Electron Paramagnetic Resonance and Electrical Properties of the Dominant Paramagnetic Defect in Electron-Irradiated *p*-Type Silicon*

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Lattice defects having strong paramagnetic resonances are introduced into *p*-type silicon that has been bombarded with electrons. We have studied the paramagnetic properties and growth of the dominant defect so introduced (the *K* center) as functions of electron flux and bombardment energy under conditions of different resistivities, impurity dopants, and illumination. The defect has a spin of $\frac{1}{2}$ and has *g* values of 2.0000, 2.0066, and 2.0056 for the principal magnetic axes, which lie along the $\langle 221\rangle$, $\langle 1\bar{1}0\rangle$, and $\langle 11\bar{4}\rangle$, crystallographic directions, respectively. No hyperfine interactions are observed. The introduction rates for the *K* center are 0.006, 0.025, 0.073, and 0.11 cm^{-1} at bombardment energies of 0.7, 1, 3, and 6.6 MeV, respectively. The *K* center is independent of the *p*-type dopant. It is not a primary defect, but requires oxygen. At high integrated electron fluxes the EPR-measured *K*-center concentration decreases; however, illumination and annealing experiments have established that the defects are still present but have a different charge state because they have trapped an electron. The EPR measurements have been paralleled by Hall-effect measurements. We have associated the *K* center with a previously reported 0.3-eV defect level on the grounds that both require oxygen, that both have about the same introduction rates and bombardment energy dependence, and that the value of the Fermi level at which the *K*-center EPR absorption decreases sharply is about 0.3 eV.

I. INTRODUCTION

ELECTRON spin resonance has been used to study the growth and structure of paramagnetic defects produced by electron irradiation.[1–3] In silicon, evidence for the existence of at least 21 species of paramagnetic centers has been presented by Watkins.[3] The conditions for observing these defects vary considerably, being dependent upon the irradiation and measurement temperatures, dopant concentration, and electron flux. In this paper we will discuss the results of studies on the dominant paramagnetic defect in *p*-type silicon produced by room-temperature electron irradiation. By dominant is meant the defect center with the highest introduction rate.

We have studied this center as functions of electron flux and bombardment energy under conditions of different resistivity, impurity dopants, and illumination. EPR measurements have been paralleled by Hall and resistivity measurements. We have found that the center requires oxygen, is independent of the particular *p*-type dopant, and is associated with a previously established defect level 0.3 eV above the valence band.

II. EXPERIMENTAL PROCEDURE

The samples studied were *p* type and doped with boron, gallium or aluminum to resistivities of 0.3 Ω cm, 2.0 Ω cm, and 6.0 Ω cm. For the most part, boron-doped material—(the most readily available)—was used in the experiments since the defect spectrum did not depend on the presence of a specific acceptor. Sample dimensions were 0.025 in×0.3 in.×0.1 in. and allowed uniform penetration of the electrons. The irradiations were performed in air at room temperature. The 0.7-the 1- and the 3-MeV bombardments were carried out with a Van de Graaff accelerator at a beam current of 5 $\mu A/cm^2$; the 6.6-MeV irradiations were performed on a linear accelerator at 10 $\mu A/cm^2$.[4] A Faraday cup monitored the current and total charge throughout the irradiations. The samples were kept cool by mounting them on water-cooled blocks. The maximum temperature rise was 25°C for the lower energy bombardments and 50°C for the 6.6-MeV irradiation.

The spin-resonance measurements were performed at liquid-neon temperature with a spectrometer operating at a frequency of 21.5 Gc/sec using superheterodyne detection. Relative defect concentrations were determined from the intensity of the defect's resonance absorption. This, in turn, was determined by comparison to the simultaneously measured resonance absorption of the conduction electrons in a (known) phosphorous-doped sample. The spin-resonance data were taken only in the dispersion mode in order to avoid errors introduced by saturation of the signal.[5,6] A modulation frequency of 80 cps and a modulation field of 0.32 G were used. Spin-resonance measurements in which the sample was illuminated were performed on a 9-kMc/sec Varian spectrometer.

