstruction of $E1$ upon annealing of $E_v + 0.13$ at 180 K. (b) EPR spectra of a Cz-Si sample irradiated at 80 K. Curve 4: the defect $(\text{Si}-\text{O})_i$ (A18 and AA13 spectra) becomes dominant immediately after irradiation. Curve 5: an intrinsic defect AA12 appears after annealing of the $(\text{Si}-\text{O})_i$ complex at 225 K. Curve 6: the defect AA12 disappears again upon injection optical annealing at 77 K with a simultaneous restoration of $(\text{Si}-\text{O})_i$.

under sample exposure at 77 K, again induces the $(\text{Si}-\text{O})_i$ complex formation. The observed reversible reactions reflect the trapping of Si_i atoms onto the impurity oxygen and their re-emission.

Thus, there exist serious grounds to identify $E1$ defects and EPR AA12 centers with one and the same self-interstitial defect. The defect $E1$ (AA12) is the most probable candidate for the role of the Si_i center which, in spite of numerous studies, has not yet been experimentally observed. The bistability of the Si_i atom has been shown theoretically: the minimum energy of the state Si_i^{++} corresponds to the position in the T_d interstice; Si_i^+ , in the BC position; and Si_i^0 , in X position [65, 66]. Experimental data on low-temperature Si_i migration also testify to the location of the Si_i atom in different positions in the lattice depending on the charge state; the recharging of the center (through low-temperature injection of carriers) or the thermal annealing at $T \sim 140$ K in n-Si, at $T \sim 190$ K in i -Si, and at $T \sim 280$ K in p-Si induces Si_i atom migration about the lattice.

Atomic hydrogen in Si. The behavior of hydrogen in semiconductors is fairly diverse [67]. Atomic hydrogen interacts with many impurities in silicon, germanium, complex semiconductors and with practically all radiation-induced defects in silicon, where it forms complexes which then change their structure, properties and electrical activity. In many cases, a change in the electrical activity causes a complete neutralization and a removal of deep defect and impurity levels from the forbidden gap, i.e., a passivation. This fact has drawn much attention to impurity hydrogen in silicon and other semiconductors. Hydrogen atoms can enter bulk silicon from a SiO_2 film, thus causing a degradation of the devices [67]. Interest has also been roused by the discovery of a residual but noticeable number of hydrogen atoms in

industrially grown silicon not specially doped with hydrogen [68].

Hydrogen in silicon may be in several forms, namely, atomic, molecular, and bound on defects. Atomic hydrogen in silicon is a bistable system with $U < 0$ [29, 69, 70]. The same evidence is provided by the data on muonium, an analog of hydrogen [71]. Hydrogen in the BC position (i.e., in the middle of the Si–Si bond) creates a donor state, the level $H_{BC}(+/0)$ being located at $E_c - 0.16$ eV, while hydrogen in the T_d interstice creates a deep acceptor state. The corresponding level $H_{T_d}(-/0)$ is located at $E_c - 0.56$ eV, i.e., almost in the middle of the forbidden gap. Therefore, the donor and acceptor electronic levels occupy inverse positions. The hydrogen atom in the lattice can be controlled by a change of the charge state. The T_d interstice is rather large, and a small lattice distortion is obviously an obstruction for H^0 in the T_d position to create a local minimum. The lifetime of the paramagnetic state H^0 in the T_d position after the transition



is small, and the state H^0 in the T_d interstice has not yet been observed by EPR as distinct from μ SR studies. Although the H_{BC}^0 state is metastable in high-resistivity silicon, it is on the contrary well observed in EPR under illumination of the sample (the Si-AA9 center [72]).

