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by

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QUENCHED-IN DEFECTS IN P-TYPE SILICON *

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ABSTRACT - P-type silicon crystals quenched from temperatures between 870 °K - - 1070 °K show an increase in donor concentration which disappears on room temperature annealing. This annealing is complete in thin samples and in crystals of relatively low acceptor concentrations. From studies of changes in resistivity on quenching, and the annealing kinetics, we arrive at the following characterization of the defect which resulted from quenching:

1. It is a donor, with a corresponding energy level at about 0.4 ev from Valence band;
2. Its activation energy for motion is about 0.3 ev and its diffusion coefficient at room temperature is 1.2×10^{-7} cm^2/sec.

The center ceases to be electrically active on reaching the surfaces of the samples. A fraction is lost during annealing in thicker samples probably because of formation of pairs with the original acceptor of the crystal. Arguments are presented pointing to the possibility that the defects discussed here are interstitial ions of silicon.

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INTRODUCTION

Silicon when heat treated shows marked changes in its resistivity and carrier lifetime. Several studies have concerned themselves with investigations of the electrical properties of the defects which are formed at temperatures above $700^{o}K$ (1-6). We are reporting here on a series of experiments concerned with one of the defects which rise to the increase in resistivity of quenched, p-type silicon. The center, once formed, anneals at room temperature, as evidenced by the return of the resistivity to its original (pre-quenching) value.

The interest in this investigation originated, in part, from the possible connection between the above mentioned center and those investigated recently in electron irradiated silicon. Detailed analysis of the paramagnetic resonance spectra has identified various radiation induced centers as those involving vacancy in association with oxygen, with phosphorus and with another vacancy [7]. More recently, observation of an isolated vacancy has been suggested [7]. In some cases a motion of vacancies has been observed at room temperature. The known electrical characteristics of irradiated silicon have been correlated with the different centers so that their ionization levels are reasonably well known [7].

We have, therefore, studied the conditions under which the quenched-in defects are formed, the kinetics of their annealing and their ionization energy, to attempt an identification of

these defects.

EXPERIMENTAL

Table I gives the essential data concerning crystals used in the present experiments. In order to investigate the influence of oxygen on formation and annealing of the centers the crystals have been divided into those of "low" oxygen concentration, grown by floating zone technique, and of "high" oxygen concentration pulled from the melt. These concentrations are known to be less than 10^{17} cm^{-3} and more than 10^{18} cm^{-3}, respectively [8].

A third group of samples was prepared from pulled crystals which have been annealed for 24 hours at $1300^{o}K$, a procedure known to lead to precipitation of oxygen in the lattice [9].

We have used samples of dimensions: 1.0 × 0.5 × 0.1 cm in all experiments with exception of those concerned with the determination of the influence of the sample thickness on the annealing process.

Quenching was performed from temperatures between $870^{o}K$ and $1070^{o}K$ after 3 minute heating, by dropping the samples into glycerine. The time involved in cooling was of the order of 10^{-2} sec. Resistivity measurements were performed at room temperatures.

RESULTS

Figure 1 shows the carrier densities, $(N_A - N_D)_2$ measured at room temperature, as a function of the temperature of quench. The densities have been obtained from resistivity measurements assuming that mobility changes were negligible. This assumption has been checked by Hall measurements in conjunction with resistivity measurements. The results are typical of all samples from crystals 1 and 4 (Table 1). The curve indicates a gradual decrease in net acceptor concentration as a function of temperature of quench followed by leveling off at values of $(N_A - N_D)_2$ of around 3.7×10^{13} cm^{-3}. This corresponds to an approximate position of the Fermi level at about 0.4 ev from the valence band.

The annealing behaviour (Fig. 2) was also identical in group 1 and 4 samples. It has been found to be independent of the temperature of quench. The curve is a plot of the fraction of centers which have annealed at time t. This fraction is defined as $f = \frac{\sigma(t) - \sigma_g}{\sigma_0 - \sigma_2}$ where σ_o is the original conductivity, σ_q the conductivity immediately after quenching and $\sigma(t)$ conductivity at time t after quenching.

DISCUSSION

The results from the figure 1 indicate that the introduced center is a donor with an energy level located at around 0.4 ev from valence band. It is also apparent that the formation of

the center is independent of oxygen concentration within the limits of concentration used in the present experiments, as long as oxygen is in dispersed state. Results with samples from crystal 3 were not reproducible and are not shown. This indicates that precipitated oxygen interfers with the formation as well as annealing of the centers. These results indicate that the observed center cannot be an oxygen-vacancy pair as observed in irradiated silicon since the latter is an acceptor type defect, with an ionization energy in the upper half of the gap [7].