After irradiation, resistivities of all samples were measured with a four-point probe. On several samples

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[1] G. D. Watkins, J. W. Corbett and R. M. Walker, J. Appl. Phys. **30**, 1198 (1959).
[2] G. Bemski, J. Appl. Phys. **30**, 1195 (1959).
[3] G. D. Watkins, *Radiation Damage in Semiconductors* (Dunod Cie., Paris, 1965).
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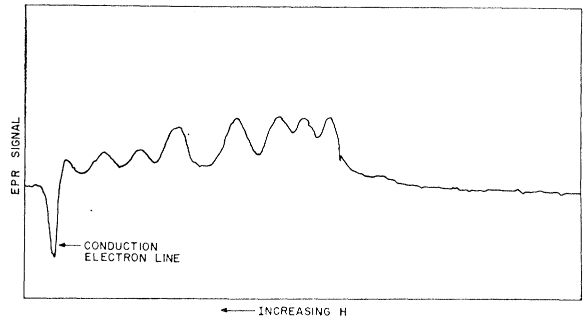

FIG. 1. EPR spectrum of the K center. The magnetic field H is oriented 10° from the ⟨110⟩ axis.

two-point probe and Hall measurements were used to determine their resistivities and thermal activation energies. In the latter measurements the Hall constant was measured over a temperature range between 200°K and 300°K.

III. EXPERIMENTAL RESULTS

A. Electron Paramagnetic Resonance Results

1. Conditions for Detecting the K Center

The samples do not exhibit any resonances before electron bombardment. After irradiation a dominant spectrum of a single center, to be referred to as the K center, is detected, (see Fig. 1). The spectrum[7] is observed in pulled silicon crystals doped with boron, gallium and aluminum. The K-center resonance is not present in silicon grown by the floating-zone technique with similar doping concentrations. Instead, one identified with the J center appears.[8,9] The main difference between these two types of crystals is that in the former there are approximately $10^{18}/\text{cm}^3$ oxygen atoms while in the latter there are only about $10^{16}/\text{cm}^3$. Oxygen thus appears to be necessary for the creation of the K center.

The J-center spectrum is observed occasionally in pulled crystals along with the K center, but generally in very much lower concentrations. There are several reasons why detection of the K center is strongly favored in our experiments. First, as we shall see, its introduction rate is higher. Secondly, the linewidth of the J center is about one half that of the K center so that the modulation amplitude (0.32 G) favors detection of the K center. Finally, and, perhaps most importantly, the two resonances are 90° out of phase with each other[9] with respect to the modulation signal. This means that when we have tuned the EPR spectrometer so as to view the K center in the dispersion mode, the J center is in the absorption mode. Since both centers give rise to saturated resonance lines, the J center will appear even more weakly.[5,6] For the remainder of this paper, we will be concerned only with the K center.

2. Symmetry Properties

The K-center spectrum consists of seven closely spaced lines as shown in Fig. 1. The angular variation of the seven-line spectrum has been fully investigated and the details have been discussed elsewhere.[10] For completeness, however, we will briefly summarize the pertinent results here. The analysis of the data on the angular variation of the spectral lines with magnetic field (see Fig. 2) is well fitted by a defect with a spin $\frac{1}{2}$ and whose three principal magnetic axes are along the ⟨221⟩, ⟨1$\bar{1}$0⟩, and ⟨11$\bar{4}$⟩ crystallographic directions. The corresponding g values are 2.0000, 2.0066, and 2.0056. Although attempts were made to discern hyperfine structure in the spectrum to help determine the physical nature of the defect, none was observed. Apparently, the interaction between the Si^{29} nuclear spin and the spin of the defect is either very small or zero.

3. Growth Rate of the K Center

The growth rates of the K center for 0.7-, 1-, 3-, and 6.6-MeV bombardment energies as measured by electron spin resonance on 2-Ω cm material are shown in Fig. 3. In this figure, the integrated resonance signal and the density of centers are plotted as a function of integrated electron dose. (The calibration of spin resonance intensity with defect concentration is most conveniently discussed in the next section on "Effects of Illumination"). For the 1- and 6.6-MeV curves, the K center grows linearly at low fluxes while at larger fluxes it decreases and finally falls below the limit of detection. No other spectrum emerges when the K center diminishes. From the relative slopes of the linear region of these two curves it is seen that the higher energy electrons are about three times more effective in producing defects. The maximum number of defects observed, on the other hand, does not appear to be strongly dependent on the bombarding energy. In the case of the 0.7- and 3-MeV irradiations the dose was not high enough to observe the decrease.

