Concerning the annealing of a dislocation EPR signal in silicon

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We investigate the kinetics of the annealing of a dislocation EPR signal (*D* centers) in silicon. The vanishing of the EPR signal from the dislocations upon annealing is attributed to the restructuring of the cores of the partial dislocations, accompanied by pairwise closing of the broken bonds in the state $S = 0$. The energy barrier to the restructuring process is ~ 2 eV. A residual nonannealing EPR signal is observed in strongly deformed silicon crystals. It is of the form of an isotropic line of width ~ 7.5 Oe with a *g*-factor $g \approx 2.006$. It is assumed that the corresponding EPR centers (*R* centers) are analogous to the EPR centers in amorphous silicon.

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1. INTRODUCTION

Numerous investigations have shown that plastic deformation of silicon single crystals at $T \lesssim 700°$ C leads to the appearance of certain centers that produce an EPR signal and are called D centers (see, e.g., Refs. 1–4). The aggregate of the available data suggests that the D centers are broken chemical bonds of the silicon atoms in the dislocation cores. In the very first investigations[1] it was shown that the D centers are effectively annealed at $T \gtrsim 650°$ C, but the causes and mechanism of the D-center annealing have not been made clear to this day.

The purpose of the present study was a more detailed investigation of the kinetics of the annealing of the dislocation EPR signal and an analysis of the possible annealing mechanisms.

2. TECHNIQUE AND SAMPLES

We used *p*-type silicon single crystals containing 10^{13} cm^{-3} boron atoms. The samples were grown by crucibleless zone melting in vacuum, and contained not more than 10^{16} cm^{-3} of oxygen atoms. The samples were plastically deformed by uniaxial compression along $\langle 110 \rangle$ or $\langle 123 \rangle$ in an argon atmosphere at 650–700° C. After deformation, a layer of not less than 0.3 mm was ground off from all the surfaces, followed by chemical polishing in a mixture 1 HF:7 HNO_3. The sample preparation procedure is similar to that used earlier.[3]

The samples were annealed at 720–780° C in an argon atmosphere. The sample, in a quartz ampoule, was placed in a large oven with a set temperature, and after soaking for a definite time it was taken out of the oven and cooled to room temperature. The EPR signal was registered with a spectrometer having a working frequency 9200 MHz.

Most measurements were made at $T = 130$ K with the magnetic field modulated at a frequency 100 kHz. Since the spin-lattice relaxation time at $T \gtrsim 100$ K did not exceed 10^{-6} for the D centers,[5] the EPR was recorded in the slow-passage regime. The signal recorded corresponded to the derivative of the absorption signal: $\partial\chi''(H)/\partial H$. The EPR signal was fed to a spectrum accumulation unit in which it was differentiated twice. The calculated result was the quantity

$$\chi = \int_{H_0 - 40\,\mathrm{Oe}}^{H_0 + 40\,\mathrm{Oe}} \chi''\, dH,$$

which is proportional to the number of paramagnetic centers in the sample. This quantity was normalized to the area of the EPR spectrum of an Mn^{++} standard calibrated against a DPPH standard. The result was a calculation of the absolute number of D center in the samples. The technique is described in detail in Refs. 3 and 5. The absolute error in the determination of the D-center density did not exceed 30%, the relative error, with allowance for the employed repeated accumulations of the signal, did not exceed 2%.

The dislocation density was measured by statistically reducing the micrograms. The thickness of the foils was determined from the number of the thickness extinction contours and simultaneously from the number of oscillations of the contrast at the dislocations under conditions of a single strong Bragg reflection. The photo-EPR procedure was similar to that described earlier.[6] The background illumination was produced by light that ensured transitions from valence band to the conduction bank over the entire volume of the sample. The light intensity corresponded in this case to saturation of the photo-EPR signal.[6] The quantity $\Delta\chi = \chi_{ill} - \chi_{dark}$, the change of the area of the EPR spectrum upon illumination of the sample, was determined after repeated accumulations and double integration of the spectra.

