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TRANSFORMATION OF THE DEFECTS OF GOLD IN SILICON: STRUCTURAL PHASE TRANSITION

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Based on the experimental data on the specific heat and photoconductivity of silicon doped with gold, the possible mechanisms of transformation of the impurity centers of gold in the crystal lattice of silicon and accordingly phase transitions are discussed.

Gold is used in semiconductor electronics as a technological impurity. This fact has stimulated a wide range of investigations devoted to the behavior of gold in silicon, and a number of interesting results have been obtained at present. It has been established that the atoms of gold in silicon in the electrically active state occupy site positions or are in the immediate vicinity of them [1, 2]. Correlation dependences between different parameters, in particular, electro- and thermophysical parameters, have been obtained [3–5]. In a number of works (for example, [6]), anomalies of the temperature dependences of the above parameters identified as phase transitions but not clearly understood have been found in the course of the investigations in a wide temperature range. From this viewpoint, a complex investigation of the temperature dependences of the thermo- and electrophysical properties of the same samples of gold-doped silicon will allow, we believe, new ideas of the behavior of the impurity centers of gold in silicon.

In connection with what has been said above, the aim of the present work is to investigate the behavior of gold in silicon by the method of specific heat and photoconductivity (PhC) at low temperatures.

Samples and Measurement Procedures. We have used single-crystalline samples of *n*- and *p*-type silicon with a specific resistance of 10–100 Ω·cm at 300 K. The technology of high-temperature doping and the use of pulsed laser radiation have been described in detail in [7]. The samples under study were subdivided into three groups. In the samples of the first group, gold was distributed uniformly over the crystal volume; these samples were specially selected out of a large number of samples, since obtaining a uniform distribution of impurity atoms throughout the silicon volume presents great technological problems. In the second group, we found the local clusters of the atoms of gold in addition to uniformly distributed atoms. The presence of such clusters of impurity atoms was revealed by the method of [3]. The third group was obtained with the use of pulsed laser radiation [7, 8].

To investigate the temperature dependence of the specific heat $C_p(T)$ and the photoconductivity PhC(T) we have used a widely known universal low-temperature thermophysical standard setup, and the procedure of measurement of $C_p(T)$ and PhC(T) has been given by us in [5, 6].

Experimental Results. Figure 1 gives experimental results on the heat capacity of gold-doped silicon. It is seen that the dependence $C_p(T)$ is substantially determined by the type of initial sample (*n*- or *p*-). A certain temperature range (~160–210 K), where the shape of the $C_p(T)$ curves has a nontypical ("nonclassical") character, is observed in all the samples investigated; depending on the type of initial silicon, these effects are both pronounced (Fig. 1a) and smoothed (Fig. 1b and c). We emphasize that in certain cases the effects are small (about 0.4–1.0%): repeated measurements of $C_p(T)$ and even the use of a differential scanning calorimeter gave no way of determining accurately the temperature and the character of anomaly.

Such effects have also been found in the temperature dependences of the Hall mobility and the dielectric properties [9]; in investigating the kinetic properties of silicon doped with gold, the dependences of these parameters on the speed of the experiment have been established. We consider this in greater detail with the example of photoconductivity.

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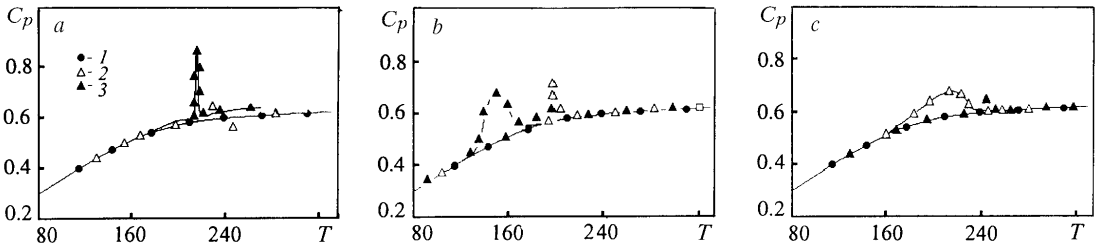

Fig. 1. Temperature dependence of the specific heat of silicon doped with gold (a–c, groups of samples): 1) initial Si; 2) *p*-Si⟨Au⟩; 3) *n*-Si⟨Au⟩. C_p, J/(g·K); *T*, K.

