Photoconductive resonance in silicon: Theory and experiment

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Measurements have been made of light-induced resonant centers at silicon surfaces which behave as power emission rather than absorption centers as applies to normal electron-paramagnetic resonance EPR. The phenomenon is analyzed as a form of photoconductive resonance, called PCR, and a theroretical expression is derived. The EPR signal then expected from PCR centers at sufficiently low power has been detected for the first time. The dependence on temperature and power of the signals from the PCR centers agrees well with the predictions from theory. The sensitivity of detection of PCR centers is found to be over 30 times that of EPR centers.

I. INTRODUCTION

Defects present in silicon oxide films in low concentrations (10^9 to 10^{13} cm^{-2}) have a significant effect on the electrical properties of the Si-SiO_2 interface.[1] It is worthwhile attempting to detect these centers (if paramagnetic) by electron-paramagnetic resonance (EPR), which, unlike electrical measurements, can provide information leading to a microscopic model of the centers involved. However, the lower limit of detectability for EPR for single-crystal Si sample interfaces is about 10^{12} cm^{-2} owing to limitations on surface area, loading of the microwave cavity, linewidth, etc. Thus, although EPR signals are obtained from damaged Si surfaces,[2] and thermally oxidized Si surfaces[3-7] (oxide films greater than 100Å), no conventional EPR signals are obtained from the thin oxide films (less than 50 Å) formed on Si at room temperature.

This situation was changed somewhat by recent reports[3-8] that thin oxide films do give an EPR-like resonance when measured at low temperatures in an EPR spectrometer while illuminated with light. However, the signals are not normal EPR signals since they are inverted in phase. It has been suggested[4-6] that this effect is due to a decrease of the photoconductivity of the sample owing to the resonant change in polarization of paramagnetic defects which also act as recombination or scattering centers.

The main aim of the present work is to obtain a theoretical expression for the dependence of a signal of this nature on temperature, microwave power, and other factors, and thus to test the above hypothesis. Excellent agreement is found between the theory and experimental results. Furthermore, for the first time, we have detected the EPR resonance which is expected to be associated with the new type of photoconductive resonance, which we call[8] PCR. The signal-to-noise ratio is more than an order of magnitude better for PCR than EPR. Thus centers present in quite low concentrations become accessible to measurement.

II. EXPERIMENTAL

Wafers of p-type Si (1 to 10 $k\Omega$ cm) and n-type Si (2 to 100 $k\Omega$ cm) were polished and etched in CP4 ($3HF:5HNO_3:3CH_3COOH$) to remove surface damage. Sample dimensions were typically 1 mm $\times$ 2.5 mm $\times$ 12 mm with the large-area face either (111) or high index. Samples were also cleaved from an n-type Si block 5 mm $\times$ 5 mm, grooved at 2-mm intervals, by striking a wedge positioned in a groove. The etch treatments were of three minutes duration at room temperature followed by a thorough rinsing in distilled water.

The EPR measurements were performed in a Varian x-band spectrometer in the absorption mode with maximum microwave power of about 300 mW. Measurements at 77 K were performed by either placing the sample directly in a liquid nitrogen Dewar in the cavity or fixing the sample in a quartz tube which was inserted in the Dewar. In the latter case liquid air formed in the quartz tube, ensuring efficient cooling of the sample. Measurements between room temperature and 77 K were performed in a variable-temperature apparatus with the crystal exposed directly to the cooled nitrogen gas stream. As a monitor of the crystal temperature in this case, which also takes into account possible cavity-sensitivity changes with temperature, the signal was simultaneously recorded from $CuSO_4 \cdot 5H_2O$ crystals attached to the end of a quartz tube pressing on the Si crystal. Width and g values were measured with respect to the lines of a MgO:Mn^{++} sample at $g = 1.9804$ and $g = 2.0326$ separated by 8.66 mT. The samples were illuminated by a tungsten lamp focused on them through a glass lens.