Crystal 2 (Fig. 2) exhibit a behaviour indicating influence of acceptor concentration on the formation and annealing of defects. The samples of this crystal show a larger increase in donor concentration on quenching and an increase in p-type resistivity during room temperature anneal (negative f). Data from figure 2 indicates the existence of two processes during the annealing stage: process A which depends strongly on the original acceptor concentration and manifests itself in an increase in resistivity (negative f) and a process B which appears in samples of lower acceptor concentration and consists of a decrease in resistivity (positive f). There exists a competition between the two processes as evidenced in the curves of fig. 2. In thicker samples the A process gradually takes over. Samples of 0.5 mm and 1mm thickness anneal fully by the B process.

In view of the results shown in Fig. 2 we have analyzed the dependence of the B process on sample thickness.

We have considered the solution of a transient, random diffusion equation for capture on the surfaces of centers initially uniformly distributed in the volume of the samples. For a parallelepiped of dimensions u, v, w one has [10]:

$$N_F = CN_{Fo} \sum_{\ell}^{\infty} \sum_{m}^{\infty} \sum_{n}^{\infty} \left[\frac{\exp(-\alpha_{\ell mn}\, t)}{(2\ell+1)^2\,(2m+1)^2\,(2n+1)^2} \right] \qquad (1)$$

where

$$\alpha_{\ell mn} = N^2 D \left[\frac{(2\ell+1)^2}{u^2} + \frac{(2m+1)^2}{v^2} + \frac{(2n+1)^2}{w^2} \right]$$

N_F is the density of defects at time t, N_{F0} density at t=0, D is the diffusion coefficient of the defect, C is a normalization constant, l, m and n are integers. One obtains a fit of this solution to the observed data with diffusion constant, $D = 1.2 \times 10^{-7}$ cm^2/sec. The 2 mm and 5 mm curves require also a bimolecular term which describes the A process. The time constant of this term is around 50 minutes. The respective contribution of the A process and B process varies with sample thickness, but time constants do not vary (see Table II).

We can interpret the two processes in the following way. The donor-like defect formed at high temperature is mobile at room temperature. During its random motion it may form donor-like pair (or more complex defect) at the acceptor site, or, if it does not come near an acceptor it ends on the surface where it loses its donor property. In such a way the kinetics of the annealing depend both on the acceptor concentration and on the

sample thickness for a given defect concentration.

We can calculate the activation energy for motion of the defect from: $V = \frac{1}{\tau} = V_o \exp(-E/kT)$ an equation which gives the jump time for a thermally activated process with an activation energy E [11]. The diffusion constant for interstitials D, is related to the jump time by the equation $D = 4\ a^2/6\tau$ [12]. Here V_o is the average lattice frequency, around 10^{13} sec^{-1}. We take a, the cube edge of unit cell equal to 5.7×10^{-8} cm and obtain $E = 0.31$ ev.

It appears improbable that the defect of interest is a vacancy. Its diffusion constant is larger by several orders of magnitude than the diffusion constant for a vacancy next to oxygen, extrapolated to room temperature [7]. One would also expect differences between the behaviour during annealing of crystals with different oxygen concentration; vacancies forming pairs with oxygen during the annealing should lead to decrease of the fraction annealed on the surfaces in crystal with high oxygen concentration.

We are also confident that the defect does not represent an impurity which diffused from the surface during heating process. We have checked this point by decreasing the heating time to one minute and still observing the introduction of centers. We have also lapped the surfaces of a quenched sample in order to check whether resistivity changes are confined to a near surface layer. We have concluded from these negative experiments that a diffusion constant at 900°K considerably in

excess of 10^{-5} cm^2/sec is necessary for an impurity to be responsible for the observed effect. This is unlikely. It is also improbable that an impurity which diffused from the surfaces would return to the surfaces during the annealing at room temperature.

It seems more probable that the defect is an interstitial silicon. Its low activation energy for motion and its high diffusion constant at room temperature point in the direction of an interstitial diffusion process. Positive ions of silicon are smaller than copper ions. The latter have very large diffusion constants in silicon at low temperatures [13], and diffuse, at least in part, interstitially.

We have unsuccesfully tried to observe paramagnetic resonance absorption at $78^{\circ}K$ and at liquid helium in quenched and annealed samples.

CONCLUSIONS

The defect which appears in quenched, p-type silicon is characterized by an ionization energy of about 0.4 ev from the valence band, by an activation energy for motion of about 0.3 ev and by a diffusion constant of 1.2×10^{-7} cm^2/sec at room temperature. The principal feature of the annealing process is that it fits into dimension dependent kinetics. This indicates that the process of elimination of the defect occurs at the surfaces of the samples and that in thicker samples only a

fraction of the centers succeeds in reaching the surfaces. The high diffusion constant makes it plausible that the defect is an interstitial silicon. It is interesting to notice that Mayburg [3] has conclude from a series of experiments that interstitials exist in large densities (10^{16} cm^{-3}) in silicon crystals as grown. He also considered their motion to the surfaces. We believe that the present experiments point to activation of interstitials during heating process. They may have existed in an electrically inactive from in the crystals as grown, i.e. near some imperfection. Their random diffusion brings them to the surfaces where again they lose their donor properties.

