PHASE TRANSITIONS IN DOPED SILICON

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The temperature dependence of the heat capacity of silicon doped with impurity atoms with deep levels has been investigated in the temperature interval of 15-300 K. Phase transitions induced by impurity centers have been discovered.

In [1], results of investigations of thermophysical properties of high-purity silicon doped with impurity atoms with deep energy levels are given. In this case, in practice, only deep impurity centers are present in silicon. However, the presence of shallow acceptor centers and deep impurity centers in silicon results in a strong localization of electrons on impurity centers and, correspondingly, the appearance of an effective phonon–electron interaction. A specific characteristic is that substitution by the impurity atom in the crystal lattice of silicon is not central. This is the so-called impurity atom of substitution, the equilibrium position of which is displaced from the node of the lattice. The complex of the type noncentral impurity-vacancy (related to the absent nodal atom) can result in the appearance of the Jahn–Teller effect [2] and, consequently, structural phase transitions [3]. In connection with the aforementioned, the purpose of the present work is to investigate the temperature dependence of the heat capacity $C_p(T)$ of silicon of p- and n-types doped with impurities with deep energy levels.

Samples and the Method of Measurement. We used single crystals of silicon of n- and p-type with resistivity $\rho = 20\ \Omega$ cm at 300 K. The content of oxygen in the original samples of silicon did not exceed 10^{16} cm^{-3}. The doping of silicon with impurities of Au, Ag, Ni, Mn, Co, S, and Sc was in accordance with technology described in [1].

Heat Capacity. In order to measure $C_p(T)$ we used a universal low-temperature thermophysical installation; the measurement error of the specific heat in the temperature interval 15-300 K did not exceed 0.3% with reference to the measurement of $C_p(T)$ of corundum.

Results of Measurements. Results of measurements of $C_p(T)$ of doped silicon are given in Figs. 1-5. As is seen, a number of domains of anomalies in the heat capacity are discovered on $C_p(T)$ of doped silicon, the temperatures of which depend on the impurity. Obtaining quasistatic thermograms has allowed us to determine that the discovered anomalies in $c_p(T)$ of doped silicon correspond to structural phase transtions. Taking account of the fact that we have found no anomalies in $C_p(T)$ of silicon samples subjected to high-temperature treatment without the source of impurities, while repeated cooling and heating of doped samples in the temperature interval of 15-300 K does not result in noticeable changes in these anomalies of $C_p(T)$, such behavior is explained by the presence of impurity atoms.

Analysis and Discussion of Results. I. Si<Au>; Si<Ag>. As was noted above, in $C_p(T)$ of Si<Au> and Si<Ag>, a phase transition has been discovered (Fig. 1). Investigations of impurity centers of Au and Ag in Si (p- and n-type) by methods of electronic paramagnetic resonance and internal friction resulted in the discovery of a noncubic center having symmetry lower than the symmetry of silicon [4, 5]. It is shown in [5] that the orthorhombic symmetry of fold with orientation <100> appears when the impurity atom is displaced from the node of the silicon lattice. Obviously, in this case the complex noncentral impurity-vacancy possesses an effective dipole moment. The direction of such dipoles, i.e., the position of the atom in the crystal lattice, is not arbitrary but depends on the crystal symmetry. In the case of Si<Au>, the impurity atom is displaced from the node of the silicon lattice in one of the six equivalent directions, transitions among which are possible due to both tunneling and thermoactivation. Therefore, dipoles are not "frozen," but can

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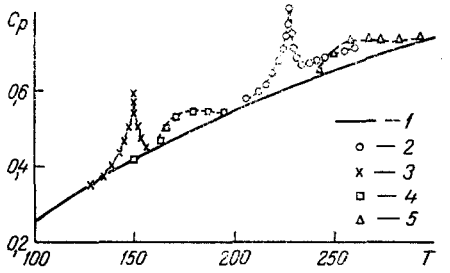

Fig. 1. Heat capacity of silicon doped with gold and silver: 1) original silicon; 2) n-S<Au>; 3) n-Si<Ag>; 4) p-Si<Ag>; 5) p-Si<Au>. C_p, J/(kg·K); T, K.

orient themselves in both external and internal electric fields. Jahn–Teller centers can be observed because of the effect of the internal electric field created by reorienting local centers. Internal fields "block" the Jahn–Teller centers in one of the minima of the adiabatic potential, transitions among which are realized not by tunneling but through thermoactivation. When the contribution of the effect of the electric field becomes comparable with kT, the process of raising the effective symmetry of the centers to cubic symmetry takes place. Therefore, the observed phase transition in Si is determined by the Jahn–Teller nature of impurity centers of Au and Ag in Si.

