rium moisture content of the material; c_0, c, c_{mo}, heat capacities of the absolutely dry, moist material, and water, kJ/(kg·K); c_e, ρ, ν, a, λ, isobaric heat capacity, kJ/(kg·K), density, kg/m^3, coefficient of kinematic viscosity, m^2/sec, thermal diffusivity, m^2/sec, and thermal conductivity, W/(m·K), all applicable to the heat-carrying agent; v, velocity of motion for the heat-carrying agent, m/sec; T_1, T_2, temperature of the heat-carrying agent at the inlet to and the outlet from the drying chamber, K.

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THERMOPHYSICAL SPECTROSCOPY OF THE DEFECTIVE STATES IN SILICON

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Experimental research into the thermophysical properties of silicon containing defects formed under a variety of external stimuli serves to demonstrate the broad possibilities of employing thermophysical methods to study the nature of defects in silicon.

We are thoroughly familiar with the fact that the physical properties of semiconductor materials and devices are extensively determined by the presence of defect states in the crystal lattice of the semiconductor. Information on the structure of the defect state, its charge state, as well as on other properties, may be revealed by studies of the electron paramagnetic resonance (EPR) spectra, as well as by optical, acoustic, and dielectric spectroscopy, as well as by a number of electric and photoelectric methods. However, these methods are subject to well-known failings and advantages [1-3].

The utilization of "nontraditional" methods to research the physical properties of the defect states in semiconductors is of great importance, since in this case it is possible to observe earlier unknown physical phenomena whose interpretation leads to a more profound understanding of the unique features involved in the behavior of the defect states in semiconductors. In studying the nature of defects in semiconductors, as demonstrated by the research covered in [4-7], the experimental studies of the relationship between temperature and the thermophysical properties of semiconductors with defects have proved to be extremely productive, and this research can be carried out successfully over a rather broad range of temperatures, and the thermophysical methods in this case exhibit a number of positive aspects. In particular, these include the rigorous thermodynamic description of the process in which the temperature, energy, and time are measured precisely. As a result we can derive information that is both purely fundamental in nature (information regarding the properties of the phonons spectrum, unique features of the relationship between defects, the ordered or disordered location of the defects in the crystalline lattice, their interaction, as well as on the various mechanisms by means of which the defect states are restructured), as well as of a practical nature (information regarding impurities, vacancies, complexes, accumulations and associations of impurities, on the kinetics of the formation and disintegration of solid solutions of impurities, etc.), thus opening real possibilities of developing new concepts regarding the mechanisms of defect-formation in semiconductors;

In this study we examine the thermophysical properties of silicon defects in the light of the possibility of using these thermophysical methods to study the structures of deep energy centers (DEC).

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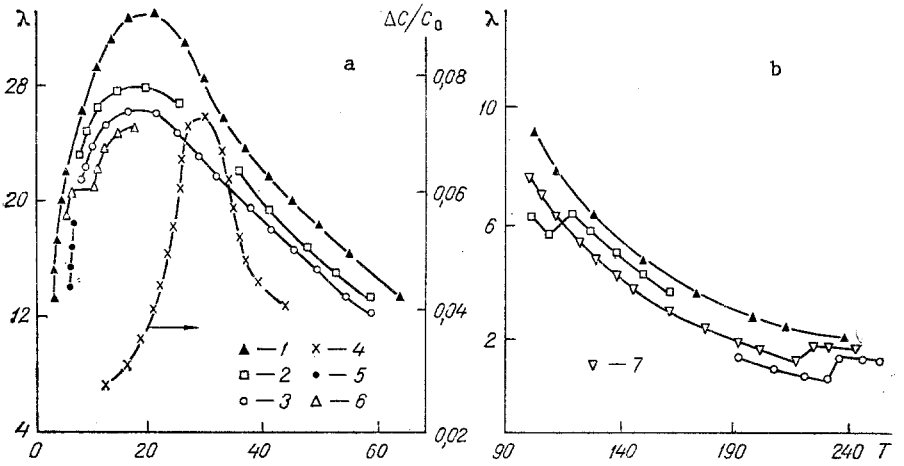

