THERMOPHYSICAL STUDIES OF DEEP IMPURITY CENTERS IN SILICON

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The thermophysical properties of silicon doped with impurity atoms having deep energy levels are studied over the temperature range 4-300°K. It is found that the temperature dependence of these properties is determined mainly by unique features of the interaction of the impurity atoms with the silicon crystalline lattice.

It is well known [1] that thermophysical studies are very convenient and effective for studying the nature of various defects in solids, in particular, semiconductors. Their main advantage is that they provide direct information on the character and concentration of various defects (impurities, vacancies, complexes, dislocations, impurity associations), on interaction of defects, on the ordered or disordered arrangement of defects, the character and features of interatomic bonds, the properties of the lattice oscillatory frequency spectrum, etc. Thus, the goal of the present study is to use thermophysical methods to detect and define the nature of deep impurity centers in silicon.

Samples and Measurement Technique. Doping of the silicon with impurities Au, Zn, S, Ni, Cr, Se, Te, Hg, Rh, Re, and Pd was accomplished by the diffusion method [2] at a temperature of 1250°C for 10-50 h with subsequent rapid cooling in air at a rate of ∿ 10 deg/sec. High purity silicon single crystals were used together with the purest possible chemical elements. The diffusion was carried out in ampuls of optically pure quartz. After diffusion the surface layer with nonuniform impurity concentration was removed from the specimens. Then neutron activation analysis and the photocapacitance method [3] were used to determine the total solubility and concentration of electrically active impurity centers. Specimens for study of thermophysical properties were than cut in the form of rectangular parallelopipeds with typical size of 5 × 5 × 40 mm. Table 1 presents some parameters of the specimens.

The temperature dependences of thermal conductivity $\lambda(T)$, specific heat $C_p(T)$, and thermal diffusivity $a(T)$ were measured using the absolute steady-state thermal flux method for $\lambda(T)$, a vacuum-adiabatic calorimeter for $C_p(T)$, and the Angstrom method for $a(T)$ over the temperature range 4-300°K. A UNTO universal low-temperature thermophysical set was used for the λ and C_p measurements, while the equipment described in [4] was used for the a measurements. Uncertainties in determining λ were no more than 5%, $C_p \sim 0.4\%$, $a \sim 10\%$.

Experimental Results. Figures 1 and 2 show the functions $\lambda(T)$ for silicon in the "pure" state and doped with the elements enumerated above. It is evident that $\lambda(T)$ is determined by the dopant impurity. Introduction of dopants leads to an abrupt fall in λ characteristic of the impurity atoms Au, Hg, Rh, Re. For the remaining impurities Zn, S, Cr, Se, Te, the suppression of thermal conductivity is relatively less. However a decrease in silicon thermal conductivity does not correlate with increasing atomic mass of the impurity atom. For example, the decrease in λ for the impurity Ni is significantly greater than for Se. Although the impurity atoms Au, Hg have similar atomic mass, the character of their effect on $\lambda(T)$ differs. Construction of curves $\Delta W(\sigma)$ showed that ΔW does not correlate with σ. Further, for the impurities Ni, Se, Te, Rh, Au, Hg the behavior of $\lambda(T)$ was anomalous, diverging from $\lambda(T)$ of pure silicon. This indicates that $\lambda(T)$ is determined not by

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TABLE 1. Some Characteristics of Specimens

Impurity	Concn. total	Concn. electrically active	Atomic mass	Impurity	Concn. total	Concn. electrically active	Atomic mass
Au	$4\cdot10^{17}$	$2\cdot10^{15}$	197,0	Se	10^{17}	$9\cdot10^{14}$	78,96
Zn	$6\cdot10^{16}$	$2\cdot10^{15}$	65,97	Te	10^{17}	$1,5\cdot10^{15}$	127,60
S	$8\cdot10^{16}$	$4\cdot10^{15}$	32,06	Hg	10^{17}	$4,8\cdot10^{15}$	200,59
Ni	$7\cdot10^{17}$	$5\cdot10^{15}$	58,71	Rh	$3\cdot10^{17}$	$5\cdot10^{15}$	102,91
Cr	10^{17}	$5\cdot10^{15}$	52,0	Re	10^{17}	$7\cdot10^{15}$	186,22
				Pd	10^{17}	$9\cdot10^{14}$	106,4