In samples of P-Si<Au> and p-Si<Ag> (Fig. 1, curves 4 and 5) we have discovered broad anomalies in $C_p(T)$; the absolute values of the anomalies are not large (3-5%) and are smoothed considerably. It is necessary to note that the application of differential scanning calorimeters does not allow one to determine clearly the temperature and the character of the anomaly in $C_p(T)$. Most likely it is determined by spreading of the phase transition. The impurity centers of Au and Ag are also quasi-Jahn–Teller centers with orthorhombic symmetry oriented in different directions (for gold in the direction <100>). Similarly to the aforementioned, the raising of the symmetry of impurity centers to cubic symmetry is possible due to the reorientation of electric dipoles and electronic redistribution among them. Two experimental facts favor the electronic mechanism of the phase transition: firstly, the observed phase transition is suppressed as a result of irradiation of samples by infrared light with energy $h\nu < E_g$; secondly, the phase transition is also suppressed in samples subjected to low-temperature annealing ($T \leq 900$ K), when impurity atoms of Au and Ag pass into electrically inactive state [6]. A physical mechanism of this phenomenon is that the Jahn–Teller effect can emerge (disappear) under the ionization (deionization) of impurity centers [7].

II. Si<Ni>. A distinctive feature of impurities of transition metals in silicon is that electronic configurations of these impurities are, firstly, nonspherically symmetric and, secondly, strongly localized. These two factors are of extreme importance for the group of so-called coordination compounds in which symmetrical distortions of the crystal lattice occur due to the Jahn–Teller effect. For sufficiently low temperatures the Jahn–Teller effect is "frozen"; however, as the temperature increases it starts reorienting. It was found by methods of electron paramagnetic resonance that the displaced atom can have two kinds of reorientation: inversion and rotation. For example, for the impurity of nickel in p-Si the reorientation excited thermally is of importance, namely, rotation, which shows itself as a phase transition (Fig. 2). In n-Si, concentration-deopendent effects are of higher significance (Fig. 3). As is seen from Fig. 1, two domains of the anomaly in $C_p(T)$ are observed. The first domain ($T \sim 25$ K) is formed due to the contribution of the tunneling, when the phase transition does not depend on concentration. The second domain of anomaly in $C_p(T)$ depend to a great degree on the concentration of the impurities. In this case a simultaneous interaction of a noncentral ion with the polarization and the lattice deformation is possible, which leads to the appearance of an additional temperature-dependent electrostriction term with the constant of electrostriction [3] Δq in the free energy of the crystal:

$$\Delta q \sim gNa^2/(kT)^2.$$

The situation when the phase transition takes effect becomes possible because electrostrictional interactions always reduce nonharmonical constants of interaction, and Δq increases when the temperature decreases.

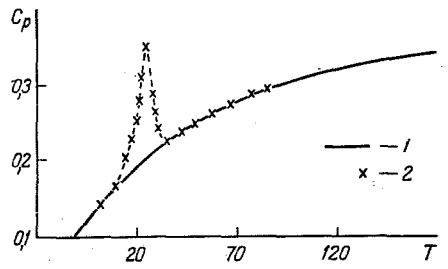

Fig. 2. Heat capacity of silicon doped with nickel: 1) original p-Si; 2) p-Si<Ni>.

It was shown in [3] that decentering, i.e., the multiminimal character of the adiabatic potential, can arise below a certain determined temperature T_0. Sometimes this situation is called "a local phase transition" or "local freezing." Actually, there is no freezing at all, and below T_0 the reorientation of the ion among different minima occurs, which shows itself as phase transition.

III. Si<Mn>; Si<Co>; Si<Sc>. In these systems the Jahn–Teller effect is also observed in spectra of electron paramagnetic resonance. The observation of cooperative effects described above presents difficulties due to the low solubility of these impurities in silicon. However, as is seen from Fig. 4, in the region of temperatures greater than 150 K, weakly manifested anomalies in $C_p(T)$ are nevertheless observed. The physical picture of observed phase transitions is apparently as follows. 1. When acceptor centers are introduced into electronic silicon, compensation of free electrons by acceptor levels of the impurity occurs, and for certain relations between concentrations of shallow and deep impurity centers, the impurity centers are in a charged state. Owing to the effective phonon–electron interaction, impurity atoms create around themselves a strong distortion of the crystal lattice determined by the displacement from the node and by the charged state. At specified temperature transition of electrons from deep levels into the C-band takes place as a result of thermal ionization, which leads to the transition of impurity atoms into an electrically neutral state; the latter is accompanied by lattice relaxation, i.e., by the decrease in distortions and, accordingly, by the phase transition.

