SILICON THERMOPHYSICAL PROPERTIES UNDER THERMAL LOADING

D. A. Vakhabov, A. S. Zakirov, Kh. T. Igamberdyev,
A. T. Mamadalimov, K. Makhmudov, Sh. O. Tursunov,
T. A. Usmanov, and P. K. Khabubullaev

UDC 536.2

The effect of thermal processing on thermal conductivity and specific heat of silicon are studied. It is determined that thermal processing causes formation of electrically active defects with deep energy levels due to interaction of thermodefects with the silicon crystalline lattice.

It is known [1] that for an appropriate choice of processing parameters (diffusion doping, thermal processing, radiation treatment), deep energy centers are formed in silicon, which have identical electrophysical parameters independent of the type of processing used. This indicates that the mechanism of deep center formation is the same for the various external actions. However, a significant role is played by processes of complex formation as a result of interaction of various defects with each other and with the silicon crystalline lattice, which makes difficult an unambiguous interpretation of experimental studies of deep center physical parameters in silicon. In conection with this, the goal of the present study is to continue further the investigation of the nature of deep energy centers in silicon commenced in [2-4]. We will consider the effects of thermal processing on thermophysical properties of silicon.

Specimens and Measurement Technique. Study of the effect of thermal processing on the electrophysical properties of silicon [5] has shown that the basic processes involved in formation of thermal defects are volume and surface ones. Distinguishing between thermal processing at high ($T > 1000$ K) and low ($T < 900$ K) temperatures makes it possible to consider volume processes ($T < 900$ K), neglecting defect diffusion from the surface, or surface processes ($T > 1000$ K), where diffusion from the surface dominates. Therefore, in the present study thermal processing was carried out at temperatures of 1500, 1100, 800 K. The parameters of original silicon specimens were as follows: type 1, high-purity silicon single-crystal; 2, silicon single-crystals with oxygen concentration $\sim 10^{18}$ cm^{-3}, with concentration of other uncontrolled impurities less than 10^{15} cm^{-3}; type 3, single-crystals of p- and n-type silicon (resistivity $\rho = 20$ Ω/cm at 300 K) with oxygen content of 10^{15} cm^{-3}. Thermal processing duration was 10 h with subsequent cooling in air at a rate of ~10 K/sec.

Measurements of the temperature dependence of thermal conductivity $\lambda(t)$ and specific heat $Cp(T)$ were performed over the temperature range 15-300 K with low-temperature reference measuring equipment. Uncertainty in determination of thermal conductivity λ did not exceed 3%, with specific heat C accurate to 0.2%.

Experimental Results. Figures 1-3 show $\lambda(t)$ for the original and thermal processed silicon. It is evident that $\lambda(T)$ is controlled by both the thermal processing temperature and the original silicon parameters. For high-temperature thermal processing $\lambda(T)$ in pure silicon is determined by the surface state or surface concentrations of defects produced by mechanical processing. In the other specimen types $\lambda(T)$ was determined mainly by the presence of oxygen, boron, and phosphorus impurities. Depending on the temperature of the thermal processing different effects are produced on the silicon $\lambda(T)$ dependence. For example, in a type-2 silicon specimen suppression of thermal conductivity is more significant at low temperatures than for high-temperature thermal processing. In type 3 specimens the behavior of $\lambda(t)$ is anomalous, departing from $\lambda(T)$ of the original material. There are also anomalies in the temperature dependence of $Cp(t)$ (Fig. 4). Measurements of quasistatic thermograms and the lattice parameter a established that the observed anomalies in λ, Cp corresponded to phase transitions. This indicates that λ, Cp are determined by interaction of defects with each other and the silicon crystalline lattice.

Polymer Chemistry and Physics Institute, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 55, No. 5, pp. 837-843, November, 1988. Original article submitted May 12, 1987.