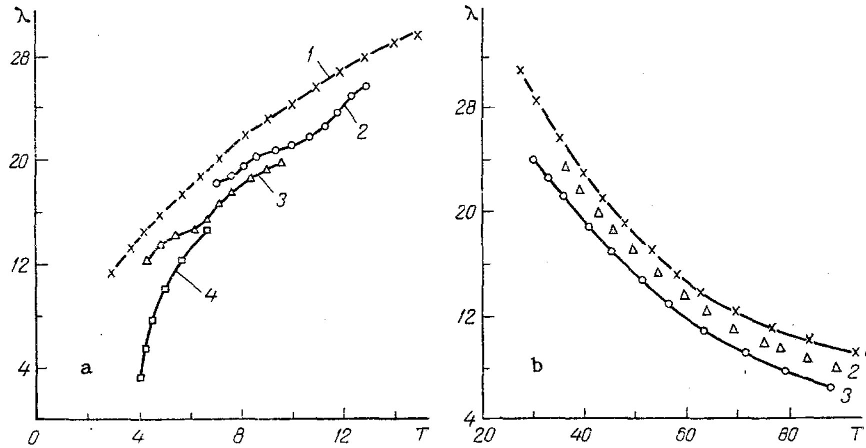

Fig. 1. Temperature dependence of thermal conductivity of doped silicon ($T < 20°K$): a) 1, Si; 2, Si<Se>; 3, Si<Ni>; 4, Si<Hg>; b) 1, Si; 2, Si<Zn>; 3, Si<Re>; λ, W/cm·K; T, °K.

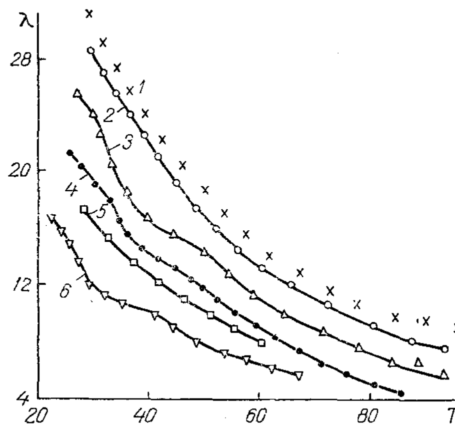

Fig. 2. Temperature dependence of thermal conductivity of doped silicon: 1) Si; 2) Si<S>; 3) Si<Te>; 4) Si<Rh>; 5) Si<Pd>; 6) Si<Au>.

impurity atom inclusion or replacement type defects, but by other defects produced by unique features of the interaction of the dopant impurity with the silicon crystalline lattice.

TABLE 2. Parameters for Phonon Scattering on Impurity Atoms

Impurity	v/L	$B+D$, CK^{-3}	A, sec^{-3}	A (calculated) sec^{-3}
Au	$7{,}56\cdot10^{-7}$	$4{,}2\cdot10^{-24}$	$5{,}5\cdot10^{-44}$	$2{,}3\cdot10^{-44}$
Zn	$7{,}44\cdot10^{-7}$	$3{,}86\cdot10^{-24}$	$1{,}56\cdot10^{-44}$	$1{,}03\cdot10^{-44}$
S	$7{,}23\cdot10^{-7}$	$4{,}6\cdot10^{-24}$	$1{,}3\cdot10^{-44}$	$9{,}9\cdot10^{-45}$
Ni	$5{,}4\cdot10^{-7}$	$4{,}1\cdot10^{-24}$	$1{,}91\cdot10^{-44}$	$1{,}2\cdot10^{-44}$
Cr	$7{,}43\cdot10^{-7}$	$3{,}74\cdot10^{-24}$	$1{,}64\cdot10^{-44}$	$9{,}6\cdot10^{-45}$
Se	$4{,}43\cdot10^{-7}$	$4{,}23\cdot10^{-24}$	$1{,}76\cdot10^{-44}$	$2{,}76\cdot10^{-44}$
Te	$7{,}32\cdot10^{-7}$	$3{,}94\cdot10^{-24}$	$2{,}1\cdot10^{-44}$	$1{,}34\cdot10^{-44}$
Hg	$1{,}01\cdot10^{-7}$	$4\cdot10^{-24}$	$5{,}1\cdot10^{-44}$	$7{,}9\cdot10^{-44}$
Rh	$7{,}62\cdot10^{-7}$	$4{,}9\cdot10^{-24}$	$2{,}9\cdot10^{-44}$	$1{,}44\cdot10^{-44}$
Re	$7{,}49\cdot10^{-7}$	$3{,}9\cdot10^{-24}$	$1{,}71\cdot10^{-44}$	$9{,}89\cdot10^{-45}$
Pd	$7{,}51\cdot10^{-7}$	$3{,}8\cdot10^{-44}$	$1{,}8\cdot10^{-44}$	$1{,}09\cdot10^{-44}$