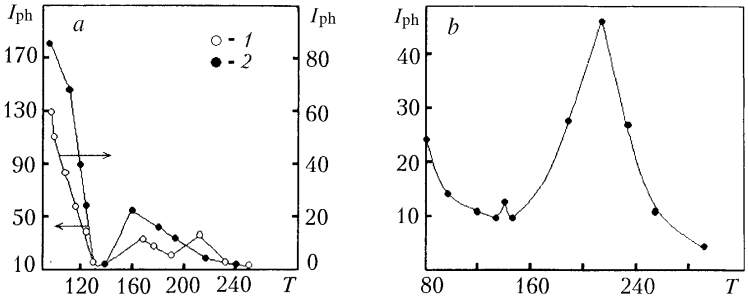

Fig. 2. Temperature dependence for the photocurrent for gold-doped silicon: a) *n*-type [1) $h\nu$ = 0.86 and 2) 0.63 eV]; b) *p*-type ($h\nu$ = 0.86 eV). I_{ph}, rel. units; *T*, K.

Figure 2 gives experimental data on the PhC of the samples investigated. It is seen that in this case, too, there is the same temperature range where photoconductivity spectra have a nontypical character. Using the spectral investigations of PhC at 77 K, we established the presence of two energy levels of gold in silicon with $h\nu$ = 0.54 eV and $h\nu$ = 0.34 eV.

For *n*-type silicon doped with gold (Fig. 2a) we observe three regions of change in the photocurrent as a function of the temperature: 1) to a temperature of 143 K, the photocurrent rapidly decreases; 2) to 165 K, we observe its small growth; 3) at high temperatures, it exponentially decreases. When a temperature of 220 K is attained, the photocurrent caused by the presence of gold totally disappears.

Figure 2b gives experimental data on PhC for *p*-type silicon doped with gold. A comparison of these dependences for *n*- and *p*-silicon shows that, beginning with temperatures higher than 160 K, their character is significantly different, i.e., whereas in the samples of gold-doped *p*-silicon the photocurrent increases, in *n*-silicon it decreases. Furthermore, at these temperatures we observe a decrease in the photocurrent amplitude from an energy level of gold of 0.34 eV and its growth from 0.54 eV; the relation of the amplitudes of the two energy levels depends on the rate of heating of the sample. It has been found experimentally that there is no change in the PhC spectrum in the case of rapid heating ($T > 0.2$–0.5 K/sec). If we plot individual curves of the change in the PhC amplitudes as a function of the temperature growth, they will not coincide, and hysteresis will be observed at the same temperature; at ~180 K, we will have a total disappearance of the 0.34-eV level and an increase in the amplitude to 0.54 eV. The latter allows the assumption that the energy levels of gold E_1 = 0.34 eV and E_2 = 0.54 eV correspond to one atom of gold in two different states in the silicon lattice rather than to two different atoms. It follows that, under certain conditions and temperatures, we have a transformation of the energy spectrum due to the transformation of the E_1 center to the state E_2. It is noteworthy that this process is reversible, i.e., as the temperature decreases to 77 K, the state E_1 is restored and PhC(*T*) acquires the previous form.

Here we emphasize that the above effects are observed in all the samples of gold-doped *p*-silicon investigated.

Investigations of silicon of all types subjected to high-temperature ($T > 1000$ K) treatment, when the atoms of gold change to the electrically active state, have shown the total absence of any observed effects. Taking into account the entire set of experimental results presented above, we may assume that such behavior of $C_p(T)$ and PhC(*T*) is caused precisely by the impurity atoms of gold in silicon.