The decrease in EPR signal in the high flux region is not due to a real decrease in K-center density. We have found that heating the samples which have been bombarded at these high fluxes to 300°C for 1 h considerably increases the spin-resonance signal. For example, a 4×10^{17}-e/cm^2 bombardment at 6.6-MeV resulted in a near-zero EPR signal. After heating at 300°C the K-center resonance appears with an intensity corresponding to 20 on the scale of Fig. 3.

[7] This center corresponds to the center designated as Si-G15 by Watkins in Ref. 3. Beyond giving the g values, however, no further work was reported on this center.

[8] J. W. Corbett and G. D. Watkins, Phys. Rev. Letters **7**, 314 (1961).

[9] G. D. Watkins and J. W. Corbett, Phys. Rev. **138**, A543 (1965).

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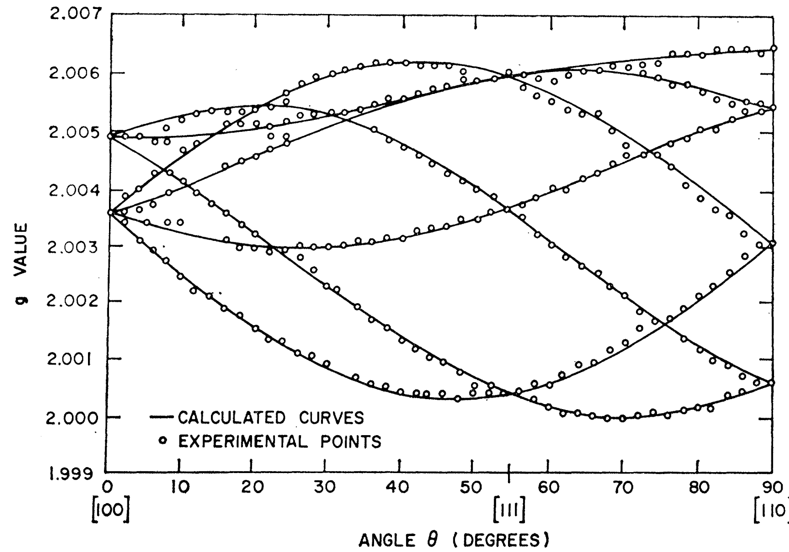

FIG. 2. Angular variation of the K-center EPR spectrum. The magnetic field H is rotated in the (110) plane. (From B. Faughnan *et al.*, Ref. 10.

The decrease in observed defect concentration may be explained by the fact that as the resistivity increases (due to the introduction of carrier removal sites by the electron bombardment) the Fermi level moves past the defect level toward the center of the forbidden energy gap. This depopulates the K center, and if our EPR measurements detect only the (hole) populated defects, the apparent K-center density would decrease. This explanation, of course, requires the presence of a level deeper than the defect level. Direct experimental evidence for such a level is discussed in Sec. III B2. One could also account for this decrease if the defects are annihilated or annealed out of the sample. However, the 300°C heat treatments described above and measurements involving sample illumination discussed in the next section have ruled this out.

