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Microwave Absorption in Silicon at Low Temperatures

Shoji Tanaka, Mineo Kobayashi, Eiichi Hanamura, and Kunimitsu Uchinokura
Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo, Japan

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The microwave conductivity of p-type and n-type silicon was studied at low temperatures at $\sim$9000 Mc/sec. Samples measured had impurity concentrations ranging from 6.7×10^{15} to 2.2×10^{16} cm^{-3}. In the impurity conduction range, the microwave conductivity varies much more slowly than the dc conductivity, becoming orders of magnitude larger in comparison at 4.2°K. Furthermore, the conductivity showed strong non-Ohmic characteristics in all the samples. The experimental results indicated that the microwave conductivity in the low-concentration range consists of two parts, one the conductivity due to direct absorption process in ionized impurity pairs, which shows saturation at low electric-field intensity, and the other, the conductivity due to hopping process, which does not show a non-Ohmic character. A simple theory of the microwave absorption in the ionized impurity pairs was developed, supporting the experimental conclusions. Theory gives a microwave conductivity due to the direct absorption process of the right order of magnitude and the same temperature dependence as measured. But the relaxation time calculated for the pairs is too long compared with the experimental results. The measured hopping conductivity was compared with calculation and reasonable agreement was obtained. The ratio of the conductivity due to the direct absorption process to the hopping conductivity was calculated and requires that a value for the effective Bohr radius of the boron impurity of 20 Å must be used in stead of the 13 Å obtained from hydrogenic approximation.

I. INTRODUCTION

SINCE Hung and Gliessman[1] first observed impurity conduction in semiconductors, many investigations[2] have been made in this field to seek better understanding of this special type of conduction mechanism. Very recently, measurements of ac impurity conduction have been made in silicon by Pollak and Geballe[3] in low-frequency range and by Tanaka and Fan[4] in microwave-frequency range. Their works succeeded to simplify the problem greatly, because the ac impurity conduction at sufficiently low temperature occurs in localized impurity pairs. The work presented here deals with the microwave absorption in silicon at low temperatures and is a development of the work by Tanaka and Fan.

In the low-impurity concentration range, the dc impurity conduction process can be described as hopping of electrons or holes from one impurity to another, the hopping being made possible by phonon interaction. In an ac field, the hopping motion of carriers could give rise to in-phase as well as out-of-phase current. Pollak and Geballe studied the ac impurity conduction in n-type silicon in the audio frequency range and found that the hopping model in the localized impurity pair accounted well for observed experimental results.

Tanaka and Fan extended the frequency range of ac measurements up to the microwave frequency in p-type silicon and observed a strong non-Ohmic characteristic of the conductivity, which could not be explained from the hopping model. They therefore suggested a possibility of measuring the conductivity due to the direct absorption process which does not require the help of phonon. According to their interpretation, the non-Ohmic characteristic of the microwave conductivity can be explained as a saturation effect of the direct absorption process in the ionized impurity pair.

In this paper the microwave absorption in p-type and n-type silicon was measured at low temperatures in order to investigate the absorption mechanisms in greater detail. The observed conductivity was interpreted as a sum of the two kinds of conductivities, one due to the direct absorption process and the other due to the hopping process. A simple theory on the microwave absorption by the ionized impurity pair was developed. The experimental results on the non-Ohmic characteristic, the temperature dependence of the microwave conductivity and the ratio of the conductivity due to the direct absorption process to the conductivity due to the hopping process were in good agreement with the theory. The observed relaxation time in the direct absorption process, however, is much shorter than the calculated one and this may come from the complexity of the impurity state.

II. EXPERIMENTS

The experimental procedure is in principle the same as described by Tanaka and Fan,[4] and the same microwave frequency of 9000 Mc/sec was used. In order to investigate the non-Ohmic characteristic of the microwave conductivity in more detail, however, the temperature range of measurement was expanded from 1.3°K up to a temperature where the conduction band or valence band conduction occurs (about 20°K), and the input microwave power was varied from 0 dB (corresponding

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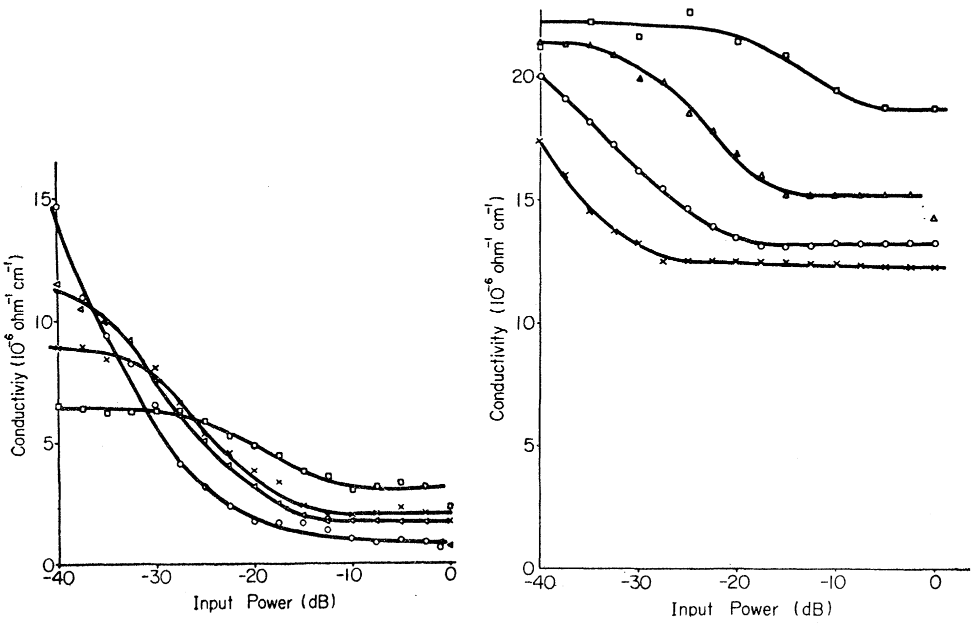
[1] C. S. Hung and J. R. Gliessmann, Phys. Rev. **79**, 726 (1950); **96**, 1226 (1954).