Early oxygen donors. As is well known, upon annealing of silicon samples grown from quartz crucibles, in the temperature range of 450–550 °C a family of double-donor centers is formed (thermal donors $nTDD$, where n varies from 1 to about 16) [73–75]. It has turned out [76, 78] that the first three terms of the series occurring in Cz-Si at early stages of annealing at $T \sim 400$ °C are defects with a negative correlation energy that can find themselves in two configurations, namely, A (deep donor) and B (shallow double donor). Residual photoconductivity is also observed. These properties make them quite similar to the well-known DX centers in complex semiconductors [79]. The concentration of $nTDD$ centers can be made sufficiently high so that these donors could determine the position of the Fermi level. With lowering temperature the population of the $A(0)$ state increases, while with heightening temperature, the population of the state $B(++)$ increases, so that within a certain interval of temperatures and free carrier concentrations the Fermi level will be stabilized approximately in the middle between the deep $E_n(0/+)$ and the shallow $E(+/++) = E_c - 0.16$ eV levels which are characterized by inverse disposition. The exchange of electrons between the deep state A and the shallow state B proceeds through an appreciable energy barrier Δ_n [78]. Three types ($n = 1, 2, 3$) of early reconstructible donors were revealed for which the parameters $E_1(0/+) = E_c - 0.75$ eV, $E_2(0/+) = E_c - 0.48$ eV, and $E_3(0/+) = E_c - 0.29$ eV were obtained and the barrier height was $\Delta_1 = 0.29$ eV, $\Delta_2 = 0.42$ eV, and $\Delta_3 = 0.58$ eV. Because of the large barrier height Δ_n , the Fermi level is stabilized at sufficiently high temperatures of ~ 300 K. Below room temperature the energy barrier is hard to overcome, and long-term relaxations of sample conductivity are thus observed which are due to the displacement of the Fermi level to an equilibrium position. On further temperature lowering, the barrier becomes insurmountable, the Fermi level stabilization becomes difficult and takes much time, and therefore the concentration of B centers can be frozen and made much higher than equilibrium. Under these conditions

(in the state B), $nTDD$ behave as normal double helium-like donors with normally positioned levels

$$E(0/+) = E_c - (0.06 - 0.07) \text{ eV}$$

and

$$E(+/++) = E_c - (0.15 - 0.16) \text{ eV}.$$

The EPR spectrum Si-NL8 [80] and the series of IR absorption lines due to the electron transitions in the region of $\sim 400 \text{ cm}^{-1}$ (the transition $D^0 \rightarrow D^+ + e$) and $\sim 1000 \text{ cm}^{-1}$ ($D^+ \rightarrow D^{++} + e$) belong to these donors. Up to 16 series are observed, the line energies decreasing with increasing n [81]. The ground state has a two-valley structure [82] which distinguishes it from the other donors in silicon described by the effective mass theory [83].

The donors formed upon a long annealing show neither bistability nor a negative correlation energy. This should be expected if the behavior of $E_n(0/+)$ and Δ_n is approximated for early thermodonors [76, 77] into a region of $n > 3$. Further annealing at ~ 500 °C leads to the formation of shallow single thermodonors (STD) to which the EPR spectrum Si-NL10 [80] and the IR absorption lines in the region of $\sim 200 - 350 \text{ cm}^{-1}$ belong [84]. STD are assumed to be formed from TDD centers by way of adjoining an impurity atom with an odd atomic number, e.g., hydrogen [85]. As has been shown in Ref. [86], along with oxygen and an intrinsic defect, the STD structure involves additional impurity (hydrogen or aluminum and possibly nitrogen) atoms.

We will make here one more remark concerning centers with $U < 0$, which may refer to both oxygen TDD and hydrogen shallow donors (the latter are discussed below). We will consider defects with $U < 0$ which have charge states d^+ , d^0 , and d^- , so that $E(d^+) + E(d^-) < 2E(d^0)$ and assume that d centers are positioned in pairs and form a defect D . Then two types of neutral pairs are possible: $D1^0 = d^+ + d^-$ and $D2 = d^0 + d^0$ [87] and, according to (10), the energy of the defect $D1^0$ will be lower than that of the defect $D2^0$. Hence, in a system of pair defects, where each component of the pair is a defect with $U < 0$, there naturally appear two identical charge states of the center with distinct energies presumably causing the bistability of such pairs. We note that the two-center model for thermodonors was proposed in paper [88]. It provides an insight into the specificity of the electronic structure of TDD.