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TABLE I			
Crystal	Method of growth	Resistivity (ohm-cm)	$(N_A - N_D)cm^{-3}$
1	Pulled	19	6.3×10^{14}
2	Pulled	1.6	2.0×10^{15}
3	Pulled *	50	-0.6×10^{14}
4	Floating zone	45	2.6×10^{14}

* This crystal is the original crystal 1 and has been heated to 1000°C for 24 hours, after which its resistivity has increased to 50 ohm-cm.

TABLE I - Characteristics of the crystals employed in the present experiments. The last column: $(N_A - N_D) = (N_A - N_D)_o - (N_A - N_D)$ indicates the maximum change in net acceptor concentration after quenching. $(N_A - N_D)_o$ - original acceptor concentration, $(N_A - N_D)$ - acceptor concentration after quenching. Resistivity measurements were performed at room temperature.

* * *

TABLE II

Time constants and fractions of defects annealed at room temperature by the two processes indicate in text. Samples quenched from 1000°K.

Crystal	Sample Thickness (mm)	f, Fraction Annealed by		T (min) (eq. below)	$D(cm^2/sec.)$ (eq. below)
		A process	B process		
1	0.5	0	1		1.2×10^{-7}
1	1	0	1		1.2×10^{-7}
1	2	0.4	0.6	50	1.2×10^{-7}
1	5	0.6	0.4	50	1.2×10^{-7}
2	1	No	B process observed		

$$f = A\left(\frac{1}{1+\frac{T}{t}}\right) + B\left[1 - C\sum_{\ell}^{\infty}\sum_{m}^{\infty}\sum_{n}^{\infty}\left(\frac{\exp\left(-\alpha_{\ell mn}t\right)}{(2\ell+1)^2\,(2m+1)^2\,(2n+1)^2}\right)\right]$$