[2] Experimental studies: H. Fritzsche, Phys. Rev. **99**, 406 (1955); H. Fritzsche, Phys. Chem. Solids **6**, 69 (1958); H. Fritzsche and K. Lark-Horovitz, Phys. Rev. **113**, 999 (1959); H. Fritzsche and M. Cuevas, *ibid.* **119**, 1238 (1960); H. Fritzsche, *ibid.* **119**, 1899 (1960); K. R. Atkins, R. Donovan, and R. H. Walmsley, *ibid.* **118**, 411 (1960); R. J. Sladek and R. W. Keyes, *ibid.* **122**, 437 (1961); R. K. Ray and H. Y. Fan, *ibid.* **121**, 768 (1961). Theoretical studies: N. F. Mott, Can. J. Phys. **34**, 1356 (1956); E. M. Conwell, Phys. Rev. **103**, 51 (1956); T. Kasuya and S. Koide, J. Phys. Soc. Japan **13**, 1287 (1958); A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960); N. F. Mott and W. D. Twose, Advan. Phys. **10**, 107 (1961).

[3] M. Pollak and T. H. Geballe, Phys. Rev. **122**, 1742 (1961).

[4] S. Tanaka and H. Y. Fan, Phys. Rev. **132**, 1516 (1963).



(a) (b)

FIG. 1. Dependence of the microwave conductivity on input microwave power at various temperatures: (a) *p*-type sample No. 2, ○ 1.3°K, △ 2.24°K, × 4.2°K, □ 6.0°K; (b) *n*-type sample No. 8, × 4.2°K, ○ 7.2°K, △ 15°K, □ 23°K.

to about 15 mW of input power to the cavity) to −40 dB.

Most of the samples investigated were B-doped, *p*-type silicon crystals. Some of them were heat treated in high vacuum to increase the minority center concentration. The P-doped and Sb-doped *n*-type crystals were added to compare the saturation characteristics of the conductivity with that of *p*-type crystals. They are all listed in Table I.

A. Power Dependence of the Microwave Conductivity

The microwave conductivity of these samples shows non-Ohmic characteristics, that is, it varies with the input microwave power as shown in Fig. 1. In the temperature range of the experiment the microwave conductivity decreases as the input power is increased. At high-power levels it becomes almost constant, that is, it saturates. At sufficiently low-power levels it is also independent of input power. This characteristic is shown in Fig. 2 schematically, and suggests the possibility of two simultaneous mechanisms of microwave absorption. We will then write the conductivity as a sum $\sigma_1(P)+\sigma_2$, where $\sigma_1(P)$ is dependent on input power and σ_2 is the high-power saturation value. It will be shown below that the former corresponds to the conductivity due to the direct absorption process by ionized impurity pairs and the latter to the hopping conductivity.

As can be seen in Fig. 1, the slope of $\sigma_1(P)$, is steep at low temperature and decreases as the temperature is raised. The power level where low-power saturation occurs shifts to higher power levels as the temperature is raised. For lower temperatures (lower than 3°K in *p*-type silicon and lower than 10°K in *n*-type silicon), the Ohmic part of $\sigma_1(P)$ (we shall refer to it as the low-power-limit conductivity $\sigma_{\mathrm{L.P.}}$ in the following) could not be reached, since the lowest microwave power used in this experiment was still too high.

TABLE I. Impurity concentration in silicon samples.

Impurity	Sample number	Majority impurity concentration (10^{16} cm^{-3})
B	1	1.5
B	2	1.4
B	3	1.4[a]
B	4	1.1
B	5	1.1[a]
B	6	0.67
P	7	2.2
Sb	8	1.8

[a] Numbers 3 and 5 were pieces adjacent to Nos. 2 and 4, respectively, in the ingots and were heat treated in vacuum at 450°C.

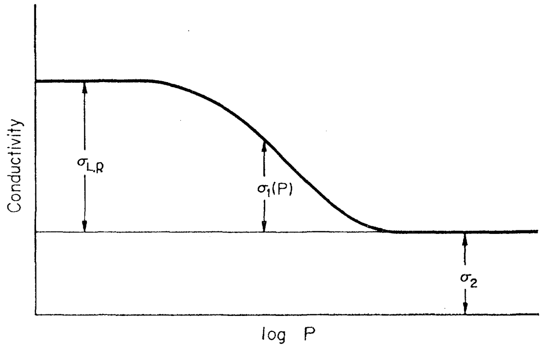


FIG. 2. Schematic representation of the power dependence of the microwave conductivity.

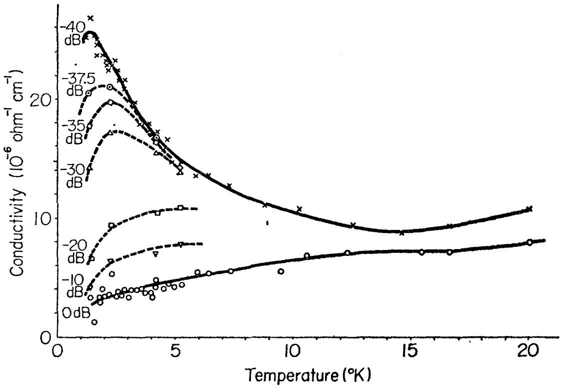


FIG. 3. Temperature dependence of the microwave conductivity at various input microwave power levels, sample No. 3.

In p-type samples the low-power saturation characteristic changes slightly with majority center concentration and also with minority center concentration. But the most marked difference was observed between p-type and n-type samples, that is, the power level where saturation occurs is larger by a factor of almost 20 in p-type samples as compared to n-type samples at 10°K. This shows that the relaxation time in the direct absorption process in n-type crystals is much longer than that in p-type crystals.

B. Temperature Dependence of the Microwave Conductivity

To investigate the hopping process and direct absorption process separately, the microwave conductivity was measured at the highest possible (0 dB) and the lowest possible power levels (-40 dB) at various temperatures, as shown in Fig. 3. The conductivities $\sigma(0\text{ dB})$ and $\sigma(-40\text{ dB})$ have quite different temperature dependences. $\sigma(0\text{ dB})$ has an increasing but weak temperature dependence, but $\sigma(-40\text{ dB})$ has a decreasing strong temperature dependence, especially at low temperatures. From a comparison with the general characteristics shown in Fig. 2, it can be seen that $\sigma(0\text{ dB})$ coincides with σ_2 throughout almost the whole temperature range, and thus $\sigma(-40\text{ dB})-\sigma(0\text{ dB})$ is the direct absorption part, $\sigma_1(P)$. This quantity is plotted against $1/T$ in Fig. 4. It is evident that it is proportional to $1/T$ except at the lowest temperatures. One can see from Fig. 1, however, that the low-power-limit conductivity was not attained at low temperature in our measurements, and therefore it can be expected that the low-power-limit conductivity $\sigma_{\text{L.P.}}$ is proportional to $1/T$ throughout the whole temperature range.