3. EXPERIMENTAL RESULTS

Electron-microscope investigations show that the vanishing of the EPR signal from the dislocations after annealing is not connected with a quantitative or qualitative change of the dislocation structure of the samples in the course of the annealing. In the entire investigated temperature and annealing-time interval (see Fig. 3 below), the corresponding dislocation-density changes, if there were any at all, did not exceed the ex-

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perimental error in the measurement of the dislocation density (usually not more than 50%), so that the decrease in the D-center density cannot be attributed to a decrease of the dislocation density.

Careful measurements have shown that the EPR signal in the non-annealed samples, deformed at $T \lesssim 680°$ C, are in good agreement with the geometrically calculated number of broken bonds corresponding to the given dislocation density. Thus, a sample deformed at 650 ° C by compression along ⟨110⟩ by an amount $\varepsilon = 1.5\%$ contained 6×10^{16} spin-cm^{-5} at a dislocation density $(3 \pm 1) \times 10^{9}$ cm^{-2}, corresponding to an average distance of 5 Å between the unpaired electrons in the dislocation cores.

With increasing deformation temperature, this correspondence is violated, with the EPR signal decreasing already at $T = 700°$ C, while in samples deformed above $T \approx 760°$ C there is no EPR signal from the D centers, even if the deformation time amounts to only several seconds.

The decrease in the EPR signal from weakly deformed samples ($\varepsilon = 2$–3%) in the course of annealing does not lead to a change in the form of the EPR spectrum. Annealing these samples leads to a smooth decrease of the EPR signal to below the noise level. In contrast, when samples with a strain $\varepsilon = 4$–6% and more are annealed, the picture observed is qualitatively different. After a prolonged annealing, the EPR signal of the D centers likewise vanishes, but a certain residual EPR signal remains and its intensity can reach 10% of the initial D-center EPR-signal intensity. Figure 1 shows EPR spectra for a sample with a strain $\varepsilon = 5\%$ at $T = 130$ K prior to annealing (upper curve) and after annealing for an hour at 720° C (lower curve). The upper curve is a typical D-center EPR spectrum recorded in the orientation H ‖⟨111⟩. The spectrum is isotropic, and the average g-factor is 2.0077. The residual spectrum (which we label R) is isotropic, its width (of the order of 7.5 Oe) is half that of the dislocation spectrum, and its g-factor is 2.0055. Figure 2 shows records of the EPR spectra before and after annealing, obtained at $T = 1.4$ K in the adiabatic fast passage (AFP) regime. In contrast to the D-center spectrum, the R-center spectrum shifts somewhat with decreasing temperature towards weak fields, and has at 1.4 K a g-factor equal to 2.007. The width of the spectrum amounts to 7.5 Oe as before. The fact that for the R centers it is possible to effect the AFP regime at 1.4 K and a modulation frequency 80 Hz is evidence of long spin-relaxation times.

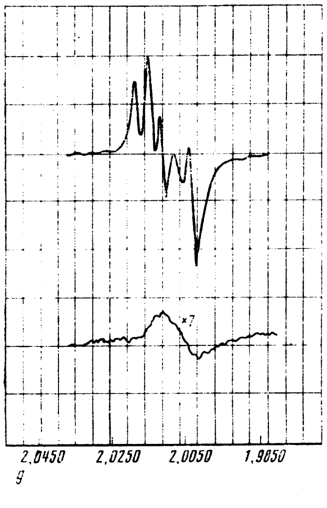

FIG. 1. Spectrum of EPR from dislocations in a sample deformed by 5% at 680° C (upper curve) and residual EPR signal (R centers) in the sample after annealing for an hour at 720° C (lower curve). $T = 130$ K.

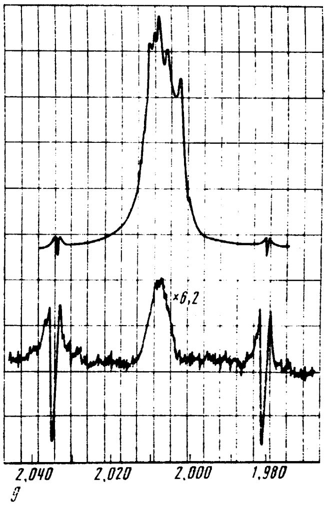

FIG. 2. Spectra of EPR from dislocations (upper curve) and R centers (lower curve), obtained in the adiabatic fast passage regime; $T = 1.4$ K.