Discussion of the Results. By the investigations of the impurity centers of gold in silicon by the methods of double electron paramagnetic resonance, internal friction, and backward scattering of neutrons [10] it has been shown that gold in the silicon crystal lattice is located at both the site of the crystal lattice and the interstitial site; a gold atom is located near the sites and the displacement is no higher than 0.2 Å. As has been noted above, the impurity atoms of gold in silicon create two levels in the forbidden band: the acceptor level (0.54 eV) corresponding to the Au^- center and the donor level (0.34 eV), which belongs to the noncentral interstitial atom of gold ($Au^0 + V$, where V is the vacancy). At low temperatures (77 K), a tunneling system of the Au^- and ($Au^0 + V$) centers is realized. At temperatures higher than 200 K, the thermal change in the charge state of impurity centers results in tunneling systems: 1) ground state at the Au^- site and excited states at ($Au^+ + V$) and ($Au^0 + V$); 2) ground state at the interstitial site ($Au^0 + V$) and excited states at ($Au^+ + V$) and Au^-. As a result we can observe two tunneling transitions

$$Au^0 + V \overset{e}{\longleftrightarrow} Au^- , \tag{1}$$

$$Au^+ + V \overset{e}{\longleftrightarrow} Au^0 + V . \tag{2}$$

As has been noted in [2], there are rapid and slow transitions in the model proposed. Reaction (1) is characterized by changes of long duration in the physical properties of the crystal (for example, specific heat and photoconductivity), which are established due to the "rapid" dipole transitions (2) (frequency dependence of the dielectric properties) [11].

It is noteworthy that in illumination of silicon with light at 77 K the measurements have shown the total absence of any effects, i.e., the photoemission of an electron will force it to transform. This means that an electron is of fundamental importance in such transformations.

In our opinion, the above transitions determine the temperature dependences of PhC and C_p of gold-doped silicon. However $C_p(T)$ substantially depends on the technology of doping of silicon, i.e., of the groups of samples indicated above. We consider this in greater detail.

Silicon Samples of the Second and Third Groups. As is seen in Fig. 1a, the temperature dependences of the specific heat of *n*-silicon doped with gold are virtually identical to the experimental results obtained earlier [4, 5]. With allowance for the data on photoconductivity and for the temperature dependences of the Hall mobility [9] we can make the following statements as far as the effects observed are concerned:

1. Such an effect on gold-doped silicon is possible only in strongly electrically inhomogeneous samples, which are characterized by the exponential dependence of the Hall mobility on the temperature in the ranges of temperatures corresponding to the transition from the power-law dependence of the Hall mobility (typical of scattering on charged impurity centers) to an exponential dependence (typical of scattering on "large" inhomogeneities). Such inhomogeneities represent regions corresponding to the minimum of a large-scale potential relief in which the donor centers of gold $Au^0 + V$ (at $T > 200$ K) are totally ionized.

2. As the temperature of the sample decreases, the strength of the internal electric field (caused by local inhomogeneities) will increase in the sample's volume, since the concentration of shielding free charge carriers decreases. The increase in the electric-field energy will lead to additional deformation of the sample due to electrostriction and to its change to an inhomogeneous state. Such an "order–disorder" transition will be accompanied by a structural phase transition; its temperature and the amplitude of the $C_p(T)$ peak must substantially depend on the concentration of gold atoms [12]. We consider this using the following experimental material.

As is seen in Fig. 1b, the $C_p(T)$ curves for the samples of silicon doped with gold by pulsed laser heating qualitatively correspond to Fig. 1a, except that the phase transitions are shifted to the region of lower temperatures and are more pronounced. The reason is that in this method of production of gold-doped silicon, the concentration of electrically active centers of gold is much (10 to 100 times) higher. An analogous result can be attained in laser treatment of silicon samples of the second group. In additional treatment of gold-doped silicon by a laser beam the concentration of electrically active centers of gold increases 4 to 10 times as compared to the initial concentration, which leads to a shift of the peak and a change in the $C_p(T)$ amplitude.