0022-0841/88/5505-1304$12.50

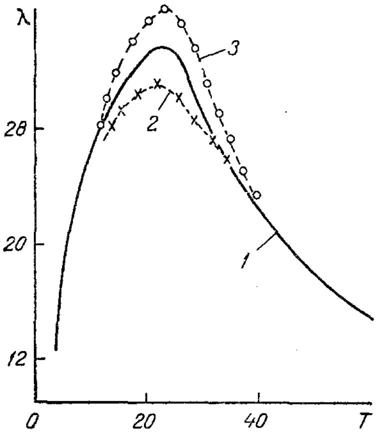

Fig. 1

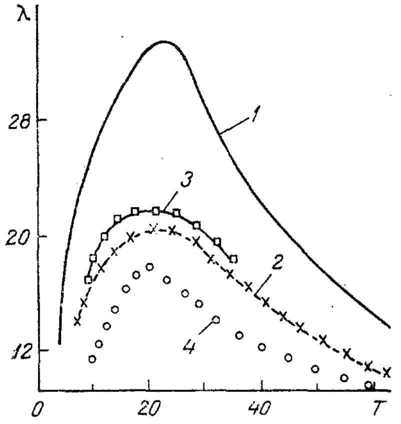

Fig. 2

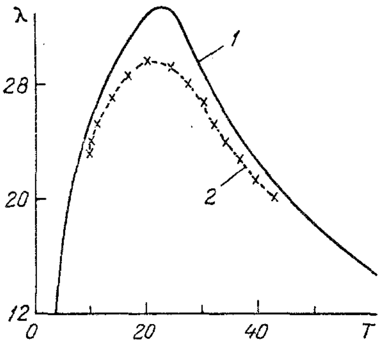

Fig. 3

Fig. 1. Thermal conductivity of high-purity silicon under thermal processing: 1) pure Si; 2) Si, thermal processing >1400 K; 3) Si, thermal processing ≥800 K. λ, W/(cm·K); T, K.

Fig. 2. Thermal conductivity of oxygen-containing silicon under thermal processing: 1) Si; 2) Si<O>; 3) Si<O>, thermal processing >800 K; 4) Si<O>, thermal processing ≤800 K.

Fig. 3. Thermal conductivity of low-resistance silicon under thermal processing: 1) Si; 2) n-Si after thermal processing.

Analysis of Thermal Conductivity Results. To analyze λ(T) the experimental results were compared with calculations using Callaway's theoretical model. The mathematical formulas used, phonon scattering mechanisms for various temperature intervals, and techniques of calculating the scattering parameters are presented in [2].

We will consider the results obtained.

Type 1 Specimens. As is evident from Fig. 1 at thermal processing temperatures $T > 1400$ K λ decreases by 12%, while for $T \geq 1100$ K the change in λ is within the limits of λ(T) determination, and at $T \geq 800$ K λ increases by 14%. Analysis of λ(T) shows that in this case only the phonon-defect scattering parameter $A = f(N, \sigma)$ changes. Change in the parameter A is caused by defect development during thermal processing. To determine the nature of the thermal defects the specimens were subjected to neutron-activation analysis, which demonstrated qualitatively that for thermal processing at $T \geq 1400$ K certain impurity atoms appeared in the specimen with a concentration $N \sim 10^{16}$ cm^{-3}. The most probable cause for the appearance of such impurities during high-temperature thermal processing is diffusion of absorbed atoms from the surface. Many researchers have observed formation of electrically active centers

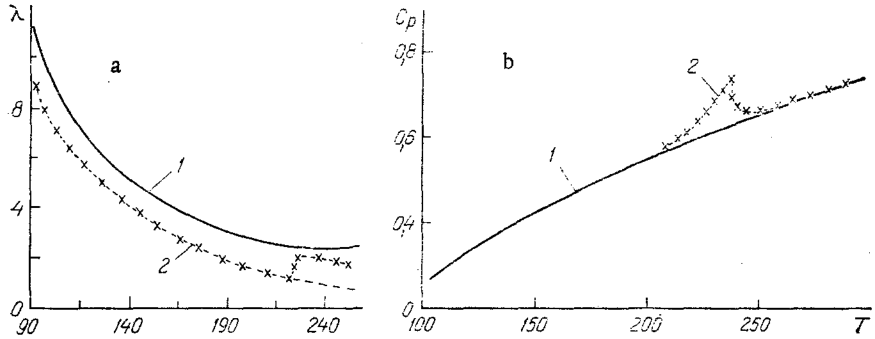

Fig. 4. Thermal conductivity (a) and specific heat (b) of silicon under thermal processing: 1) Si; 2) Si for thermal processing, $\rho = 20\ \Omega\cdot\text{cm}$. λ, W/(cm·K); Cp, J/(kg·deg).

during thermal processing and termed them thermal defects. These thermal defects have quite specific electrophysical parameters [6]. Measurements of induced photocapacitance and photoconductivity spectra reveal that the electrophysical parameters of the thermal defects coincide with the corresponding parameters of iron centers in silicon [6], while the presence of iron in the silicon after thermal processing was also confirmed by EPR data. Although the concentration of the thermal defects formed is relatively small, their electrical activity significantly suppresses λ.