C. Effect of Minority Center Concentration

In several p-type samples the minority center concentration was increased by heat treatment at 450°C in high vacuum. The microwave conductivity is increased by this heat treatment, as can be seen by comparing Figs. 1 and 4. There is a slight difference in the saturation characteristics before and after heat treatment. But the temperature dependence of $\sigma(0\text{ dB})$ and $\sigma(-40\text{ dB})$ is almost the same. From these results, we conclude that the ratio $\sigma_{\text{L.P.}}/\sigma_2$ is not changed appreciably by the increase of minority center concentration. As will be discussed later, the hopping conductivity is roughly proportional to the minority center concentration in the low concentration range, and therefore it can be concluded that the conductivity due to the direct absorption process is also proportional to the minority center concentration.

III. DISCUSSION

To explain the experimental results, we must investigate the microwave absorption mechanisms by the impurity pairs in detail.

In the compensated semiconductor, some of the majority impurities are ionized and the compensating minority impurities are oppositely charged. The ionized majority impurities are considered to be occupied by carriers, and the carrier tends to be bound near the ionized minority impurity by the Coulomb attractive force. At sufficiently low temperatures it can be shown that the carrier moves only between the majority impurities nearest and next nearest to the minority impurity. Therefore the microwave absorption by the carrier occurs only in such an ionized impurity pair.

As shown in the next section, the wave function of the carrier in the pair is expressed by a linear combination of two impurity wave functions. The extreme case appears when there is no potential difference between pair impurities. In this case, the occupation probabilities of the carrier on the two impurities are the same, and we have a molecule ion. With the hydrogenic approximation, the two molecular wave functions are called the bonding state and antibonding state, respectively, and the energy separation between them is $2W$, where W is the resonance energy [see Eq. (7)]. We call such a pair

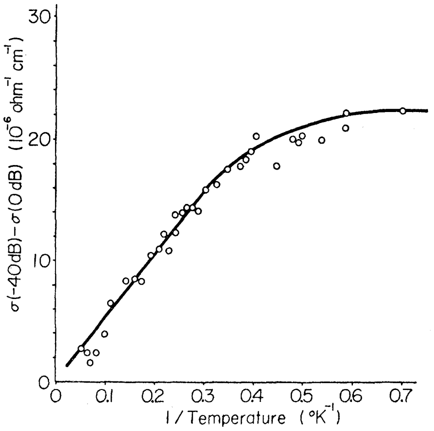


FIG. 4. Temperature dependence of $\sigma(-40\text{ dB})-\sigma(0\text{ dB})$, sample No. 3.

a homopolar pair. On the other hand, when the potential difference Δ in the pair is much larger than $2W$, one of the pair wave functions is concentrated around one of the pair impurities, and the other wave function is concentrated around the other impurity. We call such a pair a polar pair, and the energy separation between these two states is almost equal to the potential difference Δ. There are two possible microwave absorption processes in such an ionized impurity pair.

Firstly, when the energy separation between the two states is equal to $\hbar\omega$, the direct process occurs. Here the transition is produced solely by interaction with the photon, without phonon participation. The effect of phonon interactions may be regarded as a broadening of the energy level. This description is appropriate if the frequency of the phonon-induced transition is small compared to the photon frequency. The transition rate of photon absorption is large when $2W>\Delta$, and decreases rapidly with the potential difference when $2W<\Delta$. The transition rate for this direct process is actually quite large and saturation is expected for quite low field intensity.

Secondly, when the energy separation does not satisfy the resonance condition $\epsilon=\hbar\omega$, the direct absorption process does not occur in the pair. But the carrier still makes transition by interaction with a phonon and the energy required is supplied by the phonon. This process is thus an indirect transition. In the homopolar pair this process gives a minor contribution to the microwave absorption and we can neglect it in the following discussion.[5] In the polar pair, on the other hand, the indirect transition is known as the hopping process or jumping process.[2] For an ac field, the potential difference changes in phase with the ac field. Then the hopping rate between pair impurities is affected, and the carrier produces in-phase as well as out-of-phase current, which results in energy absorption.

In the following we will calculate the conductivity due to the direct absorption process (Sec. A) and the conductivity due to the hopping process (Sec. B). In Sec. C it will be shown that the microwave conductivity can be expressed as the sum of these two kinds of conductivities.

A. Direct Absorption Process

We will discuss the case of the n-type semiconductor, and the results obtained can be applied to the p-type semiconductor in the hydrogenic approximation.

In the effective-mass approximation, the Hamiltonian of a hole bound to the ionized pair is described by the following equation:

$$H_0=\frac{1}{2m^*}(-i\hbar\,\mathrm{grad})^2+V_a-\frac{e^2}{\kappa_0|\mathbf{r}-\mathbf{R}_A|}-\frac{e^2}{\kappa_0|\mathbf{r}-\mathbf{R}_B|}\,, \tag{1}$$

where κ_0 is the dielectric constant, m^* is the effective mass which gives a donor ionization energy in reasonable agreement with experiment, and $\mathbf{R}_A$ and $\mathbf{R}_B$ are the position vectors of two donor centers. V_a is the potential due to other ions, and is dominated by the contribution from the minority center.