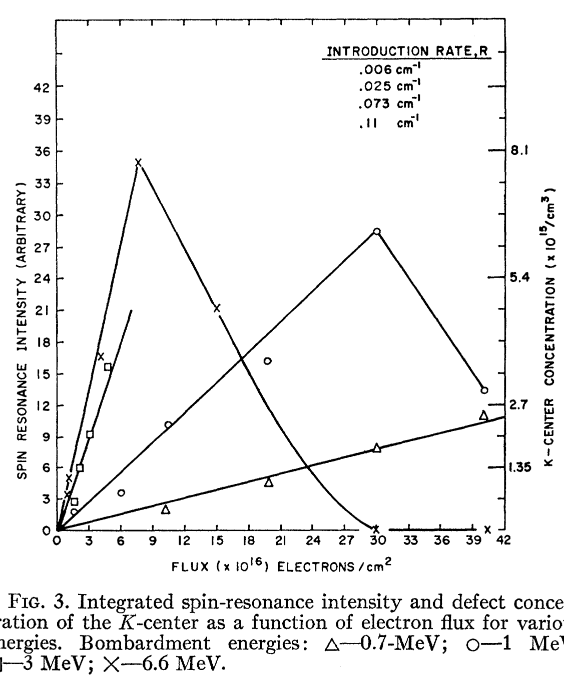

FIG. 3. Integrated spin-resonance intensity and defect concentration of the K-center as a function of electron flux for various energies. Bombardment energies: △—0.7-MeV; ○—1 MeV; □—3 MeV; ×—6.6 MeV.

The energy dependence of K-center production is obtained by plotting the initial slopes of the curves in Fig. 3 versus energy. This is shown in Fig. 4 along with the energy dependence of the production of a previously reported defect level 0.3 eV above the valence band.[11–15] The similarity between these two curves in shape and magnitude was one of our first indications that the K center should be associated with this level.

4. *Effects of Illumination*

Our hypothesis that the electron bombardment raises the Fermi level and thus depopulates the K centers was tested by illuminating heavily bombarded samples with white light. This illumination should produce holes which could repopulate the K centers. Accordingly, EPR spectra were taken of heavily bombarded samples first in the dark and then in white light. In all cases, the K-center resonances were stronger, by factors of up to 20, for those samples which were illuminated.

Another important result of these experiments was that they furnished the calibration for the actual concentration of K centers produced by the electron bombardment. We had found that at electron fluxes below the flux ϕ_c at which the EPR signal was maximum, illumination had no effect on the K-center resonance.

[11] G. K. Wertheim, Phys. Rev. **110**, 1272 (1958).
[12] Interim Report MR32, Contract No. NAS 5-1851, 1964 (unpublished).
[13] R. L. Novak, Ph.D. thesis, University of Pennsylvania, 1964 (unpublished).
[14] D. E. Hill, Phys. Rev. **114**, 1414 (1959).
[15] References 11–14 place the defect level between 0.27 and 0.32 eV above the valence band. The reported production rates for different bombardment energies are sufficiently close to indicate that the levels in question arise from the same defect. We will refer to this defect as the 0.3-eV defect level.

TABLE I. Summary of four-point-probe measurements.

			1 MeV					6.6 MeV	
	Crystal #S-1295		Crystal #N-341		Crystal #S-1295			Crystal #N-341	
Flux (e/cm^2)	ρ (Ω cm)	E_F-E_V (eV)[a]	ρ (Ω cm)	E_F-E_V (eV)[a]	ρ (Ω cm)	E_F-E_V (eV)[a]	Flux (e/cm^2)	ρ (Ω cm)	E_F-E_V (eV)[a]
2×10^{16}	0.3	0.12	2.4	0.18	10	0.23	1.5×10^{16}	3.2	0.19
5×10^{16}	0.3	0.12	...	...	25	0.25	4.5×10^{16}	5.7	0.22
6×10^{16}	...	...	3.1	0.19	...	...	7.5	**50**	**0.27**
1×10^{17}	0.3	0.12	3.7	0.20	**60**	**0.27**	1.5×10^{17}	560	0.34
2×10^{17}	0.3	0.12	5	0.21	10^3	0.35	3×10^{17}	10^3	0.35
3×10^{17}	...	...	**70**	**0.28**	$>10^3$	>0.36	4×10^{17}	$>10^3$	0.36
4×10^{17}	1.0	0.17	190	0.32	$>10^3$	>0.36			
6×10^{17}	1.8	0.18							
8×10^{17}									
1×10^{18}	**8.5**	**0.22**							
2×10^{18}	$>10^3$	>0.36							

[a] For these calculations the mobility was assumed to be independent of electron flux.

At $\phi=\phi_c$, illumination produced only about a 10% increase, indicating that essentially all the K centers are occupied. Since the starting resistivity determines the hole concentration, and hence the maximum populated K-center density in the dark, the measured K-center density at $\phi=\phi_c$ is then approximately equal to the acceptor concentration. We have used this to convert the EPR resonance signal into the absolute K-center concentrations plotted, for example, in Fig. 3.