Fig. 1

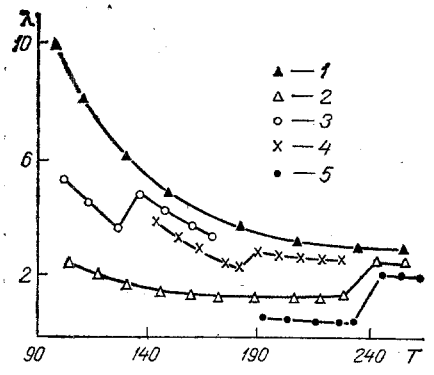

Fig. 2

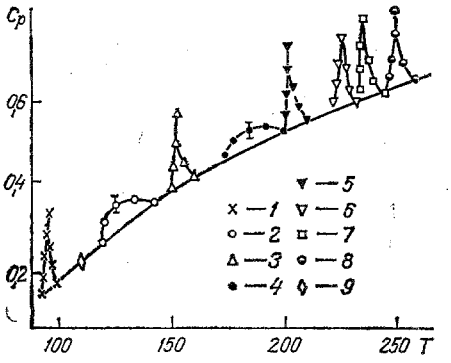

Fig. 3

Fig. 1. Thermal conductivity and heat capacity of defective silicon: a) T < 90 K; b) T > 90 K; 1) original Si; 2) Si<ER>; 3) Si<NR>; 4) Si<Te>; 5) Si<Hg>; 6) Si<Ni>; 7) Si<HT>. λ, W/(cm·K); T, K.

Fig. 2. Thermal conductivity of silicon impurity: 1) original Si; 2) n-Si<Au>; 3) n-Si<Pd>; 4) p-Si<S>; 5) n-Si<Ni>.

Fig. 3. Phase transitions in defective silicon: 1) Si<ER>; 2) n-Si<Mn>; 3) Si<Ag>; 4) Si<Co>; 5) n-Si<S>; 6) n-Si<Au>; 7) Si<NR>; 8) Si<HT>; 9) original Si. C_p, J/(g·K).

Specimens and Measurement Methods. We use monocrystalline silicon specimens of the n- and p-type with the specific resistances of 10-100 Ω·cm at 300 K. The silicon defect specimens were produced under the following external treatments: heat treatment at high temperatures; neutron and electron radiation at 300 K; diffusion alloying with impurity atoms at high (T ≥ 1200 K) temperatures. Let us note that the technology of producing these defect specimens has been described in detail in [5-8]. To study the relationship between temperature and thermal conductivity λ(T), and the heat capacity $C_p(T)$, we made use of the widely known universal low-temperature standard reference unit of the scientific production enterprise called "Dal'standart" (in the city of Khabardusk), where the determination error for λ is no more than 3%, and that of C_p 0.4%.

Experimental Results. Figures 1-3 show the relationships between the thermophysical properties of the defective silicon and temperature. We see that λ(T), $C_p(T)$ is determined by the kind of defect. We have observed a number of anomalous regions in the thermophysical properties of the silicon, and the temperature regions in these are also determined by the kind of defect. Let us note that in the case of λ(T), given superlow temperatures, we have characteristic anomalies which appear in the form of little steps, or in a more pronounced elevation in the thermal conductivity than is the case in the original silicon. At higher temperatures the thermal conductivity of the defective silicon experiences a jumpwise in-

increase virtually to the magnitudes of the thermal conductivity of the original silicon. In $C_p(T)$ we observe clearly defined anomalies characteristic of structural phase transitions (SPT). Indeed, for example, as can be seen from Fig. 3, the shape of the maxima in $C_p(T)$ of a λ-type function is well described by the following relationships:

$$C_p(T) \sim (T - T_c)^k, T > T_c;\ k \simeq -2,$$
$$C_p(T) \sim (T - T_c)^k, T < T_c;\ k \simeq -3/2,$$

where T_c is the temperature for maximum of $C_p(T)$. However, as we can see from Figs. 1 and 3 we observe smoother anomalies in the $C_p(T)$ of the defective silicon. It should be noted that repeated measurements of heat capacity, nor the utilization of a differential scanning calorimeter (DSC), did not enable us clearly to determine the temperature and nature of the anomaly in $C_p(T)$, most probably because this is a consequence of the smearing of the phase transition [9, 10].

Analysis of Thermal-Conductivity Results. In order to analyze $\lambda(T)$ we compared the experimental $\lambda(T)$ results with the theoretical data from the Callaway model [11], whose details can be found in [5]. Let us examine the results of our analysis.

Region of Superlow Temperatures ($T \leq 10$ K). The predominant mechanism of heat resistance in this region of temperatures is represented by the boundary processes of phonon scattering, i.e., the scattering of phonons at the boundaries of the specimen. However, in our case the mean-free path of the phonons does not correlate to the geometric dimensions of the silicon. As was demonstrated in [5], this can be explained by the scattering of the phonons at the "large-scale" accumulations of defects, for example, into impurity associations, which is characteristic of silicon with an admixture of nickel. Studies of $\lambda(T)$ for silicon with an admixture of mercury at these superlow temperatures demonstrated that $\lambda(T)$ is independent of the dimensions of the specimen, i.e., the mechanism of thermal resistance differs from that of boundary scattering. Studies of the electrophysical properties of alloyed silicon revealed that the charged state of the impurity center may be retained all the way to the superlow temperatures [3]. Therefore, in accordance with [4] it might be hypothecated that the unique features of $\lambda(T)$ can be explained within the framework of the resonant scattering of the phonons at the separated levels (singlet, triplet) of the electron states of the impurity center, generated by the presence of intracrystalline electric fields.