As has been noted above, the effects in $C_p(T)$ are insignificant in certain electrically inhomogeneous samples of gold-doped *p*-silicon. Earlier [4], we presented experimental data on the PhC and the dielectric properties of *p*-silicon, where we also observed the above effects. But here we must point to certain differences. Thus, in measuring the temperature dependence of PhC we observe a shift of the ionization energy of the impurity center of gold from 0.54 eV at 77 K to 0.39 eV at 178 K and the appearance of an "arm" at 0.43 eV, which is also related to the thermooptical transitions through excited states. However, another theoretical model has been proposed in this case. Vikhnin [13] has considered the system of defects which possess a multiminimum potential with absolute symmetry minima corresponding to a lattice site and relative minima processing nonzero low-symmetry distortions. Considering defects with a multiwell potential in excited states, Vikhnin has shown that in this case two typical effects can occur: 1) discontinuous increase in the order parameter in the sample (phase transition of first order) due to the discontinuous increase in the population of the excited states of the defects; 2) local configuration instability of first order, when the excited defect states corresponding to a distorted configuration become ground states. Both effects are cooperative and concentration-dependent and they are induced as the point of phase transition is approached.

Silicon Samples of the First Group. Investigations of the temperature thermophysical (specific heat, thermal conductivity) and kinetic (photoconductivity, dielectric loss tangent, frequency dependence of electrical conductivity) [2, 5, 11] dependences of these silicon samples allow the most accurate identification of the phase transition observed (Fig. 1c).

Unlike the above effects, in the silicon samples uniformly doped with gold the experiments on superfast cooling (immersion of silicon at room temperature in liquid nitrogen) and subsequent measurement of the kinetic parameters for different rates of heating have revealed the presence of a "new" center of gold with an ionization energy of 0.30 eV (E_3) corresponding to the excited states of the impurity center, i.e., the tunneling transition

$$E_1 \rightarrow E_3 \rightarrow E_2 + e \ . \tag{3}$$

The experimental data presented above are very typical of the so-called configuration-bistable transformations of defects [10, 14]. These transformations can also be considered in the context of the Jahn–Teller effect. If the impurity center of gold is filled with electrons at $T < T_c$, the metastable configuration must correspond to the state with a higher symmetry. Relaxing, the system changes to a stable configuration with a lower symmetry. At $T > T_c$, the transformation from the metastable configuration to a stable one will be accompanied by an increase in the symmetry of the center.

It is well known [12] that phase transitions of second order are often related to a symmetry change; phases with a higher symmetry are observed at higher temperatures. Consequently, the equilibrium transformation of the impurity center of gold from one configuration to another can be considered as a phase transition of second order, while the temperature of inversion of states T_c can be considered as the "point" of phase transitions of second order. In this case, for the system of centers indicated [10] we can introduce the notion of the degree of order

$$\eta = \frac{W_A - W_B}{W_A + W_B} = \frac{\tau_A - \tau_B}{\tau_A + \tau_B} \ .$$

The quantity η changes its sign with change in the configuration and it is equal to zero at the point of transition.

The ratio of the frequency factors in the general case is in proportion to the entropy factor and the ratio of the static weights of the states. For ordinary point deflects the ratio of the frequency factors is determined by the static weights of the states, since the change in the entropy with change in the state due to electron capture is nearly zero. However, in configuration transformations due to the change in the symmetry of the defect, the entropy change can be large.

NOTATION

$C_p(T)$, temperature dependence of the specific heat at constant pressure; T, temperature; PhC(T), temperature dependence of the photoconductivity; h, Planck constant; ν, frequency; $h\nu$, light quantum; E_1, E_2, and E_3, energy lev-

els; I_{ph}, photocurrent; e, electron; T_c, temperature of inversion of impurity centers; W_A and W_B, probabilities of the center being in two different states; τ_A and τ_B, characteristic transformation times.

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