Shallow hydrogen donors. Another class of shallow donors is associated with defects due to proton implantation and a subsequent short-term (~ 20 min) annealing at $T \sim 350 - 550$ °C. In this case, as in the formation of oxygen thermodonors, a supersaturated solution of impurity (hydrogen) in silicon is decomposed with a simultaneous interaction with radiation-induced defects, which causes the formation of various families of defects. At early stages of annealing and with relatively low hydrogen concentrations, deeper, perhaps double HDD, donors form; higher-temperature annealing and a large hydrogen concentration lead to the appearance of shallow ($E_c - 0.035$ eV) hydrogen donors (SHD) [89–91]. HDD⁺ centers are connected with the EPR spectrum Si-AA1 [91] which is practically identical in parameters to the Si-NL8 spectrum and belongs to the oxygen $nTDD^+$ centers [80]. Since an oxygen atom does not enter into the composition of the AA1 center, and since the piezospectroscopic tensor and the parameters of the atomic reorientation of the AA1 and

NL8 centers are substantially different [92], one can state that these centers have different microscopic structures and their similitude may be due to the similarity of the electron spectra of double helium-like donors. No bistable behavior of HDD centers was revealed.

SHD centers also show similarity with oxygen STD centers and have a series of IR absorption bands in the range of 200–350 cm^{-1} [93]. However, as distinct from oxygen STD centers, SHD centers occurring at early stages of annealing are bistable [94, 95].

In this case, the Fermi level in the sample is stabilized in a wide range of temperatures and implantation doses. The data [95] on the Hall effect imply that the Fermi level is stabilized at $\sim E_c - 0.30$ eV. Leveling of the Fermi level with a slight change of temperature proceeds at a still lower rate than in the case of oxygen TDD, and long-term relaxations of conductivity are observed at temperatures $T \sim 100\text{--}200^\circ\text{C}$, while at lower temperatures the leveling of the Fermi level is practically frozen. Aging at 90°C leads to a free carrier concentration $n \sim 10^{15} \text{ cm}^{-3}$, which means a removal of the shallow state $E_c - 0.035$ eV, and quenching from 250°C leads to its formation and dominance with a concentration $n \sim 10^{17} \text{ cm}^{-3}$. This is a clearly pronounced bistable behavior. The transition between bistable states can be repeated arbitrarily many times without a noticeable loss of oxygen donor concentration. The possibility of a negative correlation energy for SHD was not discussed in Ref. [95]. However, the existence of a limiting SHD concentration ($\sim 10^{17} \text{ cm}^{-3}$), which cannot be heightened by increasing the hydrogen implantation dose, the Fermi level stabilization, and the bistable behavior of the defects suggest that, as in the case of early oxygen donors, bistable SHD are centers with $U < 0$. A more rigorous proof calls for further studies.

When saturated with hydrogen, irradiated by electrons and annealed at $300\text{--}400^\circ\text{C}$, oxygen-containing silicon samples exhibited a defect with $U < 0$ [96]. This defect was not observed in samples with a low oxygen content or in those which had not been specially implanted with hydrogen or had not been irradiated with electrons. It was therefore concluded that the defect contained impurity oxygen and hydrogen atoms and a radiation-induced defect. The donor state was located at $E_c - 0.043$ eV and the acceptor state at $E_c - 0.11$ eV, that is, we dealt with the inverse position of the levels. The study of the occupation function of centers has shown that it corresponds to the centers with a negative correlation energy.

Thus, the precipitation of impurity oxygen and hydrogen and their interaction with intrinsic defects in silicon have similar features and lead to the formation of various donor families; the centers occurring at initial stages may exhibit bistability and have a negative correlation energy.

The common property of systems with $U < 0$ is the presence of two stable (E_n and E_{n+2}) and one unstable (E_{n+1}) state separated by an energy barrier. At low temperatures the barrier becomes insurmountable and the system typically becomes bistable.

3.3 DX-type centers in semiconductors

There now exists an extensive body of information on bistable defects in complex semiconductors. We will briefly dwell here only on the *DX* centers and *EL2* defects in GaAs which have an analogous nature [79, 97].