As was noted earlier, at these superlow temperatures, for defective silicon in certain cases we note a rise in thermal conductivity that is more pronounced than that of the original silicon. In general, in the presence of these separated states the interaction of the phonons with the electrons of the impurity center in this case can be explained by two factors [4]. The first of these factors is geometric and is associated with the dimensions of the electron orbit of the impurity state. With certain relationships between the wavelengths of the scattered phonons and the radius of the electron orbit, the scattering cross section attains a maximum and then diminishes, which leads to a growth in the mean-free path of the phonons and to a corresponding increase in the thermal conductivity. The second factor is purely resonant in nature and is associated with the virtual electron transitions between the separated levels of the main state. This factor is responsible for the sharp spike in the scattering at specific phonon wavelengths.

The Temperature Region $20 \leq T \leq 90$ K. For this temperature interval a most pronounced effect exerted by the defects on $\lambda(T)$ is characteristic. As we can see from Fig. 1a, we observe anomalously high values for the additional heat resistance, despite the exceedingly low concentrations of defect states ($N_d \leq 10^{18}$ cm^{-3}), and here it is impossible to bring the theoretical and experimental values of the phonon-defect scattering into agreement, even when the charged state of the defect is taken into consideration.

Studies of the physical properties of defect silicon [3, 5, 12] showed that for the formation of a deep defect state the defects must interact with each other and the silicon crystal lattice. As a result of such interaction various complexes fall into substantial concentrations, significantly affecting the physical properties of the silicon. In particular, with appropriate selection of the parameters of the external actions (heat treatment, radiation, diffusion alloying) defect states are formed within the silicon and these are identical in terms of their physical parameters, independent of the kind of external action, thus

providing a basis for the assumption of a single mechanism for the formation of defects with DEC. It has been established in [12] that the defects with DEC, in particular, the impurity atoms, because of the configuration of the external electron shells, cannot simply penetrate into the nodes of the crystal lattice. For these, obviously, penetration into those cells of the crystal lattice is possible where vacancies have formed, i.e., there where they can form a link with the silicon crystal lattice with the smallest possible number of electrons, i.e., thermodynamically an advantageous formation of the "vacancy-impurity" complex. With heat and radiation treatment we most frequently achieve an analogous "vacancy-impurity" complex; however, boron and phosphorus play the role of technological impurities, whereas oxygen, carbon, etc., are impurities that cannot be controlled.

As a result of the considerable localization of the electrons in the defect states, the strong phonon-electron interaction leads to a displacement of the impurity atoms from the node of the crystal lattice, i.e., we achieve a noncentrality of displacement that is characteristic of the Jahn-Teller effect (JTE). It is clear that a similar electrically charged complex is represented by the noncentral impurity, i.e., the vacancy exhibits an effective electric dipole moment. The dipole direction, i.e., the position of the ion, is not arbitrary, but is determined by the symmetry of the crystal. For example, because of the limited solubility of palladium in silicon, because of the comparatively great difference in their covalent radii, and because of polarizability, an orthorhombic elastic dipole moment of orientation <100> appears as a consequence of the displacement of the palladium ion from the node of the silicon lattice in the direction <100>. These features of the defect state in the silicon lead to the formation of noticeable regions of elastic distortions and correspondingly to a sharp increase in the thermal resistance, the latter being a function exclusively of the charged state of the defect. An evaluation of the intensification due to the charged state show that this was a quantity larger by a factor on the order of 3-5 times.