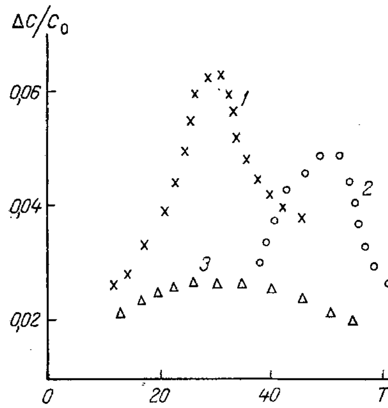

Fig. 3

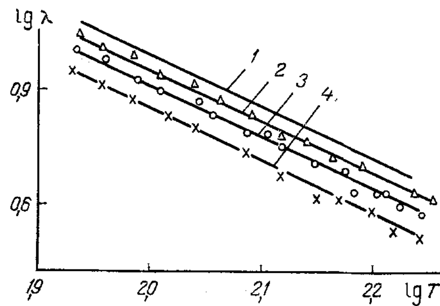

Fig. 4

Fig. 3. Heat capacity of doped silicon: 1) Si<Au>; 2) Si<Rh>; 3) Si<Re>.

Fig. 4. Thermal conductivity of doped silicon: 1) Si; 2) Si<Cr>; 3) Si<Ni>; 4) Si<Au>.

Analysis of Thermal Conductivity Results. To analyze $\lambda(T)$ the experimental $\lambda(T)$ results were compared to calculations with Callaway's theoretical model [5]. In this model $\lambda(T)$ is described in the scattering relaxation time approximation by the following expression:

$$\lambda = \frac{k_0}{2\pi^2 v}(I_1 + \beta I_2).$$

The parameters I_1, I_2, β are functions of relaxation times: $\tau_b^{-1} = v/L$, $\tau_{p-p}^{-1} = (B+D)^2\omega_2 T_2$, $\tau_{p-d}^{-1} = A\omega^4$. The scattering parameters v/L, $(B+D)$, A were determined numerically by the method of least squares, by selecting these parameters for best agreement of the calculated $\lambda(T)$ with experimental $\lambda(T)$ curves (Table 2).

We will consider the calculation results for the low-temperature range ($T < 10°K$).

In this temperature range the dominant thermal resistance mechanism is boundary scattering with relaxation time τ_b^{-1}. The phonon free path length, determined by τ_b^{-1} using the expression $l = \tau v$ for impurity atoms Au, Zn, S, Cr, Te, Rh, Re, Pd, agrees well with the actual dimensions of the specimens. For example, for the impurity Zn l = 0.513 cm. However, for Ni, Se, Hg, the values differ greatly from 0.5 cm; l_{Ni} = 0.26 cm, l_{Se} = 0.287 cm, l_{Hg} = 0.065 cm. For Ni, Se (Fig. 1a) the behavior of $\lambda(T)$ is anomalous, which is characterisc of phonon scattering on accumulations (colloids) of atoms [1]. The temperature at which the $\lambda(T)$ anomaly is observed depends on the impurity, because of the different geometric dimensions of the atomic accumulations. For Hg l = 0.065 cm, which is unrealistic. For Hg $\lambda \sim T^{4.3}$, while λ is independent of specimen dimensions, i.e., the thermal resistance mechanism is not

boundary scattering. Apparently, this is caused either by the charge state of the impurity atoms in the silicon lattice or intense phonon–electron interaction.

Temperature Range $20 < T < 90°K$. This temperature interval is characterized by the most intense effect of impurity atoms on $\lambda(T)$. From Figs. 1b, 2 it is evident that in this temperature range $\lambda(T)$ is determined by the dopant impurity. For the impurity atoms Au, Rh, Te there is an anomaly in $\lambda(T)$ in the form of an inflection. It was predicted by Kagan and Iosilevskii [6] that in the presence within the crystal of "heavy" impurity atoms resonant oscillations appear in the phonon spectrum, leading to anomalies in physical, in particular, thermophysical, properties. The $\lambda(T)$ anomaly can be described well by introducing into the total scattering process relaxation time a "resonant" term of the form $\tau_{res}^{-1} = A\omega^2T^2/(\omega_0^2-\omega^2)^2$. The resonant frequency is a function of the atomic mass and ionic radius of the impurity and main atoms. To clarify the phonon scattering mechanism, measurements were made of $a(T)$ for silicon doped with Au, Rh, Re, Te. It was established that at certain temperatures, depending on the impurity involved, there is a low-temperature anomaly in $a(T)$, expressed in the form of a sharp minimum. Inasmuch as $a = v/L$ is a direct measure of the phonon free path length, the presence of the sharp minimum indicates an intensification of scattering processes. Since there are no crystal structure transitions in silicon in the temperature range studied, intensification of scattering processes may be caused by resonant phonon scattering processes.