III. THEORY

The most notable features of the signals from thin SiO_2 films, reported previously and in this work, are that they are only observed in the presence of light and that their phase is inverted with respect to a normal EPR signal. The latter result shows that less microwave energy is being absorbed by the sample *at* resonance than *off* resonance. There are a number of ways in which this could occur, for example, population inversion of the Zeeman levels as a result of illumination.[9] However, in the explanation here discussed, PCR is a manifestation at microwave frequencies of the resonant change in conductivity already detected by Lèpine at zero frequency[10] (direct current). By monitoring the dc conductivity of an Si single crystal during an otherwise conventional EPR experiment, Lèpine found that a resonant decrease occurred in the conductivity of the sample. This effect was attributed to a resonant increase in the recombination rate of the electron-hole pairs produced by light, owing to interaction with recombination centers. The interaction rate was altered since, owing to microwave power absorption, the populations of parallel spin and antiparallel spin centers were altered. The resulting change in spin polarization of these centers results in the observed resonant decrease of the zero-frequency photoconductivity of the sample. If this conductivity decrease (or recombination-rate increase) also occurs at microwave frequencies, it will produce an increase in cavity Q. If sufficiently large to be detected, this would result in an apparent EPR signal of phase opposite to that of normal EPR, which corresponds to a decrease in Q.

In deriving an expression for PCR, we first obtain the signal strength in terms of the photoconductivity change and then relate the latter to the microscropic properties of the defect. When the detector crystal of the spectrometer is operating in the linear range, the signal voltage ΔV is given by

$$\Delta V \propto \Delta Q \sqrt{\Pi}/Q ,$$

where Q is the quality factor of the microwave cavity, ΔQ is the change in Q during resonance, and Π is the microwave power incident on the cavity. In the usual EPR case, ΔQ is due to a resonant change of the magnetic losses in the sample. This term can be treated in the usual way.[11] In the present case we include an additional term due to a resonant change of the electrical losses in the sample, for which new expressions are obtained. Including these, one obtains for ΔV the expression

$$\Delta V \propto -Q(\delta\chi''\eta + \delta\epsilon''\alpha)\sqrt{\Pi},$$

where $\delta\chi''$ is the change in the imaginary part of the relative susceptibility due to magnetic resonance losses, $\delta\epsilon''$ is the change in relative permittivity of the sample, and the "filling factor" η (or α) is the ratio of the magnetic (or electric) energy stored in the volume occupied by the sample to the magnetic (or electric) energy stored in the cavity. If the photoconductivity of the sample changes by $\Delta\sigma_p$ when the microwave field is applied,

$$\Delta V \propto -Q(\delta\chi''\eta + \Delta\sigma_p\alpha/\epsilon_0\omega)\sqrt{\Pi}, \tag{1}$$

where ϵ_0 is the average dielectric constant and $\omega/2\pi$ is the microwave frequency.

The magnetic susceptibility term $\delta\chi''$ due to the paramagnetic centers is proportional to the spin polarization of the centers $p_0 = (n_0^- - n_0^+)/(n_0^- + n_0^+)$, where n_0^+ (n_0^-) is the number of electrons in the upper (lower) Zeeman level in equilibrium. If one assumes that the spin system interacts homogeneously, then, in the presence of the microwave field, the polarization changes from p_0 to $p = p_0 S$, where the saturation factor S is given by

$$S = [1 + \tfrac{1}{4}\pi\gamma^2 H_1^2 T_1 g(H - H_0)]^{-1}, \tag{2}$$

where γ is the gyromagnetic ratio, H_1 (proportional to $\sqrt{\Pi}$) is the microwave magnetic field amplitude, T_1 is the spin-lattice relaxation time, $g(H - H_0)$ is the line-shape function, and H_0 is the resonant magnetic field.

The conventional EPR signal height is given by[11,12]

$$\Delta V_{\mathrm{EPR}} \propto p_0 g(H - H_0) S\sqrt{\Pi}.$$

For a Lorentzian line shape,

$$g(H - H_0) = (T_2/\pi)[1 + T_2^2\gamma^2(H - H_0)^2],$$

where the spin-spin relaxation time T_2 is a measure of the linewidth. One usually detects the first derivative of ΔV_{EPR} with respect to the magnetic field, the maximum value A_m of which occurs when $(H - H_0)^2 = (3\gamma^2 T_2^2/S)^{-1}$,

$$A_m = A_m^0 p_0 S^{3/2}\sqrt{\Pi}, \tag{3}$$

where A_m^0 is a constant.