The wave functions of the ionized pair are written on the analogy of the molecular orbital method:

$$\begin{aligned}\Psi_{\text{bond}}&=aU_A(\mathbf{r})+bU_B(\mathbf{r})\,,\\ \Psi_{\text{antibond}}&=a'U_A(\mathbf{r})+b'U_B(\mathbf{r})\,,\end{aligned} \tag{2}$$

where $U_A(\mathbf{r})$ and $U_B(\mathbf{r})$ are hydrogenic wave functions of the ground state of donor centers centered on $\mathbf{R}_A$ and $\mathbf{R}_B$, respectively. One should, of course, use the complicated impurity wave functions as discussed by Kohn and Luttinger.[6] We have instead, however, chosen the hydrogenic wave function

$$U_A(\mathbf{r})=(\pi a^{*3})^{-1/2}\exp(-|\mathbf{r}-\mathbf{R}_A|/a^*)\,, \tag{3}$$

in order to simplify the calculation. In the above equation, a^* is the effective Bohr radius in the material; $a^*=\kappa_0\hbar^2/m^*e^2$. The coefficients a, b, a', and b' for bonding and antibonding states are determined as follows:

$$\begin{aligned}a&=\frac{1}{\sqrt{2}}\left(1+\frac{\Delta^2}{4W^2}\right)^{-1/4}\left[\frac{\Delta}{2W}+\left(1+\frac{\Delta^2}{4W^2}\right)^{1/2}\right]^{1/2},\\ b&=\frac{1}{\sqrt{2}}\left(1+\frac{\Delta^2}{4W^2}\right)^{-1/4}\left[\frac{\Delta}{2W}+\left(1+\frac{\Delta^2}{4W^2}\right)^{1/2}\right]^{-1/2},\\ a'&=-\frac{1}{\sqrt{2}}\left(1+\frac{\Delta^2}{4W^2}\right)^{-1/4}\left[-\frac{\Delta}{2W}+\left(1+\frac{\Delta^2}{4W^2}\right)^{1/2}\right]^{1/2},\\ b'&=\frac{1}{\sqrt{2}}\left(1+\frac{\Delta^2}{4W^2}\right)^{-1/4}\left[-\frac{\Delta}{2W}+\left(1+\frac{\Delta^2}{4W^2}\right)^{1/2}\right]^{-1/2},\end{aligned} \tag{4}$$

where the overlap integral S was neglected compared to unity, Δ is approximately the potential difference between two centers, $\Delta=\langle U_A|V_a|U_A\rangle-\langle U_B|V_a|U_B\rangle>0$, and W is the resonance energy:

$$\begin{aligned}W&=L-SJ+\langle U_A|V_a|U_B\rangle-S\langle U_A|V_a|U_A\rangle\,,\\ L&=-\langle U_A|(e^2/\kappa_0|\mathbf{r}-\mathbf{R}_A|)|U_B\rangle\,,\\ J&=-\langle U_A|(e^2/\kappa_0|\mathbf{r}-\mathbf{R}_B|)|U_B\rangle\,,\\ S&=\langle U_A|U_B\rangle\,.\end{aligned} \tag{5}$$

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[5] M. Kikuchi considered the loss of the pair generally and recently got the same results to our calculations. He found that the main contribution to the loss consists of two parts, the one corresponds to the direct process which is described by the off-diagonal elements of dipole moment and the other corresponds to the indirect process which is described by the diagonal elements of dipole moment. The terms including the cross product of the diagonal and off-diagonal elements give minor contributions to the loss. This means that the indirect process is unimportant in the homopolar pair (private communication).

[6] See W. Kohn, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 258.

When the separation r_d between pair impurities is much larger than a^*, the resonance energy W is approximated as follows[7]:

$$W=\frac{e^2}{\kappa_0 r_d}\left[\frac{2}{3}\left(\frac{r_d}{a^*}\right)^2-1\right]\exp[-r_d/a^*]$$
$$\approx\frac{2e^2}{3\kappa_0 a^{*2}}r_d\exp[-r_d/a^*]. \quad (6)$$

We have neglected terms of the order of $\exp[-2r_d/a^*]$ compared to unity and a local field effect, $\langle U_A|V_a|U_B\rangle-S\langle U_A|V_a|U_A\rangle\ll 2W$. The energy difference between the bonding and antibonding states in the ionized pair, which we call the excitation energy and denote by ϵ, is as follows:

$$\epsilon=[\Delta^2+(2W)^2]^{1/2}. \quad (7)$$

Now, let us consider the two limiting cases.

Case 1. In one limiting case $2W\gg\Delta$, i.e., the homopolar pair, the electronic states in the ionized pair are represented by the following wave functions:

$$\Psi_{\text{bond}}=(1/\sqrt{2})(U_A(\mathbf{r})+U_B(\mathbf{r})),$$
$$\Psi_{\text{antibond}}=(1/\sqrt{2})(U_A(\mathbf{r})-U_B(\mathbf{r})), \quad (8)$$

and the energy gap ϵ between these two levels is approximated by $2W$.

Case 2. In the other limiting case $2W\ll\Delta$, i.e., the polar pair, the wave functions for bonding and antibonding states are given as follows:

$$\Psi_{\text{bond}}=U_A(\mathbf{r})+(W/\Delta)U_B(\mathbf{r}),$$
$$\Psi_{\text{antibond}}=U_B(\mathbf{r})-(W/\Delta)U_A(\mathbf{r}), \quad (9)$$

and the energy gap ϵ is approximated by Δ.

In the homopolar pair with $r_d\approx 10a^*$, the energy separation $\epsilon\approx 2W$ is 3.7×10^{-2} meV, which corresponds to the energy of a microwave quantum at 9000 Mc/sec. In B-doped *p*-type silicon, $a^*=13$ Å in the hydrogenic approximation, and r_d is then about 130 Å for the microwave absorption by the direct process.

