Microwave conductivity and inverted ESR signal from new centers in oxygen-containing silicon

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The microwave conductivity and ESR signal from the new centers, which correlates with the conductivity, were detected in a heat-treated oxygen-containing silicon at low temperatures. The results are interpreted in a model which takes into account the formation of precipitates with dislocation dipoles and the transfer of oxygen to the lattice sites accompanied by the formation of paramagnetic centers.

It has now been established that annealing of silicon crystals with a high oxygen content at $T \cong 920$ K leads to the formation of thermal donors-11 (TD-11) which are attributable to SiO_x precipitates. This process causes the formation of quasicontinuous energy levels in the band gap at depths[1] $E = 0.01–0.3$ eV.

In the present letter we report the observation of new properties of these crystals which appeared as a result of prolonged annealing.

We studied silicon samples in the temperature range $T = 1.8–40$ K by the ESR method ($\nu_{mw} = 9.3$ GHz). These *n*- and *p*-type samples ($N_P = 5\times10^{14}$ and $N_B = 1\times10^{15}$ cm^{-3}, respectively), grown by the Chokhral'skiĭ method ($N_0 \cong 8\times10^{17}$ cm^{-3}), were annealed at $T = 920$ K for 20–200 h. The $3\times3\times10$-mm samples were placed in a magnetic field of a cylindrical resonator (H_{011}).

At liquid-helium temperatures the test samples were found to have an appreciable microwave conductivity which manifested itself in the reduction of the *Q*-factor of the resonator by a factor of several units. This effect correlates with the appearance of new paramagnetic centers (referred to below as Si-2*K*) which have several unique properties. Figure 1 shows the ESR spectrum of the Si-2*K* centers with $h \parallel [001]$, which was recorded by a superheterodyne spectrometer. We see that the spectral lines are narrow (≈ 0.03 mT) and the phase of the signal is opposite to the phase observed normally at the ESR. The measurements carried out at different values of T, $f_{\rm mod}$, and P_{mw} and also measurements of the relaxation rate, τ_1^{-1}, by the pulse-saturation method show that there is no connection between the observed inversion of the ESR lines of the spectrum of the Si-2*K* centers and the transmission conditions. For an arbitrary orientation of the crystal, the spectrum is comprised of 12 lines of equal intensity. A rotation of the field **H** in the $(1\bar{1}0)$ plane simplifies the spectrum, and its angular dependence behaves as shown in Fig. 2. The angular dependence is described by the spin Hamiltonian C_s of symmetry with $s = 1/2$ and by the following *g*-tensor values: $g_1 = 2.0018$, $g_2 = 1.9980$, and $g_3 = 2.0014$. Figure 2 shows that certain lines are seen

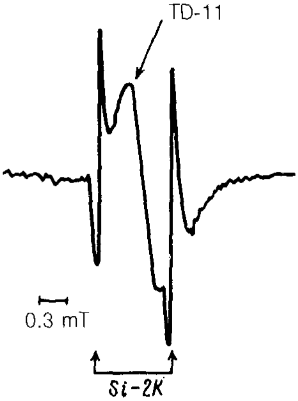

FIG. 1. The ESR spectrum of the Si-2*K* centers. The broad line at the center is the ESR signal of the thermal donors (TD-11). $H \parallel [001]$; $T_{\text{meas}} = 10$ K; $P_{mw} = 10^{-7}$ W; $f_{\text{mod}} = 4.3$ kHz.

only in a limited interval of angles, indicating the presence of clearly identifiable orientations of the Si-2*K* centers.

Interband illumination causes the ESR spectrum of the Si-2*K* centers and the microwave conductivity to vanish. The *Q*-factor in this case becomes comparable to its value in the absence of a sample. Removal of illumination leads to a restoration of the ESR spectrum and the microwave conductivity in a time which depends on the temperature and the presence of fine, uncompensated TD-11 which are thermally excited at the measurement temperatures. At $\lesssim 4.2$ K no such restoration occurs in the original *p*-type samples.

Using the Hall and ESR data, we found that the described effects are accompanied by the appearance of donor and acceptor levels in the band gap. We also found that the concentration of the Si-2*K* centers increases appreciably when the samples are subjected to an ultrasound ($f = 1$ MHz). The concentration of these centers increases even more strongly when the samples are annealed (for ≈ 3 h) at $T \cong 1000$ K the application of ultrasound. Annealing of the samples at $T = 1150$ K for ~ 0.5 h and bombardment by 1.5-MeV electrons and γ rays destroys the Si-2*K* centers and microwave conductivity.

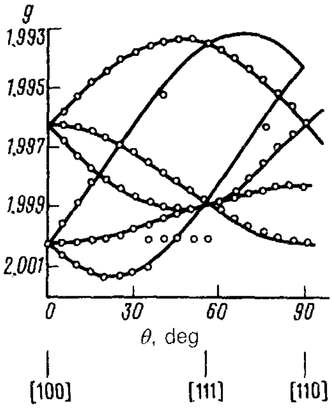

FIG. 2. The angular dependence of the ESR spectrum of the Si-2*K* centers. The magnetic field roated in the $(1\bar{1}0)$ plane. $T_{\text{meas}} = 20$ K. The points represent the experimental results and the solid lines denote the theoretical calculation.

The experimental data obtained by us can be explained by using the following model. As was shown in Ref. 1, a prolonged annealing of oxygen-containing samples at $T \cong 920$ K leads to the appearance of extended oxygen precipitates with dislocation dipoles oriented predominantly along the $\{110\}$ direction. We can assume that the elastic fields of the dislocation dipoles facilitate the embedding of oxygen into the lattice sites near the dislocation center, accompanied by the formation of the paramagnetic state (the Si-2*K* center). The *Q*-factor decreases because of the nonresonant rf conductivity, which is caused by the motion of electrons trapped in the dislocation dipoles, by analogy with the manner in which this process occurs in a plastically deformed silicon.[2,3] Illumination causes the holes to be trapped in the dislocation dipoles. These holes then recombine with the electrons, cancelling out the microwave conductivity. The illumination-induced disappearance of the ESR spectrum of the Si-2*K* centers occurs either as a result of their charge exchange or as a result of the fact that the spin-dependent conductivity signal, which vanishes along with the destruction of the microwave conductivity, is seen in the absence of illumination.

The exposure of a crystal to ultrasound increases the length of some of the dislocation dipoles, and the annealing that follows (1–3 h) at 1000 K leads to an increase in the number of oxygen substitution centers, i.e., an increase in concentration of the paramagnetic centers. The electron and γ-ray bombardment, as well as annealing at $T \cong 1150$ K, destroy the dislocation dipoles, causing the ESR spectrum and microwave conductivity to disappear.

The opposite phase of the ESR signals from the Si-2*K* centers may be associated with the population inversion of the paramagnetic centers in the spin system due to the interaction of these centers with the current carriers,[4] with the spin-dependent conductivity,[3] or with the manifestation of a combined electron resonance in a quasi-one-dimensional system, by analogy with its manifestation in a plastically deformed silicon.[5]

We are now attempting to resolve these problems.

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