Returning to the second term of Eq. (1), $\Delta\sigma_p$ is the variation in the photoconductivity due to the change in polarization $(p - p_0)$ produced at resonance. As pointed out by Solomon,[13] the dependence of the photoconductivity on the polarization of the recombination centers can arise because the probability of a conduction electron (or, alternatively, a hole) being absorbed by the recombination center in the parallel spin (triplet) configuration is much less than when spins are

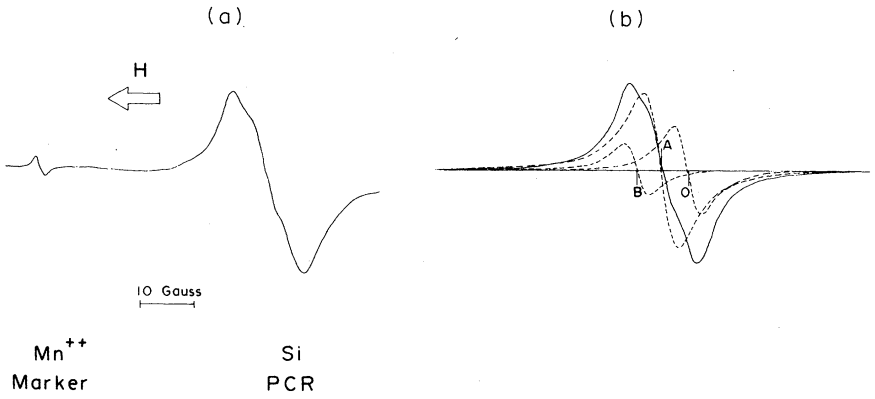

FIG. 1. (a) Photoconductive resonance (PCR) signal at 77 K from etched Si. The computed curve superimposes with this curve very closely. (b) Computed curve and its three Lorentzian components.

antiparallel (singlet).

Assuming that triplet recombination is negligible, the photoconductivity σ_p depends on pP, where P is the polarization of the conduction electrons. The change $\Delta\sigma_p$ in σ_p in the microwave field is due to the alteration in p,

$$\Delta\sigma_p \propto -Pp_0(1-S)\sigma_p^0,$$

where σ_p^0 is the photoconductivity in zero microwave field. Thus the signal height due to the second term in Eq. (1) becomes

$$\Delta V_{\mathrm{PCR}} \propto Pp_0(1-S)\sqrt{\Pi}\,\sigma_p^0.$$

Since, in this case also, one detects the first derivative with respect to the magnetic field of this voltage, the peak-to-peak detected signal is given by

$$A_e = -A_e^0 p_0 P(1-S)\sqrt{S}\,\sqrt{\Pi}, \tag{4}$$

where A_e^0 is a constant which contains σ_p^0. The total signal is then

$$A = [A_m^0 p_0 S^{3/2} - A_e^0 p_0 P(1-S)\sqrt{S}\,]\sqrt{\Pi}. \tag{5}$$

The first term in Eq. (5) is the normal EPR voltage, and the second term is the PCR voltage. The two contributions have opposite sign, which explains the inverted phase of the PCR signal. It is difficult to estimate theoretically the relative magnitudes of each. However, the results of Sec. IV B show that the EPR spectrometer is much more sensitive to the PCR component. The applicability of Eq. (5) can be tested in two ways. Firstly, the polarizations p_0 and P vary as T^{-1}, and so the PCR signal should vary more rapidly with temperature than EPR. Secondly, the saturation factor S decreases with the microwave power level. Thus the EPR component should approach zero at high powers while the PCR component approaches a limiting value. Both these predictions are borne out by the experimental results of Sec. IV B.