A conductance of the ionized pair $G_D(\omega)$ due to the direct absorption process can be derived from the imaginary part of the electrical susceptibility $\chi(\omega)$ as follows:

$$G_D(\omega)=\omega\,\mathrm{Im}\chi(\omega). \quad (10)$$

The dipole moment induced by the electric field $F(t)=F\cos\omega t=\mathrm{Re}(Fe^{-i\omega t})$ is

$$P(t)=\mathrm{Re}(\chi Fe^{-i\omega t}). \quad (11)$$

On the other hand, with the aid of the quantum-mechanical density matrix $\rho(t)$, the dipole moment is

$$P(t)=\mathrm{Tr}P\rho(t), \quad (12)$$

where P is the dipole moment operator. Combining Eqs. (11) and (12) and using the results of Karplus and Schwinger,[8] we get the electric susceptibility

$$\chi(\omega)=\sum_{m,n}\tfrac{1}{3}|P_{mn}|^2\left(1-\frac{\omega}{\omega-\omega_{mn}+i/\tau}\right)\times\frac{\rho_n^{(0)}-\rho_m^{(0)}}{\hbar\omega_{mn}}, \quad (13)$$

where $\rho_n^{(0)}$ is the population of the nth state in equilibrium and $\hbar\omega_{mn}$ is the energy difference between the mth and nth states. Then we get

$$G_D(\omega)=\sum_{m,n}\tfrac{1}{6}|P_{mn}|^2\frac{\omega^2}{kT}\times\left[\frac{1/\tau}{(\omega-\omega_{mn})^2+1/\tau^2}+\frac{1/\tau}{(\omega+\omega_{mn})^2+1/\tau^2}\right]\times\frac{1-\exp[-\hbar\omega_{mn}/kT]}{\hbar\omega_{mn}/kT}\rho_n^{(0)}. \quad (14)$$

In the two level case,

$$G_D(\omega)=\tfrac{1}{3}|P_{12}|^2\frac{\omega^2}{kT}\frac{1/\tau}{(\omega-\omega_{21})^2+1/\tau^2}\rho_1^{(0)}, \quad (15)$$

where τ is the relaxation time due to the electron-phonon interaction which will be discussed in Sec. C. The matrix element P_{12} is calculated as follows:

$$P_{12}=\langle\Psi_{\text{bond}}|ex|\Psi_{\text{antibond}}\rangle$$
$$=-\left(\frac{a^*}{6}\right)\left(\frac{r_d}{a^*}\right)^3\exp[-r_d/a^*]e(ab'+a'b)$$
$$+eaa'[\langle U_A|x|U_A\rangle-\langle U_B|x|U_B\rangle], \quad (16)$$

where a, a', b, and b' have been given in Eq. (4). Since $r_d/a^*\gg 1$ in our case, Eq. (16) becomes simpler:

$$P_{12}=er_d aa'. \quad (17)$$

In the homopolar pair case, i.e., $2W\gg\Delta$,

$$|P_{12}|^2=\tfrac{1}{4}e^2r_d^2 \quad (18)$$

and in the polar pair case, i.e., $2W\ll\Delta$,

$$|P_{12}|^2=\tfrac{1}{4}e^2r_d^2(4W^2/\Delta^2). \quad (19)$$

Comparing Eqs. (18) and (19), we can say that the homopolar pair makes the dominant contribution to the direct absorption process. Therefore, in the following, we approximate the ionized impurity pairs which have potential difference Δ smaller than $2W$, by the homopolar pairs.

To calculate the conductivity, we choose only homopolar pairs among all the ionized pairs having various

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[7] This expression is the same as Miller and Abraham's result (Ref. 2).

[8] R. Karplus and J. Schwinger, Phys. Rev. 73, 1020 (1948).

impurity separations r_d and various potential differences Δ, and sum up the conductances of the homopolar pairs. Since the minority concentration is small compared with the majority impurity concentration (several percent) in our samples, we can assume that the volume of crystal is divided into cells, each centered around the minority impurity. Each cell contains a carrier and the carrier is mainly on the majority impurity nearest to the minority impurity at quite low temperatures, forming an ionized impurity pair with another majority impurity. The probability of finding the nearest majority impurity at a distance between R and $R+dR$ from the minority impurity is $(3R^2dR/R^{*3})\exp[-(R/R^*)^3]$, where R^* is the average distance between majority impurities. The probability of finding the other majority impurity at a distance between r_d and r_d+dr_d from the first majority impurity and at a smaller potential difference than $\hbar\omega$, is $3r_ddr_d\Delta R/2R^{*3}$, where ΔR is derived from the equation

$$\frac{e^2}{\kappa_0 R}-\frac{e^2}{\kappa_0(R+\Delta R)}=\hbar\omega\,,$$

and then $\Delta R\approx R\hbar\omega/(e^2/\kappa_0R)$ (see Fig. 5).

The crystal conductivity is derived as follows:

$$\begin{aligned}\sigma_D(\omega)&=\int\int G_D(\omega)f(R,r_d)dRdr_d\\&=\int\int\tfrac{1}{3}|P_{12}|^2\frac{\omega^2}{kT}\frac{1/\tau}{(\omega-\omega_{21})^2+1/\tau^2}\\&\qquad\times\rho_1{}^{(0)}f(R,r_d)dRdr_d\,,\end{aligned}\qquad(20)$$

where

$$f(R,r_d)=\frac{3R^2}{R^{*3}}\exp[-(R/R^*)^3]N_{\min}\frac{\frac{3}{2}r_d}{R^{*3}}\Delta R\,.$$

For the change of $\hbar\omega_{21}=\epsilon$ such that $|\omega-\omega_{21}|\approx1/\tau=10^6$ sec^{-1}, other quantities in the integrand are almost constant, so that $(1/\tau)/[(\omega-\omega_{21})^2+1/\tau^2]$ may be replaced by $\pi\delta(\omega-\omega_{21})$ without serious error. The total conductivity is then

$$\begin{aligned}\sigma_D(\omega)&=\frac{3(\hbar\omega)^2}{16kT}\pi\kappa_0R^{*2}N_{\min}\\&\qquad\times\int_0^\infty\left(\frac{r_D}{R^*}\right)^3\left(\frac{dr_D}{d\epsilon}\right)\left(\frac{R}{R^*}\right)^4\exp[-(R/R^*)^3]d\left(\frac{R}{R^*}\right)\\&=\frac{\pi\hbar\omega^2}{16kT}\kappa_0N_{\min}\frac{a^*r_D{}^3}{R^*}\Gamma(\tfrac{5}{3})\,,\end{aligned}\qquad(21)$$

where r_D is the pair separation at which $2W=\hbar\omega$ holds.

B. Hopping Process

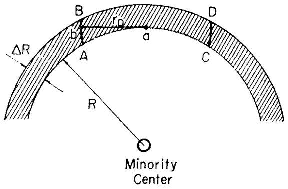

FIG. 5. Schematic diagram of the region of integration in the calculation of the conductivity. A majority impurity a nearest to the minority impurity forms an ionized impurity pair with another majority impurity b. When the impurity b is in the hatched region, the potential difference in the pair is less than $\hbar\omega$. The ionized pair, with the impurity b near the lines AB or CD, contributes to the conductivity due to the direct absorption process.