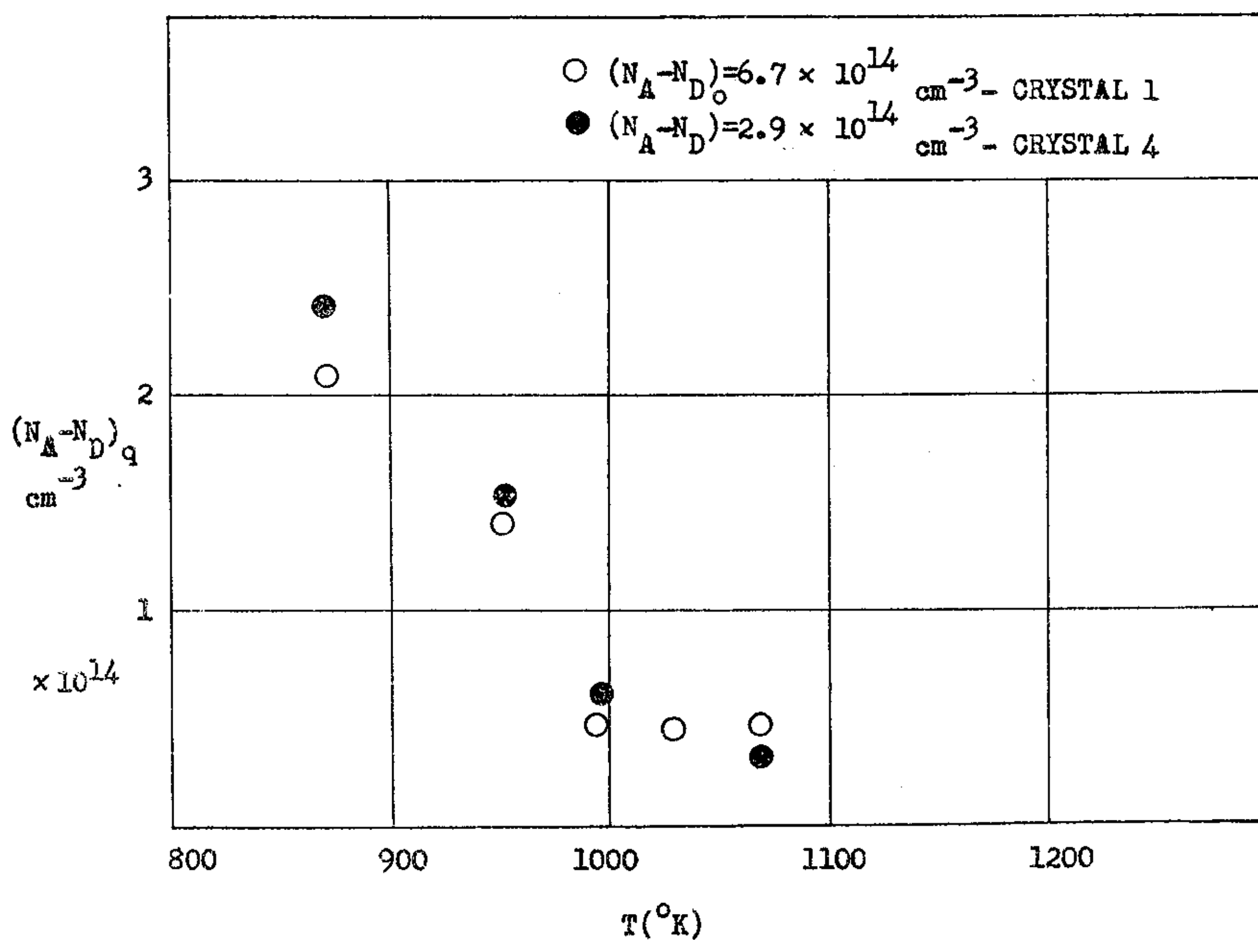

Fig. 1: Net acceptor concentration $(N_A-N_D)_q$, measured at room temperature immediately after quenching from various temperatures (Crystals 1 and 4).

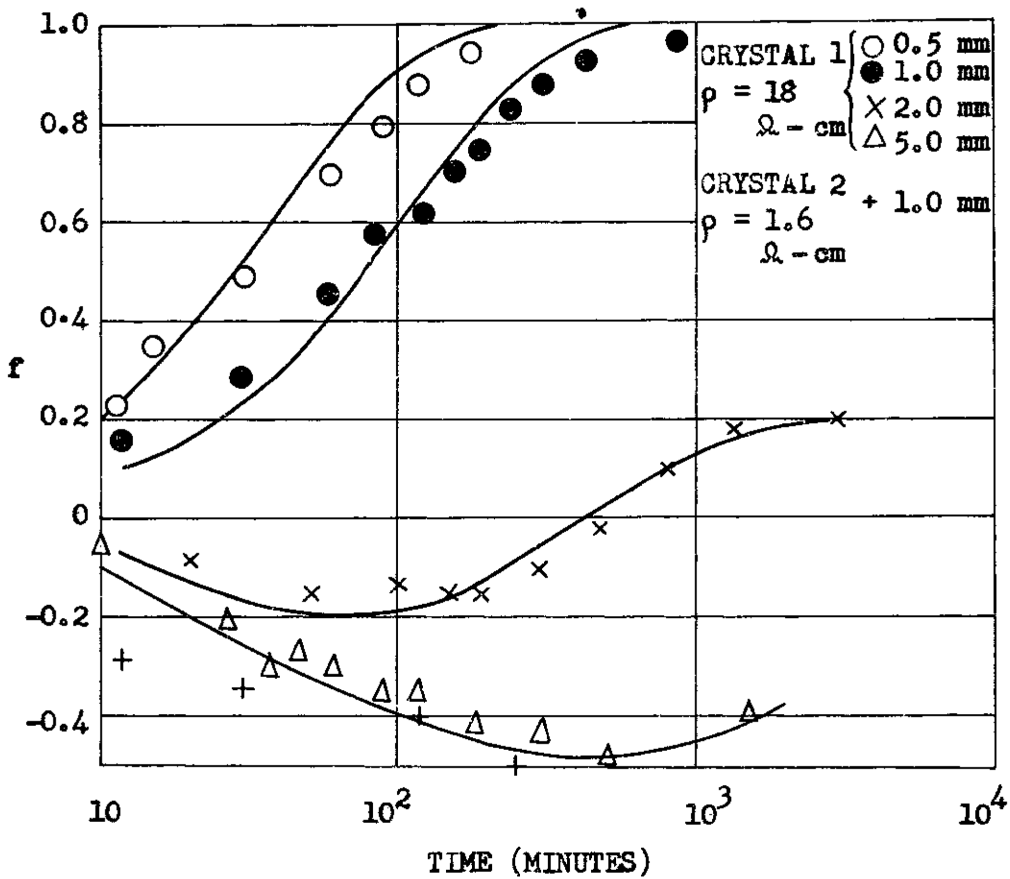

Fig. 2: Fraction of introduced defects, f, annealed at room temperature as a function of time in samples of various thicknesses. The samples were quenched from 1000°K.

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