At thermal processing temperatures $T \leq 1100$ K the changes in thermal conductivity are within the limits of uncertainty in λ determination. Subsequent experiments revealed that at such thermal processing temperatures the thermal defects formed are unstable over time and practically decay at room temperature. In general high-temperature heating with subsequent abrupt cooling leads to development within the crystal volume of defects of a different type, which may be preserved in a nonequilibrium state at lower temperature due to abrupt cooling. To clarify the role of volume processes on λ(T) during thermal processing the following experiments were performed. To remove impurity atoms absorbed on the silicon surface before thermal processing the specimens were washed in a polishing (high-purity) solution, removing a layer 0.1-0.2 mm thick from the surface. Detailed study of the electrophysical properties after thermal processing revealed that the thermal defect concentration did not exceed $5\cdot10^{11}$ cm^{-3} even after 20 h of processing. A marked reduction in λ (of the order of 10%) after thermal processing was found only when a layer was removed from the silicon surface by cleaving or mechanical polishing. In that case the λ decrease is caused by formation of vacancy clusters.

Type 2 Specimens. Figure 2 shows the effect of thermal processing on λ for oxygen-containing silicon. In this case the result λ(T) depends on T. At high ($T > 1100$ K) the decrease in λ due to thermal defect formation is insignificant. In connection with the significant oxygen concentration in the original specimen the most probable cause producing additional thermal resistance is formation of a vacancy—oxygen cluster, a so-called A-center. The oxygen atom binds two of the four broken bonds existing in the vacancy, while the two remaining ones are redistributed between the oxygen atoms closest to the vacancy and are capable of capturing an additional electron, which is the cause of the electrical activity of the defect. Measurements of optical absorption spectra revealed a peak at 884 cm^{-1} which corresponds to a charged A-center [7].

It is evident from Fig. 2 that the greatest effect of thermal processing on λ occurs at temperatures $T > 800$ K, with significant suppression of λ occurring. Calculations revealed that in this case the phonon-defect scattering parameter increases greatly. The present authors had previously [3] established that such a phenomenon is found only upon development of electrically active centers. At low thermal processing temperatures the concentration of vacancies, and thus A-centers, formed is quite small. At such temperatures thermal defect formation is related to formation of oxygen complexes. In silicon interstitial oxygen atoms and molecular oxygen exist in a dynamic equlibrium, i.e., $O_i + O_i = O_2$ [8]. Since the O_2 is not bound to the lattice atoms it must have a large diffusion coefficient, since for the O_2 the diffusion process is not accompanied by breakage of any bonds, and upon interaction of two O_2 molecules the complex $O_2 + O_2 \rightleftarrows O_4$ is formed. It has been proposed [8] that O_4 complexes may ionize in a manner similar to impurity centers $O_4 = O_4^+ + e^-$.

The effect of processing at T = 800 K on $\lambda(T)$ is significantly less, there even being some increase in thermal conductivity in contrast to other processing temperatures. This is because at such a temperature oxygen complex formation is retarded by the carbon which exists in any type of silicon specimen. Optical absorption spectrum studies showed a decrease in the absorption peak at 9.1 μm and formation of a new peak at 29 μm, caused by formation of SiO_2 complexes. These complexes are electrically inactive so that their formation leads to a reduction in the concentration of oxygen centers which scatter phonons, thus affecting the value of the thermal resistance.

Type 3 Specimens. No marked changes in $\lambda(T)$ were observed in the n-type silicon specimens at the thermal processing temperatures used. In the p-type specimens there was some (of the order of 8-10%) decrease in λ. Abrupt cooling of the specimens (quenching in oil) after high-temperature annealing leads to intensification of the effect of thermal processing on $\lambda(T)$. Development of additional thermal resistance in this case is caused by formation of electrically active silicon lattice vacancy defects [9]. It was shown in [9] that a silicon lattice vacancy defect is thermally unstable and decays into simpler defects with formation of a vacancy—boron defect. In fact, if after high-temperature thermal processing p-type silicon specimens are subjected to low-temperature annealing ($T \approx 150\text{-}200°C$) the suppression of thermal conductivity becomes significant (Fig. 3), which can be explained by increased concentration of the vacancy—boron complex.