Now we will discuss the conductivity due to the hopping process and compare this with the conductivity due to the direct absorption process. The following is an expression for the ac conductivity due to the hopping process as given by Tanaka and Fan[4]:

$$\begin{aligned}\sigma_H&=\sigma_1+\sigma_2\,,\\\sigma_1&=\frac{\pi^2}{3}\omega r_H{}^4(\Delta r_H)\frac{e^2}{kT}N_{\min}N_{\text{maj}}{}^2\\&\qquad\times\int_0^{R'}g_1R^2\exp(-\tfrac{4}{3}\pi N_{\text{maj}}R^3)dR\,,\\\sigma_2&=\frac{\pi^2}{3}\omega r_H{}^4(\Delta r_H)\frac{e^2}{kT}N_{\min}N_{\text{maj}}{}^2\\&\qquad\times\int_{R'}^{R''}g_2R^2\exp(-\tfrac{4}{3}\pi N_{\text{maj}}R^3)dR\,,\end{aligned}\qquad(22)$$

where R is the distance from minority impurity to the nearest majority impurity and R' is the radius corresponding to the critical condition

$$1+\beta=\alpha\beta\,,\qquad(23)$$

$$\alpha=(1/4kT)(e^2/\kappa_0R)\,,\quad\beta=r_H/R\,,$$

and R'' is the radius of the unit cell. g_1 and g_2 are functions of α and β. r_H is the separation of the ionized impurity pair absorbing the microwave power by the hopping process, and Δr_H is the half-width of microwave absorption. In order to compare this expression with Eq. (21) for the conductivity due to the direct absorption process, Eq. (22) can be simplified for the condition $1+\beta\ll\alpha\beta$ (a low-temperature approximation):

$$\sigma_H\approx\tfrac{1}{8}\omega r_H{}^3(\Delta r_H)\kappa_0N_{\min}(1/R^*)\Gamma(\tfrac{5}{3})\,.\qquad(24)$$

The prominent differences between Eqs. (21) and (24) are the frequency dependence and temperature dependence of the conductivity. The conductivity due to the direct absorption process is roughly proportional to ω^2/T, while the conductivity due to the hopping process is roughly proportional to ω. The ratio σ_D/σ_H is

$$\sigma_D/\sigma_H=\frac{\pi}{2}\left(\frac{\hbar\omega}{kT}\right)\left(\frac{a^*}{\Delta r_H}\right)\left(\frac{r_D}{r_H}\right)^3.\qquad(25)$$

The impurity separations r_D and r_H are determined mainly from the resonance energy W, as shown in Eqs. (6) and (26) respectively and are approximately proportional to a^* at a fixed frequency. Therefore the term $(r_D/r_H)^3$ is almost independent of a^*. The half-width Δr_H is also proportional to a^*. Thus σ_D/σ_H is almost independent of a^*, although both σ_D and σ_H are sensitive to the magnitude of a^*. Therefore σ_D/σ_H is approximately independent of the detailed features of the impurity wave functions and the majority and minority impurity concentrations in the low-impurity concentration range.

C. Electron-Phonon Interaction in Impurity Pairs

The electron-phonon interaction in the impurity pairs plays an important role in determining the relaxation time in the direct absorption process and the hopping rate in the hopping absorption process. The hopping rate ν_{12} has been calculated by several authors.[2] Miller and Abraham[2] give

$$\nu_{12}=(E_1^2/\pi\rho_0 s^5\hbar^4)W^2\Delta\left\{\begin{matrix}\dfrac{1}{e^{\Delta/kT}-1}\\[2ex] \dfrac{1}{e^{\Delta/kT}-1}+1\end{matrix}\right\},\qquad(26)$$

where E_1 is the deformation potential, and ρ_0 and s are the density and the velocity of longitudinal sound respectively. On the other hand, the relaxation rate in the direct absorption process can be calculated by using a deformation potential approximation as follows:

$$\begin{aligned}(1/\tau)&=\tfrac{1}{2}(W_{21}+W_{12})\\ &=\frac{E_1^2W^3}{\pi\rho_0 s^5\hbar^4}\left(1+\frac{\Delta^2}{4W^2}\right)^{1/2}\\ &\quad\times\left(\frac{2}{e^{\epsilon/kT}-1}+1\right)\left(1-\frac{\sin qr_D}{qr_D}\right),\qquad(27)\end{aligned}$$

where q is the phonon wave number, given by $\hbar sq=\epsilon=\hbar\omega$. It is noted that both calculations use the assumption of a single phonon process in the electron-phonon interaction.

In B-doped silicon ($a^*\approx 13$ Å), the hopping distance r_H corresponding to a frequency of 9000 Mc/sec is about 80 Å and the resonance energy W is about 0.2 meV. On the other hand, in the direct absorption process the impurity separation r_D is almost 130 Å and the resonance energy is about 0.02 meV. Then the relaxation rate $1/\tau$ is estimated as 1.7×10^4 sec^{-1}. This value is quite small because of the smallness of the resonance energy and the inclusion of the phase factor $(1-\sin qr_D/qr_D)$. q was estimated as 6×10^4 cm^{-1} for the 9000 Mc/sec direct absorption process, and then qr_D is about 0.08. As a result $(1-\sin qr_D/qr_D)$ is of the order of 10^{-3}. In the hopping process, on the other hand, the energy difference Δ can be taken up to the order of kT, 0.4 meV at 4°K, and the qr_D becomes the order of unity.