The kinetics of the restoration of the R-center EPR signal intensity after saturation of the EPR spectrum by repeated passages through resonance in a regime close to AFP, at $T = 1.4$ K, is well described by the usual exponential law, and it is possible to determine the spin-lattice relaxation time τ_1. The value $\tau_1 = 230$ sec obtained at $T = 1.4$ K is three times larger than the D-center spin-lattice relaxation time at the same temperature.[1,3,5] The parameters of the EPR signal of the R centers practically coincide with those of the EPR spectrum of the ground surface of silicon. We note therefore that we have especially verified that the intensity of the R-center EPR signal decreased linearly with decreasing volume of the sample in the course of prolonged chemical polishing, whereas the EPR signal from a ground surface vanishes completely already after 3–5 minutes of chemical polishing.

Figure 3 shows in a semilog scale the dependence of the area of the EPR absorption signal on the annealing time at various temperatures. The value of χ for R centers (χ_a) was calculated from the experimentally measured values of χ, so that Fig. 3 represents the annealing kinetics of the D centers. (Since the spectrometer was not sensitive enough, we did not investigate in detail the annealing kinetics of the R centers. We point out, however, that annealing of one of the samples for two hours at $T = 720°$ C did not lead to a noticeable decrease in the EPR signal of the R centers). Curve 1 of Fig. 3 corresponds to annealing of a sam-

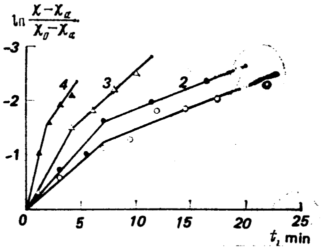

FIG. 3. Dependence of the logarithm of the area of the D-center EPR-absorption signal in Si samples deformed by 5% at 600° C on the annealing time. Annealing temperature: *1*, *2*) 720° C, *3*) 750° C, *4*) 780° C. Sample was grown by the Czochralski method, samples 2–3 were grown by crucibles zone melting in vacuum. χ_0—signal in the initial sample, χ_a—residual signal.

ple grown by the Czochralski method, with an oxygen concentration 10^{18} cm^{-3}, larger by two orders of magnitude than the oxygen content in samples obtained by crucibleless zone melting in vacuum.

One can observe on the experimental curves of Fig. 3 two exponential sections (slow and fast) with different time constants τ_s and τ_f. Figure 4 shows plots of τ_s and τ_f against temperature. The activation energies for τ_s and τ_f are equal within the limits of experimental error and amount to 2.0 ± 0.1 eV. It should be noted that in order to obtain the observed difference of τ_s and τ_f, it suffices to assume that for identical pre-exponential factors the activation energy for τ_s is higher by 0.08 eV, i.e., by 4%, than the activation energy for τ_f; these values are within the limits of experimental error.

We have previously observed[6] an increase in the EPR signal of the D centers when the sample was illuminated, This increase reached its maximum value at a certain illumination intensity, and did not increase further with increase of the light intensity. We note that at $T = 130$ K saturation was reached at rather low illumination intensities. The dark intensity of the spectrum after turning off the light was restored after long time intervals, that increased rapidly with decreasing temperature. In the present study we measured this effect in annealed samples. At $T = 130$ K we recorded the EPR spectrum in the absence of illumination, and then applied light that ensured the transition from the valence band to the conduction band over the entire volume of the sample. Both spectra were integrated and their difference was determined. Table I lists some quantitative data obtained as a result of these measurements. The first column indicates the degree, temperature, and access of the sample deformation, the second describes the heat-treatment regime. In the third column is given the area of the EPR signal in the illuminated sample, normalized to the EPR signal from the standard. This quantity gives the number N_D of D centers in arbitrary units. In the fourth column is given the quantity $\Delta\chi = \Delta\chi_{\text{ill}} - \Delta_{\text{dark}}$, which is the change of the area under the spectrum when the illumination is turned on, i.e., the increase in the number of spins that produce the D-center EPR spectrum. The fifth column lists the values of $\Delta\chi/\chi_{\text{ill}}$.