IV. RESULTS

A. PCR spectrum

A typical PCR spectrum is shown in Fig. 1. The spectrum was recorded from a CP4 etched sample

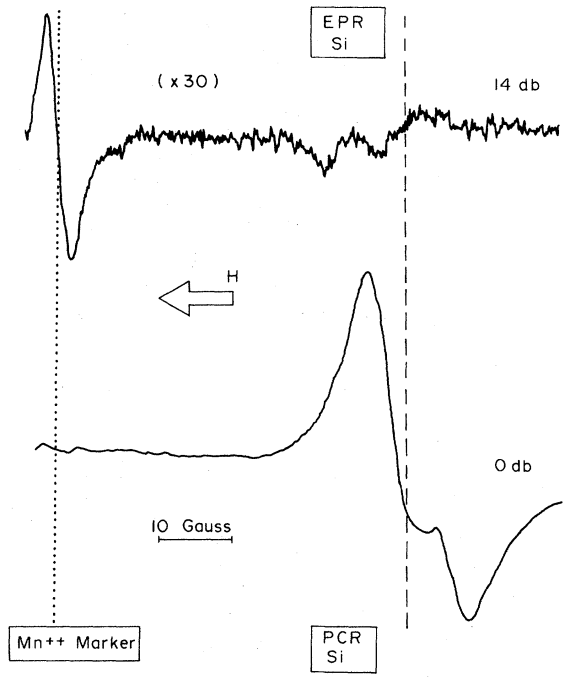

FIG. 2. Experimental spectra at 77 K of the recombination centers detected by both EPR (upper) and PCR (lower). The EPR signal (recorded at 14 dB attenuation) has been accumulated 30 times and has the normal phase. The PCR signal (recorded immediately afterwards at 0 dB attenuation) has not been accumulated and has the reverse phase. The relative sizes of the Mn^{++} marker signals demonstrate the superior sensitivity of the PCR signal. The EPR spectrum (at low power) shows an additional line which is saturated at the gain used for the PCR display, at $g = 2.0022 \pm 0.0003$.

at 77 K with the magnetic field parallel to the (111) surface, which was the illuminated face. By simultaneous measurement of the Si signal and a signal from a paramagnetic sample, e.g., pitch in KCl or $CuSO_4 \cdot 5H_2O$, it was ascertained that the Si signal was indeed inverted in phase with respect to a normal EPR resonance. A similar spectrum was obtained from air-cleaved Si, but not from Si cleaved and measured while continuously immersed in liquid nitrogen before it was exposed to air (several minutes). These results show that the signals are not due to contamination from the etchant, which was suggested before.[6] Other experimental results designed to elucidate the origin of the signals will be reported subsequently.