Next it will be shown that in the 9000 Mc/sec range the direct absorption process and the hopping absorption process contribute to the microwave absorption independently in the different pairs. In the direct absorption process, the impurity separation is about 130 Å, and in such a pair the hopping frequency is very low compared with the microwave frequency, i.e., 10^7 to 10^8 sec^{-1}. Thus the hopping process does not contribute to the microwave absorption at all. On the other hand, the impurity separation in the hopping absorption process corresponding to the microwave frequency is about 80 Å. The direct process occurs in such a pair only in the 90 000 Mc/sec range, and therefore in the 9000 Mc/sec range the direct process does not occur in such a pair. Therefore, these two absorption processes at fixed frequency occur in different pairs, independently, and the microwave conductivity can be expressed as follows:

$$\sigma=\sigma_D+\sigma_H.\qquad(28)$$

D. Comparison with Experimental Results

As noted in Sec. II, the microwave conductivity in both n- and p-type silicon shows a non-Ohmic characteristic for field strengths of less than 1 V/cm at 1.3°K. In the hopping model, non-Ohmic characteristics are not expected for fields less than 100 V/cm. This result suggests that the observed conductivity comes from a microwave absorption mechanism other than the hopping mechanism. The model of microwave absorption by a direct absorption process in localized pairs discussed in the preceding sections seems to explain the experimental results satisfactorily. Before discussing these in detail, we must examine the validity of the localized pair model in our samples. In general, the localized pair model is valid when R^* is much larger than the separation r_D or r_H in the pair, where R^* is the average distance between majority centers. In our samples, $N_{\rm maj}$ is 1.5×10^{16} cm^{-3} at most, and this corresponds to R^* of 240 Å. r_D is estimated as $10a^*$, where a^* is the effective Bohr radius. In the hydrogenic approximation a^* is 13 Å in B-doped p-type silicon. Schechter,[9] however, calculated the magnitude of a^* and estimated it as 17 Å. Even though 17 Å is used for a^*, r_D is still shorter than 240 Å. Therefore, the localized pair model should have satisfactory validity in our p-type samples. In P-, and Sb-doped n-type samples, a^* is 21 and 22 Å, respectively. r_D's corresponding to these values are still shorter than R^*. Therefore, the pair model should be valid in all samples used in this experiment. We now turn to a discussion of the microwave absorption mechanism.

At first we assume that the non-Ohmic character of the microwave conductivity comes from saturation of the direct absorption process in the homopolar pair,

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[9] D. Schechter, Phys. Chem. Solids 23, 237 (1962).

TABLE II. σ_D and σ_H at 4.2°K in B-doped samples.

Sample number	σ_D 10^{-6} ohm^{-1} cm^{-1}	σ_H 10^{-6} ohm^{-1} cm^{-1}	σ_D/σ_H
1	16.8	9.2	1.8
2	5.6	2.9	1.93
3	12.6	9.2	1.4
4	3.5	4.0	0.9
5	16.6	4.2	3.9
6	6.0	5.2	1.15

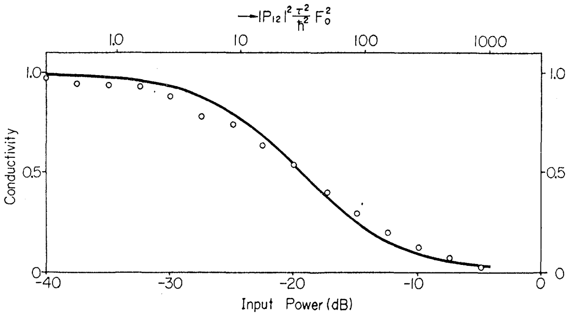

FIG. 6. Dependence of the microwave conductivity on input microwave power. Solid curve is the calculated one and open circles are the experimental results from sample No. 1. The upper scale is for the calculated curve and the lower scale is for the experimental results.

that is, the microwave power used in this experiment is strong enough to make the populations of carriers in the ground and excited states equal. Second, we assume that after complete saturation occurs, the conductivity due to the hopping process in the polar pairs still exists, and this does not show non-Ohmic characteristics in the whole microwave power range of this experiment. As discussed in the preceding section, the direct absorption process and hopping process at 9000 Mc/sec occur in the different pairs independently, and then the conductivity obtained can be divided in two parts, i.e., $\sigma_1(P)$ and σ_2; $\sigma_1(P)$ which depends on the input microwave power, is due to the direct absorption process, and σ_2 is due to the hopping process. The Ohmic part of $\sigma_1(P)$ at low enough input power, that is, $\sigma_{\text{L.P.}}$, then corresponds to the conductivity σ_D expressed by Eq. (21). σ_2, on the other hand, corresponds to the conductivity σ_H expressed by Eq. (24).

The experimental results show that $\sigma_{\text{L.P.}}$ decreases with temperature as $1/T$. This agrees well with the theoretical results. It must be pointed out that in these p-type samples, the number of molecule-ion traps[4] which may strongly affect the temperature dependence of conductivity is negligibly small in such low concentration samples. Therefore the temperature dependence of $\sigma_{\text{L.P.}}$ can be considered as that of the direct absorption process. The magnitudes of $\sigma_{\text{L.P.}}$ and σ_2 in all p-type samples at 4.2°K are listed in Table II. Assuming $a^* = 13$ Å, theory gives the magnitude of σ_D at 4.2°K as 5.5×10^{-7} ohm^{-1} cm^{-1} for the conditions: $K = N_{\text{min}}/N_{\text{maj}} = 5\%$, $N_{\text{maj}} = 10^{16}$ cm^{-3}, $\omega = 5.6\times10^{10}$ sec^{-1}. Unfortunately, the compensation degree K is not known exactly, but is estimated as several percent in samples which were not heat treated. Then the theoretical results give too low a value of the conductivity compared with the experimental results. The theoretical hopping conductivity σ_H, however, is also too small, i.e., $\sigma_H = 7.6\times10^{-7}$ ohm^{-1} cm^{-1} for the same experimental conditions.

The ratio σ_D/σ_H in Eq. (25) will give information about this disagreement. The ratio $\sigma_{\text{L.P.}}/\sigma_2$ obtained experimentally at 4.2°K is in the range from 0.9 to 1.9, except for sample No. 5, as shown in Table II, and these values are close to the expected value of 0.7. Since σ_D/σ_H excluded the uncertain quantities, i.e., N_{min} and a^*, it is reasonable to obtain closer agreement with the theoretical results. If we further take an effective Bohr radius of about 20 Å instead of 13 Å, the theoretical calculations of both σ_D and σ_H are in good agreement with the experimental results. This also agrees with Schechter's calculation[9] on the effective Bohr radius.