5. *Effects of Resistivity*

The effects of the initial resistivity on K-center production are shown in Fig. 5. The same growth behavior is found as that described in Fig. 3. The K-center concentration increases linearly with flux until a certain value ϕ_c is reached, beyond which it descresaes. As the initial resistivity increases, ϕ_c decreases. These effects can be understood again in terms of Fermi-level location and charge state of the K center. At higher resistivities, the acceptor concentration, N_a is smaller. Therefore, to move the Fermi level past the K-center level requires the formation of fewer carrier removal sites. This, in turn, requires a smaller flux ϕ_c. Note also that in Fig. 5 the product of ϕ_c and the introduction rate, R, of Fig. 3 is equal to N_a for the different resistivities. This further substantiates our earlier resoning that at ϕ_c the K-center density should equal N_a.

For the 0.3 Ω-cm curve, ϕ_c occurs at a lower value than N_a/R. However, this is probably due to the fact that at high flux levels the defect concentration is approaching the oxygen concentration, and so might be expected to have a somewhat lower production rate. This would mean that fewer carrier removal sites (deeper than the K center) would be required to move the Fermi level past the K-center level, resulting in a smaller ϕ_c. The rates of decrease of the K-center resonance intensity in Figs. 3 and 5 indicate that the deeper level is being produced at comparable rates.

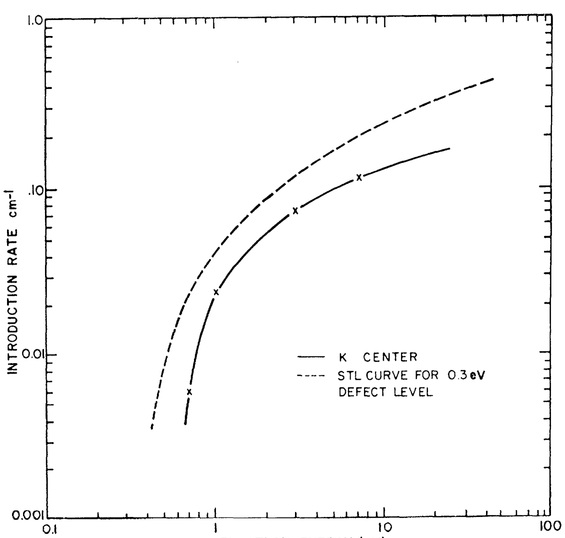

FIG. 4. Introduction rates of the K center and the 0.3-eV defect level as a function of energy.

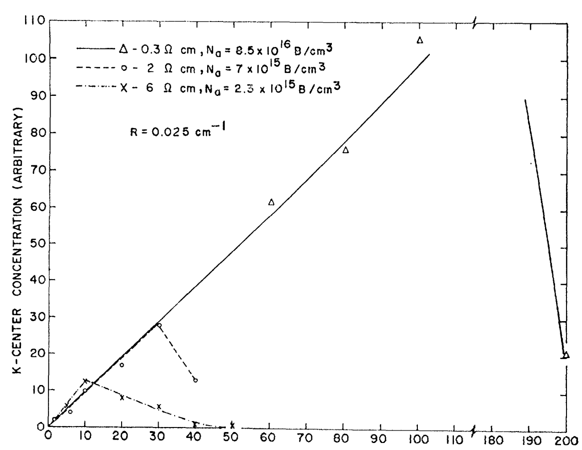

FIG. 5. Growth rate of the K center as a function of flux for three different resistivity crystals.