As shown in Fig. 1(b), the spectrum can be fitted

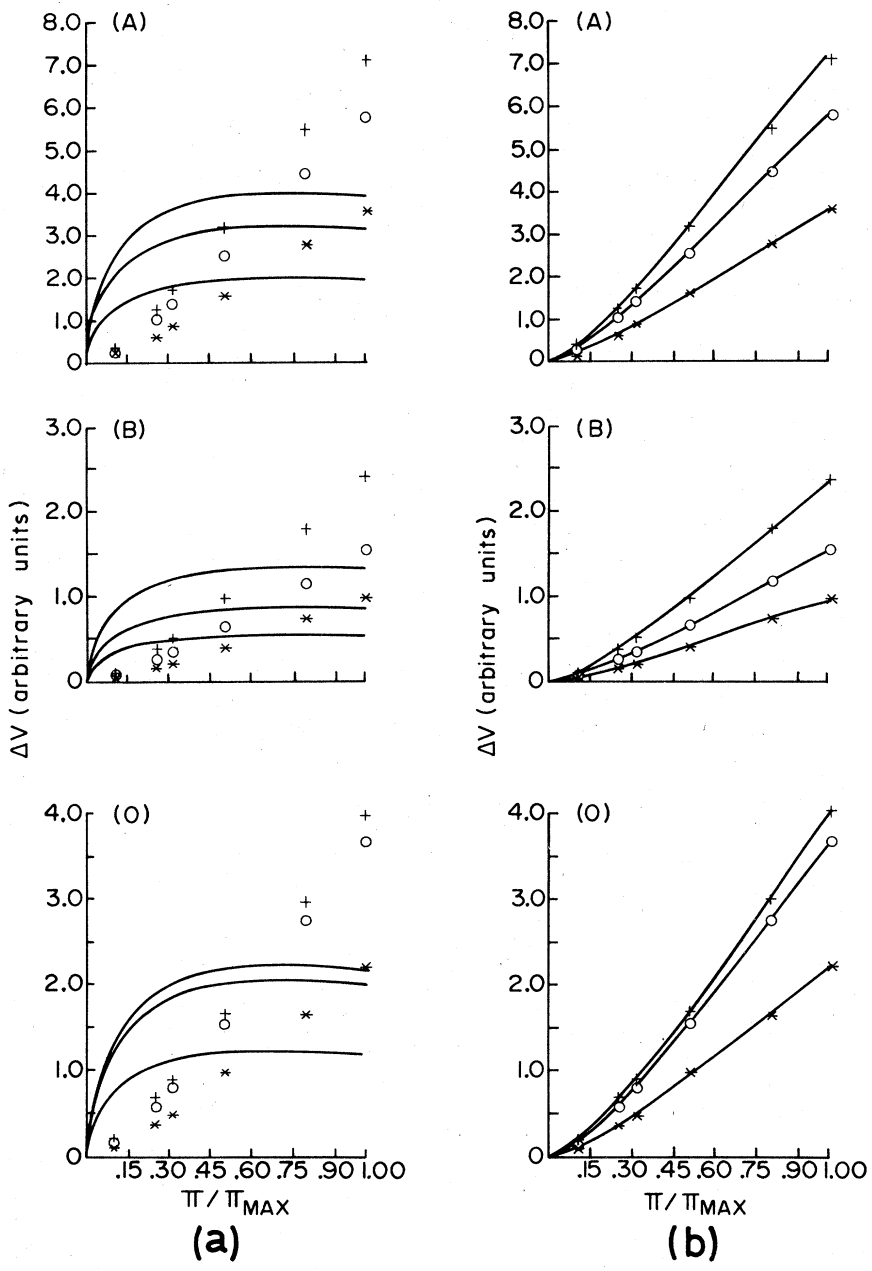

FIG. 3. PCR signal magnitude (77 K) of the constituent lines *A*, *B*, and *O* as a function of the microwave power. For each line, the three different sets of experimental points represent light intensities of 8.2 (*), 47.2 (○), and 83.3 (+) units. In (a), the full line is the least-squares fit to the EPR formula, Eq. (3); in (b) the full line is the least-squares fit to the PCR formula, Eq. (4).

by the sum of three Lorentzian curves. In the subsequent sections, the heights and widths of lines A, B, and O refer to the parameters obtained from a similar computer fit to experiment. It is quite deceptive to estimate the heights and widths of overlapping lines directly from the recorded spectrum. The parameters used in Fig. 1 are line A: width $W = 0.68$ mT, height $H = 4.45$ units, and $g = 2.0088$; line B: $W = 0.44$ mT, $H = 1.4$ units, $g = 2.0063$; line C: $W = 0.513$ mT, $H = 2.6$ units, $g = 2.0103$ from a spectrum whose overall height was 5.4 units.

According to the theory of Sec. III, there is a paramagnetic resonance associated with the observed PCR signal. At sufficiently low powers, the PCR signal should no longer be observable [$S \approx 1$ in Eq. (4)], and there is the possibility of detecting the underlying EPR signal. Indeed, Fig. 2 shows that there is an EPR signal at the same magnetic field at which the PCR signal (reversed phase) appears at high powers. The signal-to-noise (S/N) ratio of the EPR is 1:3 (before enhancement by signal averaging), and the S/N of the PCR signal is 12:1. Thus, for this sample and the microwave powers used, the spectrometer is over 30 times more sensitive to the PCR effect than to the EPR effect.