2. In the other case the effective phonon–electron interaction can result in the following effect. The impurity atom in the ionized state occupies a position in the crystal lattice of silicon for which its orbital moment is not equal to zero, and due to that the Jahn–Teller effect can show itself. Under the influence of thermal ionization the orbital moment becomes equal to zero as a result of the recharging of the deep impurity center and the Jahn–Teller effect is removed [7]. It means that under recharging the position of the impurity in the crystal lattice changes, which is followed by lattice relaxation and, therefore, by the phase transition too. It is necessary to note that a similar effect of displacement of the impurity atom under recharging was discovered in [8].

IV. Si<S>. There are practically no direct experimental data conforming the decentering of ions of S in Si. We suggested that the decentering takes place in Si<S> [9]. Indeed, an extremely large value of the additional heat resistance (at sufficiently small concentrations of impurities of sulfur $N < 10^{17}$ cm^{-3}) cannot be explained by the scattering of phonons on lattice defects, it is only possible at strong phonon–electron interaction. The decentering of substitution is also supported indirectly by a considerably difference in the ion radii: Si (1.90 Å) and Si (0.30 Å). It has been found in [9] that a steep jump in the thermal conductivity is observable on the temperature dependence of the thermal conductivity Si<S> at temperatures T ~ 200 K. As is seen from Fig. 5, the anomaly in $C_p(T)$ is observed at temperatures T ~ 200 K expressed as a λ-function. A physical picture of the observed phase transition is apparently conditioned by the Jahn–Teller nature of impurity centers in Si<S>.

Apparently, consideration of displacements of atoms due to phonon-electron interaction and, therefore, for the Jahn–Teller effect is a phenomenon regular enough for centers with deep levels in semiconductors [8]. This is supported by the data on electron paramagnetic resonance and by experimental results of the present work. Further, the Jahn–Teller effect can be treated as the formation of complexes of the type impurity atom-vacancy. Indeed, as has been shown in [1], concentrations of electrically active impurity centers are of the

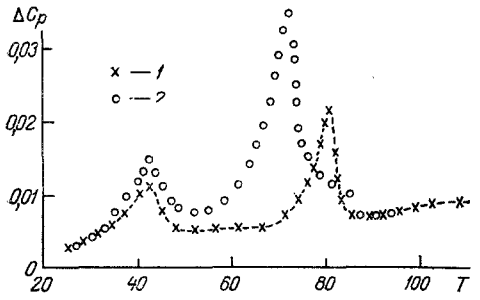

Fig. 3

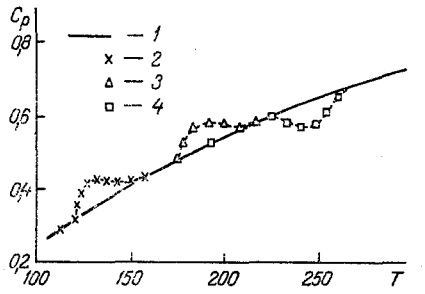

Fig. 4

Fig. 3. Heat capacity of silicon doped with nickel. 1) n-Si<Ni>, $N = 7 \cdot 10^{17}$ cm^{-3}; 2) n-Si<Ni>, $N \sim 10^{17}$ cm^{-3}.

Fig. 4. Heat capacity of silicon doped with deep impurity centers: 1) original Si; 2) Si<Mn>; 3) Si<Co>; 4) Si<Sc>.

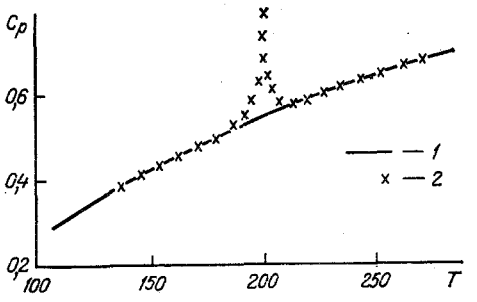

Fig. 5. Heat capacity of silicon doped with sulfur: 1) original Si; 2) Si<S>.

same order of magnitude as the equilibrium concentration of vacancies formed at the same temperatures of diffusion, i.e., formation of the complex of the type vacancy-doping impurity is possible.

Therefore, the conducted investigations of the temperature dependence of the heat capacity of silicon doped with impurities with deep energy levels have shown that this dependence is determined by the impurity atom and by peculiarities of its interaction (nature) with the silicon lattice.

NOTATION

$C_p(T)$, temperature dependence of the isobaric heat capacity; ρ, resistivity; h, Planck constant; ν, incident light frequency; E_g, the width of the forbidden band in silicon; Δq, electrostriction term; g, interaction constant of the decentralized ion with elastic deformations; N, impurity concentration; d, dipole moment determined by the magnitude of the central displacement; k, Boltzmann's constant.

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