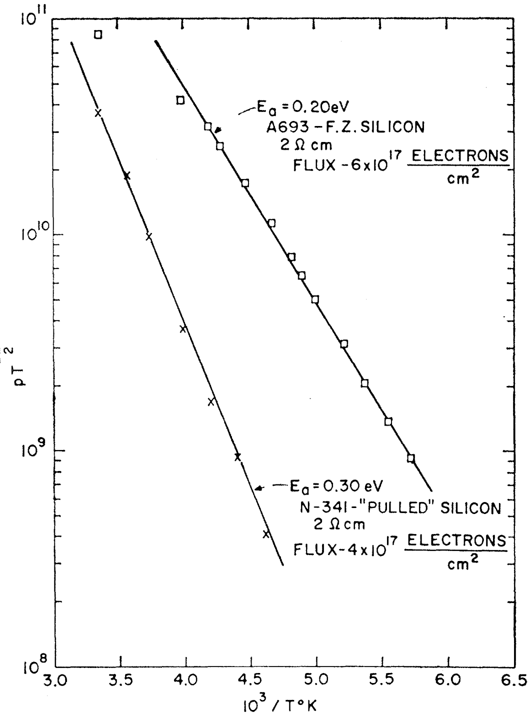

FIG. 6. Plot of $pT3^{3/2}$ versus $10^3/T$°K for "pulled" and "float-zone" silicon irradiated with 1-MeV electrons showing that a 0.3-eV level is dominant in the former while a 0.2-eV level is dominant in the latter.

B. Electrical Measurements

1. *Resistivity Measurements*

Our earliest evidence that the K center is associated with the 0.3-eV defect level stemmed from the fact that their introduction rates and the energy dependence of these rates were the same. Additional evidence for this association has been derived from the correlation of resistivity measurements described below with our earlier EPR results.

The resistivity measurements were taken by standard four-point probe techniques at room temperature, and are summarized in Table I for the 1- and 6.6-MeV irradiation energies. The bold-face entries are those for which the irradiation flux produced the maximum K-center EPR signal. Note that at these fluxes, the Fermi level is always close to 0.3 eV above the valence band. At fluxes greater than this, the Fermi level lies further from the valence band and the K-center EPR signal begins to decrease (see Figs. 3 and 5), i.e. the flux at which the Fermi level moves past (and thus depopulates) the 0.3-eV level is the same at which the K-center EPR signal decreases. This is, of course, consistent with our suggestion in Sec. III A 5 that hole depopulation of the K center is responsible for the decrease in its EPR signal.[16]

2. *Hall Measurements*

The association of the K center with the 0.3-eV defect level in pulled silicon and the failure to observe the K center in float-zone silicon led us to make Hall measurements to see if the 0.3-eV level itself depended on oxygen. Hall samples of both pulled and float-zone silicon (2-Ω cm, p type) were irradiated with 1-MeV electrons with fluxes of 4×10^{17} and 6×10^{17} e/cm^2, respectively, and Hall measurements were performed from 200 to 335°K. The data are plotted in Fig. 6. The thermal activation energy for conduction obtained in float-zone silicon is 0.20 eV while for pulled material it is 0.3 eV. These results demonstrate that the 0.3-eV defect level is indeed associated with oxygen and so adds further evidence for the connection between it and the K center. The terminal resistivities after the same amount of irradiation indicate that the production of carrier removal sites is smaller by a factor of 5 in the float-zone silicon.

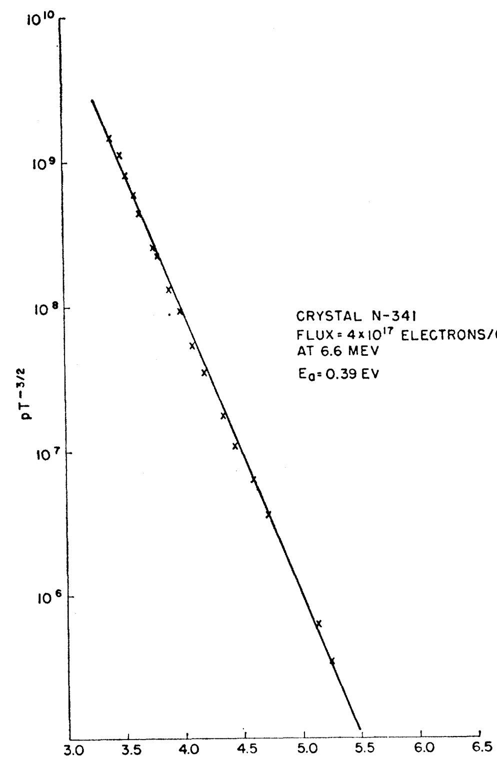

FIG. 7. Plot of $pT^{-3/2}$ versus $10^3/T$°K for "pulled" silicon irradiated with 6.6-MeV electrons showing that at high total fluxes a 0.39-eV energy level is dominant.