B. Saturation

To test Eq. (5), the signals from etched Si, illuminated at 77 K, were measured as a function of microwave power. The microwave power was varied by an attenuator whose calibration was checked under similar conditions from measurements on a copper sulfate sample. At each power level, the heights of the constituent signals were found from computer fits and plotted against the ratio of the relevant power level to the maximum power of approximately 300 mW. As shown in Fig. 3(b), the experimental data agree well with a least-squares fit to Eq. (4) for the PCR formula for the signal voltage. The factor S was replaced by $(1+\beta\Pi)^{-1}$ where β is a constant which should depend on the linewidth through Eq. (2). Indeed, the best-fit value of β is found to scale with measured linewidths and be independent of the light intensity. On the other hand, the best-fit value of A_e^0 increases with light intensity, as expected from its dependence on the photoconductivity σ_p^0. Figure 3(a) shows that a least-squares fit to the EPR formula, Eq. (3), does not fit the data, which demonstrates a fundamental difference between the EPR and PCR mechanisms.

C. Temperature dependence

The predicted temperature dependence of the EPR signal is T^{-1} from the dependence of the magnetic susceptibility of the spin polarization of the centers, p_0. The PCR signal temperature dependence is T^{-2} from the terms p_0 and P in Eq. (4). (The spin polarization P of the majority carriers goes as T^{-1} for the temperatures and samples studied.) To test the experimental temperature dependence, signal heights and widths were determined at different temperatures by computer fitting spectra recorded at three different light levels to check any dependence on light intensity. The signal intensity was calculated as the height times width squared since the experimental spectra could be fitted by a Lorentzian line shape throughout. Figure 4 shows that the signal intensity of each of the three lines follows an approxi-

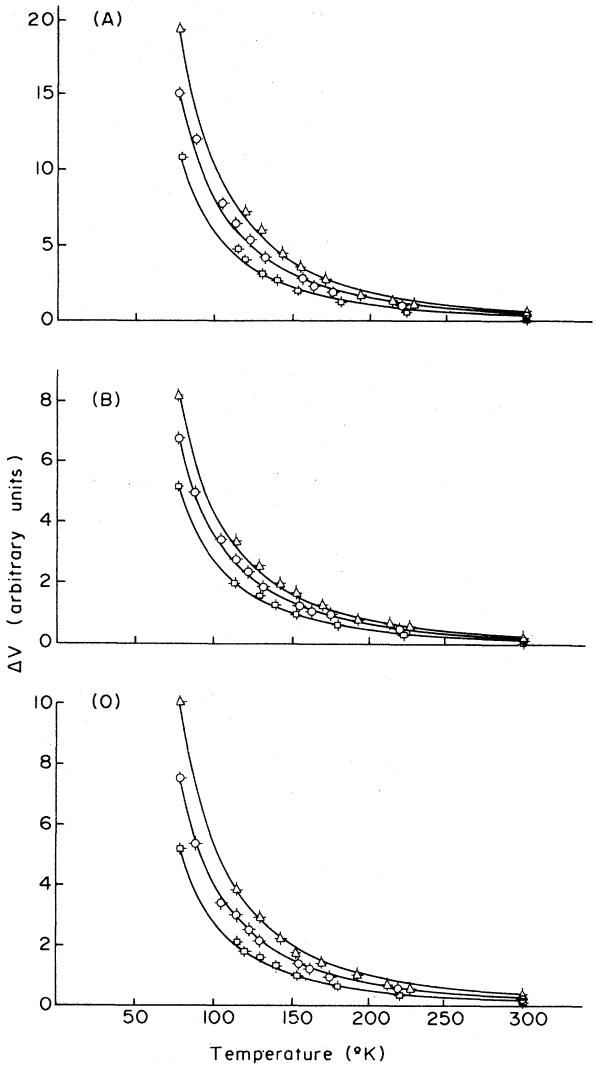

FIG. 4. PCR signal magnitude as a function of temperature for the three lines A, B, and O at the light levels of Fig. 3. The full lines vary as $T^{-2.4}$.

mate $T^{-2.4}$ dependence, in reasonable agreement with the T^{-2} prediction for PCR.

V. CONCLUSION

Paramagnetic centers in Si single crystals have been measured for the first time on the same specimens using both PCR and EPR methods. It has thus been possible to establish that the former technique can be more than one order of magnitude more sensitive than the latter. PCR is thus shown to be a powerful new technique for the study of electrically active paramagnetic species on surfaces or at interfaces.

A theoretical explanation for photoconductive resonance has been obtained and tested against experimental results, yielding excellent agreement between experiment and theory.

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