The presence of resonant oscillations of impurity atoms significantly changes the silicon spectrum, and thus should have the greatest effect on low-temperature heat capacity. Thus, the function $\Delta C/C_0(T)$ ($\Delta C = C-C_0$) in the low-temperature range $T/\Theta \ll \omega_0/\omega_D$ passes through a sharp maximum [6]. It is evident from Fig. 3 that in the case of silicon doping by impurity atoms Au, Rh, Re an anomaly is found which qualitatively confirms the theory of [6]. However, the function $\Delta C/C_0(T)$ shows no clearly expressed maximum. Evaluation of the resonant frequency with the expression $\omega_D^2 = 1/3|E_\lambda|$ (where E is defined by the physical properties of the impurity and main atoms) and comparison with the resonant frequency determined from $\lambda(T)$ showed, for example, that for Au these quantities differ by a factor of several times: $\omega_0^e/\omega_0^r = 124\ cm^{-1}/42\ cm^{-1}$. Therefore, the absence of a clearly expressed maximum in $\Delta C/C_0(T)$ is caused by resonant oscillations of the complex with participation of impurity atoms [7]. Formation of complexes comes about because the total solubility and concentration of electrically active impurity centers for the majority of impurities differ by a factor of several times. Further, it is evident from Table 1 that the concentration of electrically active impurity centers is equal in order of magnitude and comparable to the equilibrium concentration of vacancies formed at the same diffusion temperatures, i.e., formation of vacancy–dopant impurity complexes is possible.

Temperature Range $T > 90°K$. At these temperatures (Fig. 4) $\lambda \sim T^{-1}$. Consequently, the dominant thermal resistance mechanism is phonon–phonon scattering processes. The component ΔW caused by impurity atoms is temperature independent. However, in this case also ΔW is determined by the dopant impurity. The independence of ΔW from T allows comparison of the scattering parameter A for impurities with calculated values. Use of the A values presented in Table 2 and analysis of phonon-defect scattering relaxation times τ_{p-d}^{-1} lead to the necessity of dividing ΔW into two components; i.e., the thermal resistance of the doped silicon can be represented in the form $W = W_0 + \Delta W_e + \Delta W_n$. The numerical values of ΔW_n determined in this manner were used to calculate A and compare the values obtained with the calculated ones presented in Table 2. The comparison shows that the order of magnitude of A is identical for both cases. Consequently, the numerical value of the experimentally selected A values is determined by phonon scattering on both neutral and electrically charged centers. The intensification of scattering due to the charge state of the impurity center is in accordance with the expression $\tau_e^{-1}/\tau_n^{-1} \sim 3\text{–}5$ times, which is apparently due to charge complexes.

Thus, the studies performed have established that under identical conditions for doping of silicon by impurity atoms with deep energy levels the temperature dependence of thermophysical properties is determined by the impurity atom and its interaction with the silicon lattice. Therefore, studies of $\lambda(T)$, $c(T)$, $a(T)$ can determine the nature of a deep impurity center.

NOTATION

λ, thermal conductivity; C_p, isobaric heat capacity; a, thermal diffusivity; ΔW, thermal resistance; σ, factor considering crystalline lattice distortion; k_0, Boltzmann's constant; v, phonon velocity; I_1, I_2, β, parameters determining intensity of scattering process relaxation times; τ_b^{-1}, boundary scattering relaxation time; L, effective crystal dimension; τ_{p-d}^{-1}, phonon-defect scattering relaxation time; ω, phonon frequency; τ_{p-p}^{-1}, phonon–phonon scattering relaxation time; A, impurity scattering parameter; l, phonon free path length; τ_{res}^{-1}, resonant scattering process relaxation time; C_0, total heat capacity of "pure" silicon; Θ, Debye temperature; ω_D, Debye frequency; ω_0, resonant frequency; W_0, thermal resistance of "pure" silicon; ΔW_e, ΔW_n, thermal resistance of electrically active and neutral impurity atoms.

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