The Temperature Region $90 \leq T \leq 300$ K. At these temperatures (Figs. 1 and 2), with the exception of certain temperature intervals, we have $\lambda \sim T^{-1}$. Consequently, the predominant mechanism of heat resistance is represented by the phonon-phonon and phonon-defect scattering processes. The additional thermal resistance caused by the defect state is independent of temperature. However, as was noted earlier, in this temperature region $\lambda(T)$ exhibits anomalies expressed in the form of a pronounced jump in the thermal conductivity, with the additional thermal resistance dropping to some minimum, i.e., additional thermal conductivity appears. Depending on the nature of the external treatment, the following physical mechanisms are possible in this case for the formation of this additional thermal conductivity: with the presence in the silicon forbidden zone simultaneously of several donor or acceptor levels (i.e., a multicharge center) as a consequence of the interelectron interaction between the carriers at the donor level and in the conductivity zone we have a resonant transition in which the electron from the donor level is excited into the conductivity zone and simultaneously an electron from the conductivity zone is captured by the donor. As a result we have a transfer of energy from one donor state to another and with the temperature gradient we have a transfer of the excess energy in the form of the conduction of heat. Characteristic of such a heat-transfer mechanism is its relationship to the degree to which the heat energy level is compensated. In another case, the appearance of additional heat conduction is caused by the so-called activation thermal conductivity [13]. At low ($T < 70$ K) temperatures the defect states are electrically charged. At certain temperatures, depending on the ionization energy of the defect, as a result of the increase in the quantity kT, we have thermal ionization of the defect state and, according to [13], additional activation thermal conductivity proportional to

$$\Delta\lambda \sim \frac{1}{T} \exp\left(-\frac{E}{kT}\right)$$

and caused by recharging of the defect state.

Analysis of Heat-Capacity Results. As was noted earlier, in $C_p(T)$ for the defect silicon we observe a number of regions of anomalous $C_p(T)$ which we have identified as SPT. Let us examine the possible physical SPT mechanisms induced by the defect states.

In the majority of cases the SPT that we have observed, as a rule, are encountered in electrically micrononuniform specimens. In this case, electrically charged local micrononuniformities are formed within the volume of the silicon and as a consequence internal electric fields are also formed. The most clearly expressed influence of the micrononuniformities

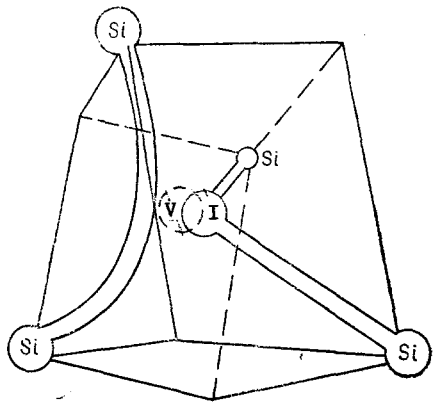

Fig. 4. Structure of defective silicon: V) vacancy; I) impurity.

on the SPT is observed in the thermal radiation treatments, as well as in the introduction of nickel into the silicon. Measurements of the Hall effect show that SPT is observed only in those specimens of silicon for which an exponential relationship between Hall mobility and temperature is characteristic [14], and the SPT appears in those temperature regions corresponding to a transition from a power relationship of Hall mobility (characteristic for the scattering of carriers in charged point defects) to the exponential (characteristic for the scattering at "large" defects). As follows from [15], such nonuniformities represents regions corresponding to a minimum in the large-scale potential relief in which the compensating deep centers when T > 300 K have been completely ionized. With a drop in temperature of the specimen we will have an increase within its volume of the strength of the internal electric field, since the concentration of the shielding free charge carriers is reduced. The increase in the energy of the electric field leads to an additional deformation of the specimen because of the electrostriction and transition of the specimens to an electrically nonuniform state. Such a "order-disorder" transition will be accompanied by the appearance of a phase transition. The rather good agreement between the SPT temperature and the temperature of the thermal ionization of the defect state provides a basis for our assumption that the observed SPT is caused precisely by this mechanism.

Investigations into the defect states caused by impurity centers by EPR methods as well as by internal friction led to the discovery of a noncubic center whose symmetry is lower than the point symmetry of the crystal. For example, it was demonstrated in [16] that the orthorhombic symmetry of the impurity center for gold with an orientation <100> arises as the impurity atom is displaced from the node of the lattice in one of six equivalent directions, the transitions between these possible due to both tunneling and thermal activation. Let us examine both of these possible mechanisms.

We know that tunnel dipole-lattice relaxation of centers with reoriented electric and elastic dipole moments determines to a considerable extent the physical properties of the crystals, and in such objects, as a rule, the internal electric fields and their distributions play an important role [17]. Although it was demonstrated in [17] that in "rigid" matrices, such as those of silicon, high-frequency optical phonons are not effective in tunnel reorientation relaxation which predominates at low temperatures; however, in the local dynamics of the lattice we find a soft resonance [18] which makes a considerable contribution to the tunnel relaxation. Moreover, the internal electric fields in crystals with SPT serve as a decisive parameter for the critical relationships of the tunnel dipole-lattice relaxations [17].