It is evident that thermal action on silicon produces primarily electrically active thermal defects. Consequently, the dominant thermal resistance mechanism involves processes of phonon scattering on charged centers. This fact, together with the significant additional thermal resistance, despite the relatively low thermal defect concentration ($N \lesssim 10^{16}$ cm^{-3}), indicates intense phonon—electron interaction. One of the manifestations of effective phonon—electron interaction is the Yang—Teller effect and the corresponding structural phase transition.

Phase Transitions in Silicon under Thermal Processing. Figure 4 shows anomalies observed in $\lambda(T)$ and $C_p(T)$ in type 3 silicon specimens. The $\lambda(T)$ anomalies appear in the form of a discontinuity in thermal conductivity, i.e., the thermal conductivity increase is of an anomalies activation character. At temperatures of the order of 237 K the most probable cause of development of additional heat transport is excitation (ionization) of a defect state. According to [10], the additional activation thermal conductivity $\Delta\lambda \sim 1/T \exp(-E/kT)$. When a defect state is ionized its charge state changes, leading to readjustment of the surrounding crystalline lattice [11].

The $C_p(T)$ anomaly is expressed as a weak λ-function. As was noted above taking quasistatic thermograms permitted us to determine that the observed $C_p(T)$ anomalies correspond to phase transitions. The physical mechanism of these phase transitions is apparently the following: as was noted above, upon thermal processing of type 3 specimens a vacancy—impurity type charged complex develops, the presence of effective phonon—electron interaction presupposes shift of an impurity atom from a crystalline lattice point, i.e., on central displacement characteristic of the Yang—Teller effect is realized, leading to a reduction in the effective symmetry of the silicon crystal. At certain temperatures because of increase in the quantity kT thermal ionization of the defect state occurs, i.e., change in its charge state, which leads to relaxation of the crystalline lattice and thus to increase in the effective symmetry of the crystalline lattice which characterizes the appearance of a phase transition.

To sum up, we offer the following conclusion: upon thermal processing in silicon defect states are formed with deep energy levels characterized by effective phonon—electron interaction. Significiant phonon—electron interaction and as a consequence, the Yang—Teller effect, are a general feature of defect centers with deep electrical levels in silicon produced by thermal processing.

NOTATION

ρ, resistivity; λ, $\lambda(T)$, thermal conductivity and the temperature dependence thereof; C_p, $C_p(T)$, specific heat and temperature dependence thereof; N, defect concentration; A, phonon-defect scattering parameter; σ, phonon scattering section due to presence of defects in silicon crystalline lattice; V, vacancy; V—O, vacancy—oxygen complex; $\Delta\lambda$, activation thermal conductivity; E, excitation activation energy; k, Boltzmann's constant; EPR, electron paramagnetic resonance.

LITERATURE CITED

1. V. V. Emtsev and T. V. Mashovets, Impurities and Point Defects in Semiconductors [in Russian], Moscow (1981).
2. D. A. Vakhabov, A. S. Zakirov, and Kh. T. Igamberdyev, Inzh.-Fiz. Zh., 50, No. 6, 984-988 (1986).
3. K. A. Adilov, D. A. Vakhabov, A. S. Zakirov, et al., Fiz. Tverd. Tela, 28, No. 6, 1918-1920 (1986).
4. D. A. Vakhabov, A. S. Zaikirov, Kh. T. Igamberdyev, et al., Fiz. Tverd. Tela, 27, No. 11, 3420-3422 (1985).
5. S. Z. Zainabidinov, Physical Principles of Deep Level Formation in Silicon [in Russian], Tashkent (1984).
6. A. A. Lebedev, A. T. Mamadalimov, and P. K. Khabibullaev, Deep Levels in Semiconductors [in Russian], Tashkent (1981), pp. 59-69.
7. S. Z. Zainabidinov, Effects of External Actions on Semiconductors and Semiconductor Devices [in Russian], Tashkent (1985), pp. 3-6.
8. K. D. Glinchuk, N. M. Litovchenko, and R. Merker, Semiconductor Technology and Microelectronics, 25th edn. [in Russian], Kiev (1977), pp. 17-25.
9. V. N. Mordkovich, Fiz. Tverd. Tela, 4, No. 8, 3640-3643 (1962).
10. B. M. Mogilevskii and A. F. Chudnovskii, Semiconductor Thermal Conductivity [in Russian], Moscow (1972).
11. V. I. Kaidanov and Yu. I. Ravich, Usp. Fiz. Nauk, 145, No. 1, 51-86 (1985).