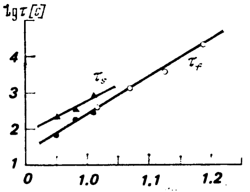

FIG. 4. Dependence of the logarithm of the time constant for the annealing of D centers on the reciprocal annealing temperature corresponding to the linear section of the curves in Fig. 3: ●) initial section of fast annealing, ○) analogous data obtained from Ref. 1, ▲) section of slow annealing.

TABLE I.

Type of sample	Annealing regime	$\chi_{\text{ill}} = N_d$	$\Delta\chi = \chi_{\text{ill}} - \chi_{\text{dark}}$	$\Delta\chi/\chi_{\text{ill}}$, %
$\varepsilon = 5\%$ $T_{\text{def}} = 700°$ C ⟨123⟩	Prior to annealing	15.4	1.2	8
	Annealing 1.5 hr at $T = 540$°C	13.9	0.4	3
$\varepsilon = 4.3\%$ $T_{\text{def}} = 680°$ C ⟨123⟩	Prior to annealing	17	2.2	13
	Annealing 6 min at 720°C	8	0.3	3
$\varepsilon = 2.8\%$ $T_{\text{def}} = 680°$ C ⟨110⟩	Prior to annealing	23	1.15	5
	Annealing 2 min at $T = 780$°C	6	1.0	17

4. DISCUSSION OF RESULTS

As already indicated above, in our experiments, the density and the character of the dislocation distribution in the crystal did not change during the course of the annealing. Probably, however, annealing is possible of various submicroscopic defects on the dislocations (such as jogs and others), which cannot be monitored with an electron microscope. The good agreement between the intensity of the EPR signal from the D centers, on the one hand, and the number of broken valence bonds geometrically calculated from the dislocation density, on the other, allows us to assume that the overwhelming contribution to the EPR dislocation signal is made by the electrons of the "dangled bonds," due to the presence of edge components of dislocation lines, and not by some singular points in the dislocation cores. In fact, the obtained value 5 Å for the average distance between the unpaired electrons corresponds approximately to the distance between the broken bonds in the core of a 60° dislocation.

The first mechanism to which one can attempt to attribute the vanishing of the broken bonds on the dislocations in the course of annealing is a possible diffusion of chemical impurities towards the dislocations and the formation of chemical impurity atom-plus-broken-bond associations. Since the density of the broken bonds N_D reaches in our samples 6×10^{16} cm^{-3}, it is necessary to consider only impurities whose concentration is high. Such an impurity can apparently by oxygen, if it is assumed that all of it can be captured by the dislocations. To check on this hypothesis, we have annealed samples grown by the Czochralski method, in which the oxygen concentration was approximately 10^{18} cm^{-3}, which exceeds by two orders of magnitude the content in samples obtained by crucibleless zone melting in vacuum. As seen from Fig. 3 (curves 1 and 2), however, an increase in the oxygen content by two orders of magnitude does not accelerate the annealing of the D centers. This fact casts doubts on this annealing mechanism, although it is apparently still impossible to reject the point of view that the impurities can influence the annealing process.

The second variant can be the following: annealing can produce in the vicinity of the dislocations, or directly on them, unique point defects that have acceptor properties and whose energy E_a lies below the energy E_1 of the electrons of the dislocation broken bonds.[6] We note that in plastically deformed silicon samples with high boron concentration[7] an acceptor level was observed with energy $E_a = E_v + 0.27$ eV. The electrons of the broken bonds should be captured by such acceptors. If these point defects are produced in the immediate vicinity of the dislocation cores, then the Coulomb charge of the nucleus will be effectively screened by them, and the coefficient f of the filling of the dislocations by the holes can be close to unity at a sufficiently large number N_a of the acceptors. In this case all the electrons of the broken bonds are captured by acceptors, and the EPR signal from the dislocations vanishes. When the sample is exposed to light capable of producing transitions from the valence band to the conduction band, the resultant electrons will be captured by dislocations and their filling coefficient will decrease. At sufficiently low temperature, the negatively charged acceptors filled with electrons serve as effective traps for the holes. As a result, the EPR signal from the dislocations will decrease upon illumination, and at high illumination intensities it will reach a value corresponding to a zero filling coefficient.