With the thermoactive SPT mechanism it becomes possible to observe the Jahn–Teller centers when the center is localized at one of the minima of the adiabatic potential. The internal electric fields "block" the Jahn–Teller centers at one of the minima of the adiabatic potential, and when the contribution of such an internal electric field becomes comparable to kT we have an increase in the spot symmetry to the cubic, and the SPT is consequently realized.

Analysis of the above-indicated SPT mechanisms showed that the most probable is, apparently, thermal activation. In the case of tunnel effects we must observe an increase in the thermal resistance that is associated with the scattering of the phonons in the tunnel state, which is not found in the experiments on heat conduction.

In the above-described SPT mechanisms, as we can see, it is the internal electric fields that play a decisive role. This factor is confirmed by experimental results relating to $C_p(T)$ under conditions of IR illumination, when there are virtually no anomalies in $C_p(T)$. Indeed, under conditions of IR illumination (i.e., optical ionization of defect states) the concentration of the free charge carriers will be maintained at a sufficiently high level, regardless of the temperature of the specimen, which leads to effective shielding of the internal electric fields generated by local nonuniformities, and it will correspondingly lead to an absence of SPT.

As was noted earlier, in $C_p(T)$ at low temperatures ($T < 60$ K) we observed an anomaly in $C_p(T)$ (Fig. 1a, curve 5). At such low temperatures it is impossible to describe the anomaly of the SPT within the scope of the appearance of SPT. Analysis of the results in a theoretical model [19] enabled us to establish that the anomaly in $C_p(T)$ can be described through the following model.

In silicon, containing impurity atoms of diverse configurations for the electron shells and atomic masses, the electrons interact with the phonons and in the case of considerable phonon-electron links the total potential of the crystal lattice is disrupted. As a result of the action of the perturbed potential, the impurity center strives to occupy a new quasi-resonant position in the crystal lattice and lattice relaxation takes place. The change in the force constant of the lattice leads to the formation of local and pseudolocal states due to the change in the shape of symmetry for the crystal lattice and correspondingly to a change in the frequency spectrum of the phonons, which must become evident in the low-temperature heat capacity. We presented a similar result in [5]; however, the appearance of local oscillations there was caused only by the difference between the atomic masses and covalent radii of the impurity and main atoms.

Certain Physical Mechanisms for the Formation of Defect States with Deep Energy Levels in the Silicon. Studies of the temperature relationship between the thermophysical properties of defect silicon revealed a number of new, earlier unknown, physical phenomena, such as structural phase transitions, anomalously high values for the additional thermal resistance caused by the defect state, scattering of phonons at the split electron states of the defect centers with deep energy levels, the appearance of local and pseudolocal oscillations, etc. The experimental results which we obtained with respect to the thermophysical properties of defect silicon allows us to draw certain conclusions with respect to the physical mechanisms involved in the formation of defect states with deep energy levels in the silicon.

As was noted earlier, various means of achieving deep centers within the silicon are thermodynamically advantageous and these include the appearance of the "vacancy-impurity" complex. The significance of the phonon-electron interaction is found in the displacement of the defect from the node of the crystal lattice, i.e., the noncentrality of substitution. The large difference in the covalent radii and the polarizability of the substituted and substituting atoms enhances the appearance of noncentrality of substitution, and here we have the disruption of the balance of polarizaton and repulsion forces in the centrosymmetric point in the cell. Such an effect can be observed in the case of a degenerate electron state which corresponds to an unstable nuclear configuration, i.e., the disruption of the overall potential of the crystal lattice [20]. The existence of such an effect significantly alters the physical properties of the crystals, anomalies arise in the heat capacity, in the conduction of heat, etc. The anomalies in $\lambda(T)$, $C_p(T)$ we have observed and the consequent anomalous high values for the additional heat resistance, the structural phase transitions, the appearance of local and quasilocal oscillations in the impurity atoms, the noncentrality of substitution as a result of the significant phonon-electron interaction, these all are characteristic of the so-called Jahn–Teller centers (Fig. 4). Therefore, apparently one of the basic physical mechanisms for the formation of defect states with deep energy levels is the Jahn–Teller nature of the defect interactions. Equally apparent is the significant phonon-electron interaction that serves as a general characteristic of the deep-level centers within the silicon, since characteristic of these is pronounced localization of the electron at the defect centers, and the interaction of the defects is accomplished not by the hybridization of the electron shells, but through the phonon subsystem. These facts enable us to note the trends for future research in the area of semiconductor thermophysics.

NOTATION

$\lambda(T)$, $C_p(T)$, temperature relationships for thermal conductivity and heat capacity, respectively; N_d, defect concentration; k, Boltzmann constant; E, ionization energy; ER, electron radiation; NR, neutron radiation; HT, heat treatment.

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