[16] Although the resistivity and the Fermi level were measured at room temperature while the spin resonance measurements were performed at 27°K, the temperature difference does not alter the nature of the above conclusion since the Fermi level moves toward the band edge as the temperature is lowered. Thus an upper limit to the Fermi level position is established by the room-temperature value which in turn places an upper limit to the K-center level. It does mean that a more precise quantitative investigation is required to place accurately the position of the Fermi level and the population of the 0.3-eV level at 27°K.

Resistivity measurements were also made on pulled silicon samples (2-Ω cm, *p* type) irradiated by 6.6-MeV electrons with fluxes of 4×10^{17} e/cm^2. It will be recalled that under these very heavy irradiations no *K*-center EPR signal was detected (see Fig. 3), and it had been suggested that this was due to hole depopulation of the 0.3-eV level. This mechanism, of course, requires that a deeper level be present in the crystal. The results of such resistivity measurements as a function of temperature are shown in Fig. 7. Although mobilities were not measured at the various temperatures, the temperature dependence of the mobility, given by Prince,[17] was used to determine the carrier concentrations. The data do indeed show the presence of a deeper level at 0.39 eV, which is being produced at a rate comparable to that of the *K* center (see Sec. III A 5).

IV. SUMMARY AND DISCUSSION

We have found that the *K* center is the dominant paramagnetic defect introduced into *p*-type silicon by electron bombardment at energies ranging from 0.7 to 6.6 MeV. Its net electron spin is $\frac{1}{2}$. Its *g* values are 2.0000, 2.0066, and 2.0056 for the $\langle 221\rangle$, $\langle 1\bar{1}0\rangle$, and $\langle 11\bar{4}\rangle$ directions, respectively. Its symmetry axis is the $\langle 221\rangle$, which is the direction from a substitutional lattice site to a next nearest-neighbor interstitial. The *K* center is not a primary defect but requires oxygen, thus suggesting that atomic motion of either (interstitial) silicon and/or oxygen may be involved.

The formation of the *K* center is independent of the *p*-type dopant. Its introduction rates at 0.7, 1, 3 and 6.6 MeV are, respectively, 0.006, 0.026, 0.073, and 0.11 cm^{-1}. At high fluxes, depending in part on bombardment energy and in part on the starting resistivity, the EPR-measured *K*-center concentration decreases. However, subsequent illumination experiments and annealing experiments show that the defects are still present, but that they have a different electronic charge state because they have trapped an electron.

We have identified the *K* center with an electrical level 0.3 eV above the valence band. This is based on the following of our measurements: Both have the same introduction rate and energy dependence for their formation; both require oxygen; and, finally, the *K*-center EPR absorption decreases sharply as the Fermi level, moving away from the valence band, passes through a value of about 0.3 eV.

Experimental results of other workers furnish strong supporting evidence for this hypothesis. For example, both Vavilov *et al.*[18] in photoconductivity studies, and Fan and Ramdas[19] in optical absorption measurements, find that a 0.3 eV-peak response is present only when the Fermi level is less than 0.3 eV. These results are analogous to our EPR findings described in Sec. III A 5. Furthermore, Fan and Ramdas[20] have annealed heavily bombarded silicon and subsequently observed a 0.3-eV optical absorption which had been absent before the anneal. This, again, is analogous to our EPR results described in Sec. III A 3.

In conclusion, it is interesting to note that Watkins[9] has recently associated the *J* center with the 0.3-eV level after measuring an optical threshold of 0.25 eV at which the *J*-center depopulates. It is suggested here that this association is inappropriate since the introduction rate for the *J* center is considerably less than that for the 0.3-eV level, and since the 0.3-eV level requires oxygen while the *J* center does not. The 0.25-eV threshold may, of course, correspond to the depopulation of the 0.2-eV level seen in Fig. 5. If this is so, it leads to the suggestion that the 0.2-eV level be identified with the *J* center, rather than the 0.3-eV level which we have associated with the *K*-center. Both levels may, in fact, be present in oxygen-containing material, but because the 0.3-eV level has a larger introduction rate, the 0.2-eV level is not readily detected.

ACKNOWLEDGMENTS

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