It is seen from the table, however, that the number of hypothetical acceptors, which in this model is equal to $N_a = \Delta\chi$, decreases in the course of annealing, but with a kinetics that differs from the annealing kinetics of the D centers, as indicated by the change in the value of $\Delta\chi/\Delta\chi_{111}$. Thus, N_a decreases faster than N_D in annealing at $T = 720$ and 540° C. This decreases the relative effect $\Delta\chi/\chi_{111}$. At $T = 780$°C, $\Delta\chi/\chi_{111}$ increases, meaning that N_D decreases more rapidly than N_a. Thus, the experimental facts can likewise not be explained by the considered annealing mechanism, which presupposes an increase of the coefficient of filling of the dislocations by holes to a value on the order of 100% as a result of the appearance of acceptors in the course of the heat treatment.

In our opinion, the most acceptable of the possible mechanisms of the vanishing of the EPR signal from dislocations upon annealing is the following: Owing to the displacement of the atoms in the dislocation cores, the cores in such a way that the joining of the dislocation broken bonds with one another in a state $S = 0$ becomes energywise favored In Ref. 8 are given theoretical calculations that show that in the joining of the broken bonds can be energywise favored in the case of split dislocations.

At the present time it can be regarded as established that in the equilibrium state the overwhelming majority of the dislocations in silicon are split.[9] There are, however, no published data on the ratio of the number of split and unsplit dislocations in silicon deformed in a regime that leads to the production of a large EPR signal from the dislocations, as for example in our samples. Thus, we cannot state with assurance that in our case the dislocations are also predominantly in a split state.

We note that the average distance 5 Å between the spins along the dislocations, obtained in the present paper, corresponds to the distances between the broken bonds in an unsplit 60° dislocation. If the dislocations are split, then the number of spins in the samples should be three times larger. It can be assumed, however, that the broken bonds in 90° partial dislocations are always joined and the EPR signal is always produced only by broken bonds in 30° partial dislocations. Indeed, the closing of the broken bonds in 90° partial dislocations calls for a much smaller deformation of the lattice than in the case of 30° partial dislocations. Thus, we can consider two versions. In the first, the dislocations in our samples are predominantly in a split state immediately after the deformation, and an activation energy 2 eV is necessary to overcome the energy barrier for the restructuring of the cores of the partial, e.g., 30°, dislocations, leading to a closing of the broken bonds along the dislocation. In the second we have dislocations in an unsplit state after the deformation, and the heat treatment causes them to split, after which the closing of the broken bonds takes place immediately. We note that in the latter case it is necessary to consider the possibility of transformation of dislocations from a "shuffled" set to a "slipping" set.[10] To separate these versions, we plan to carry out an investigation using electron microscopy of higher resolution.

We turn now to Fig. 3. It is easy to see that a change in the rate of annealing, at a fixed temperature, takes place in pure samples after annealing of approximately 60–65% of the broken bonds. This change in slope can be attributed to the presence on the dislocations of specific "pinning points" near which the restructuring of the nucleus requires a somewhat larger activation energy. The fact that in "dirtier" samples, grown by the Czochralski method, the change of the slope occurs earlier, namely after annealing of approximately 50% of the bonds (see Fig. 3), agrees with this assumption.

We discuss now the nature of the residual EPR signal, which we have ascribed to some R centers. As already mentioned above, its parameters differ greatly from the parameters of D centers. The R centers have an isotropic EPR line without a resolved structure, with a g-factor 2.0055 and with a width 7.5 Oe, and another spin-lattice relaxation time. We assume that the R centers have a somewhat different nature than the D centers.