A very large number of studies have been devoted to the *EL2* center. Since this center is a predominant defect in GaAs, the understanding of its nature is quite important for

applications. In a stable state (*A*), the *EL2* defect has a deep level $E_c - 0.75$ eV. The optical excitation with an energy of ~ 1.15 eV at $T < 120$ K brings the *EL2* center into an excited state *EL2** (*B*) undetectable by optical and EPR methods. For the explanation, two models of the *EL2* center were proposed, namely, an As atom in a Ga site (As_{Ga}) and an $\text{As}_{\text{Ga}} - \text{As}_i$ pair [5]. Both models were confirmed by experimental data, which made a choice between them rather difficult. Comparison with experiment of the shapes of the EPR signal obtained theoretically for both the models has recently given evidence in favor of the model of *EL2* center as an As_{Ga} defect [98]. Furthermore, electrical measurements have been reported [99] showing that the *EL2** state corresponds to the shallow donor state at $E_c - 40 \pm 10$ meV which is associated with the Brillouin zone minimum at the point *L* and is an excited state of the *EL2* center. The metastability of the *EL2** state is due to the fact that a reverse transition to the ground state is to be accompanied by a change in the electron localization around the defect (a transition from the point *L* to the point Γ) and, therefore, by a change in the atomic configuration around the defect. This creates a barrier for the transition from the excited to the ground state and is responsible for the observed deep level–shallow state transition. There are also indications [100] of the fact that the term ‘*EL2*-center’ cannot be used to identify a defect with a strictly defined structure, but refers to a whole class of structurally related defects in which the As_{Ga} atom plays a significant role.

DX centers that are formed upon doping of $A^{\text{III}}B^{\text{V}}$ materials with donor impurities [101] also demonstrate a deep level–shallow state transition, like *EL2* in GaAs. *DX* donors are also observed in semiconducting Group II–VI systems [102] and a similar behavior is shown by elements of Group III in Group IV–VI compounds [103]. In all the cases, the concentration of *DX* centers is approximately proportional to the donor impurity concentration, and the occurrence of *DX* centers is associated with the existence of several microscopic configurations of the donor atom. The properties of *DX* centers have been most thoroughly investigated in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. Although there is a lack of detailed understanding now, there exist theoretical results [102] and direct experimental data [104] pointing to the two-electron process as being responsible for the creation of the deep state. In III–V and II–VI compounds, when the coordination number assumes its normal value 4, a shallow hydrogen-like state is formed. Owing to the strong electron–phonon interaction and the lattice relaxation in the $\langle 111 \rangle$ direction (or a more complicated relaxation [102]), the carrier may pass over from the shallow to the deep level with a reduction of the coordination number of the impurity atom (or a near-by metal atom). The acceptor effect of the *DX* center in a material of n-type conductivity testifies in favor of the negative correlation energy of the electrons localized at the deep level. This is also confirmed by theoretical calculations.

Note that there exists at least an outward resemblance between the properties of *DX* centers and early oxygen and hydrogen donors in silicon. This resemblance may be a manifestation of the close nature of the bistability phenomena observed in these cases. Examination of the nature of the TDD and SHD centers in silicon is hampered by impurity (oxygen or hydrogen) precipitation. The separation of manifestations of precipitation processes and the examination of the nature of the bistability of shallow donor levels in silicon is a topical problem for future studies.

4. Conclusion

Thus, the bistability of defects is one of the intriguing issues of solid state physics. The principal condition of the existence of bistable states is the existence of a multiwell adiabatic potential for a defect or an impurity atom. The above examples demonstrate that, as distinct from static phenomena, bistability is a complicated and diversified dynamic process which depends on a fine balance of various factors. However, several basic interactions responsible for bistability in semiconductors can be singled out:

— the Coulomb interaction between defect-constituting components. A characteristic example is the $\text{Fe}_i^+ - \text{Al}_s^-$ complex in Si.

— Variation of the chemical interaction for various defect configurations. An example is the $\text{C}_i - \text{C}_s$ complex in Si in which the configuration number of the carbon atom may change.

— Electron–electron interaction. A typical example is obviously the $EL2$ center in GaAs.

— Electron–phonon interaction. It plays an important role in all the known examples. Moreover, it may lead to self-capture of the carrier and the transition from a shallow electronic state to a deep one. In some cases, a strong electron–phonon interaction may compensate for the repulsion between electrons, thus leading to a negative correlation energy for the electrons localized on the defect (V and B_i centers, early thermodonors in Si, and DX center).

The explanation of each case of bistability requires consideration of all the indicated factors, for they create various metastable states and control switching among them.

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