Next we will discuss the non-Ohmic characteristics of the microwave conductivity due to the direct absorption process, and this will lead us to the examination of the relaxation time in the homopolar pair. Karplus and Schwinger[8] also discussed the saturation effect of the resonance absorption in gas molecules in a strong monochromatic microwave field and indicated that the electric susceptibility of the molecule is expressed as follows:

$$\operatorname{Im}\chi = \frac{1}{\hbar}|P_{12}|^2 \frac{\omega}{\omega_{21}} \frac{1/\tau}{(\omega-\omega_{21})^2 + 1/\tau^2 + |P_{12}|^2 F^2 \cos^2\varphi/\hbar^2} \times (\rho_1^{(0)} - \rho_2^{(0)}), \tag{29}$$

where φ is the angle between the field direction and the molecular axis. This equation indicates that when $|P_{21}|F\cos\varphi$ becomes comparable with $\hbar/\tau$, the absorption line begins to widen, and the peak absorption coefficient correspondingly decreases.

Under our experimental conditions, however, the field strength F in the cavity is not uniform and it distributes as shown in the following relation:

$$F \propto (\omega\mu_0/k_c) J_0'(k_c r), \tag{30}$$

where $k_c = 3.83/a_1$ and a_1 is the radius of TE_{011} mode cavity containing the sample. The orientation of the molecular axis to the direction of the field must also be taken into account in a discussion of the saturation effect. Therefore, the dependence of the microwave conductivity $\sigma_1(P)$ on the input power in our experiment becomes much smoother than expected from Eq. (29), and the saturation field strength F_s defined as the maximum field strength F_0 in the cavity corresponding to the relation $\sigma_1(P) = \sigma_{\text{L.P.}}/2$ becomes much larger. The saturation curve was computed numerically against $|P_{12}|^2 F_0^2 \tau^2/\hbar^2$ with an inclusion of such experimental conditions and the result is shown in Fig. 6. This result

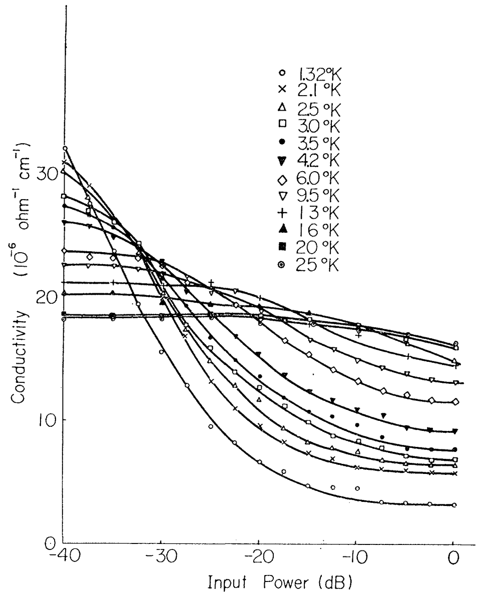

FIG. 7. An example of the detailed measurements of the dependence of the microwave conductivity on the input power at various temperatures, sample No. 1.

indicates that the conductivity has just half of the magnitude of the low-power-limit conductivity, $\sigma_{\text{L.P.}}$, when $|P_{12}|^2F_s^2\tau^2/\hbar^2$ is about 25. One of our experimental results is also plotted in Fig. 6, and the calculated curve fits the experimental results fairly well. The saturation power P_s into the cavity which corresponds to the saturation field F_s in the cavity was measured in p-type samples in detail and some of the results are plotted against temperature in Figs. 7 and 8. Since the low-power-limit conductivity could not be obtained at temperatures lower than 4°K, we extrapolated the $1/T$ variation of $\sigma_{\text{L.P.}}$ and estimated the saturation power. Figure 8 indicates that the saturation power increases with temperature as T^2 above 4°K, and below this temperature the temperature dependence of P_s becomes rather steeper. Since P_s is proportional to F_s^2, the saturation field F_s varies linearly with temperature above 4°K. Since the relation $|P_{12}|F_s\tau/\hbar=5$ holds in the whole temperature range, the relaxation time τ is proportional to $1/T$ above 4°K. This temperature dependence seems to agree well with the theoretical results, Eq. (27), but the magnitude obtained experimentally (10^{-9} sec at 4°K) is quite different from the theoretical result of 6×10^{-5} sec at 4°K. The minority impurity concentration seems to affect the saturation power P_s in p-type samples as shown in Fig. 8 and there is also an appreciable difference in the saturation power between p- and n-type samples (Fig. 1). But even with these differences, we expect that the agreement cannot be improved much.

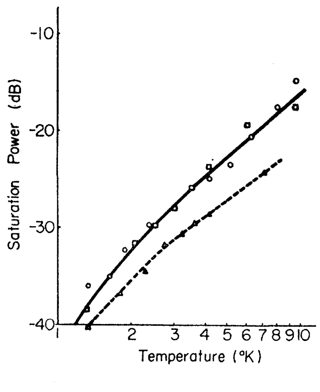

FIG. 8. Temperature dependence of the saturation power P_s. □ for sample No. 1, ○ for No. 3, and △ for No. 6, respectively.

This discrepancy probably comes from the simplicity of the model used in this paper. For instance, we used the hydrogenic approximation for the wave function of the impurity pair, and also used the simple single-phonon process for the relaxation process. In fact, the acceptor states in silicon are degenerate and they are easily split into two twofold-degenerate states by internal strain.[10] The donor states are also split by valley-orbit interaction. The molecular states, therefore, may be more complicated than the one assumed in this paper. It is thus expected that the relaxation process in such an complicated molecule ion is much more complicated. In order to clarify the problem, further investigations are now in progress.

IV. SUMMARY

The non-Ohmic characteristics of the microwave conductivity of silicon were measured at low temperatures in the 9000 Mc/sec range. The process of direct absorption of microwave photons in the ionized impurity pair was discussed in detail. Reasonable agreement between theoretical calculations and the experimental results is obtained. The relaxation process in the impurity pair is also discussed and the discrepancy between experimental results and calculations is appreciable. Comparison between the conductivity due to the direct absorption process and the conductivity due to the hopping process was made, and the ratio of both types of conductivity shows fairly good agreement with theoretical results.

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[10] G. Feher, J. C. Hensel, and E. A. Gere, Phys. Rev. Letters **5**, 309 (1960).