The fact that in samples of amorphous silicon there is observed an isotropic EPR signal with a g-factor 2.0055 and with a width that fluctuates in the range

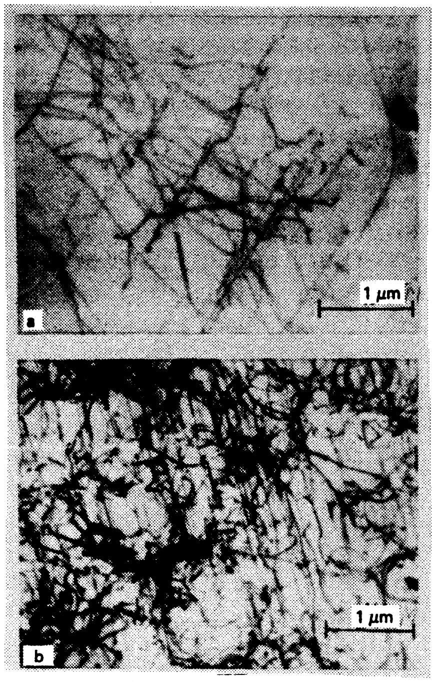

FIG. 5. Micrograms of the dislocation structure of silicon crystals deformed by compression along ⟨110⟩ at 680° C: a) $\varepsilon = 1.5\%$, b) $\varepsilon = 4.5\%$.

5.0–15 Oe, depending on the method of sample preparation,[11] suggests that the nature of the R centers and of the centers that produce the EPR signal in amorphous silicon is one and the same. It is possible that at high degrees of deformation in samples of plastically deformed silicon there are produced microscopic regions of the amorphous phase. Figure 5 shows typical micrograms of the dislocation structure in a sample with a strain $\varepsilon = 1.5\%$ (average dislocation density 3×10^9 cm^{-2}) and in a sample with $\varepsilon = 4.5\%$ (average dislocation density 6×10^9 cm^{-2}). We did not observe any R centers in the first sample, while in the second their concentration, as obtained from EPR data, was 5×10^{15} cm^{-3}. As seen from Fig. 5, the sample with $\varepsilon = 4.5\%$ contains a rather large number of clusters with very high dislocation density, which cannot be resolved by the electron microscope. It is possible that it is precisely in these regions that the amorphous phase can be produced. Indeed, when the distance between the dislocations is of the order of several lattice constants, we can no longer speak of either dislocations or of a crystal lattice, at least when referring to some specially ordered structure. This is not a new idea, and a dislocation model of the amorphous state was considered earlier.[12] There is also another possible explanation of the nature of the centers: if the dislocations have a large number of defects due to their mutual intersections, then in the course of the restructuring of the dislocation cores, which should close the broken bonds, the broken bonds in such defects may remain open because of the strongly distorted geometry of the core in the intersection region. The EPR signal from such spins can be narrower than the signal of the D centers, owing to the smaller dipole-dipole interactions, since the distance between the residual spins should exceed by many times the lattice constant. This explanation corresponds to a system of randomly disposed isolated EPR centers, which apparently are similar to the EPR centers in amorphous silicon.

We note in conclusion that the possibility of formation of R centers must be taken into account when speaking of investigations of the electronic properties of dislocations in silicon. Thus, a spin-dependent recombination signal was observed in silicon[13] plastically deformed at $T = 800°$ C, when according to our data there is no EPR signal of D centers associated with broken bonds in dislocation cores. The observed signal had $g = 2.004 \pm 0.001$ and an approximate half-width 6 Oe, which correlates well with the characteristics of the D centers. It is therefore natural to assume that the observed effect[13] is due precisely to R centers and is apparently analogous to spin-dependent recombination in amorphous silicon. In contrast to Ref. 13, we have observed[14] a spin-dependent photoconductivity signal in plastically deformed silicon whose g-factor, shape, and width practically coincide with those of the D-center EPR signal.

We note in the same connection that no D-center EPR signal was observed in our samples when the deformation temperature exceeded 760° C, but at a sufficiently large deformation we observed an R-center signal. It can be assumed that it was precisely this signal which was observed in Ref. 15, where the first observation of EPR in deformed silicon was reported.

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