

Electron Scattering by Dipole Centers in a Semiconductor

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A genuine dipole scattering of electron is explored in silicon crystal. One unsuccessful trial was a possible dipole center of LiB. Another rather successful trial has been due to permanent dipoles created in the Si-O-Si bonding in Czochralski grown silicon crystal. Scattering cross section is derived from electron cyclotron resonance linewidth measurement and compared with one of the existing theories.

I. INTRODUCTION

Electron scattering by various kinds of impurities in semiconductors has been studied with the help of cyclotron resonance. The prototypes of impurities are neutral impurities either donors or acceptors. One example is a substitutional phosphorus in silicon crystal, a donor, which is compared to a hydrogen atom in the free space. Electron scattering by a neutral donor, accordingly, is discussed in terms of e^- -H scattering. A similar but interestingly different case is an electron scattering by a neutral acceptor, say neutral boron atom in silicon, again substitutional. In view of the sign readjustment of relevant charges, this scattering can be simulated by the e^+ -H scattering. Difference in cross section, for example, between these two types of scattering is mentioned and discussed in detail elsewhere [1]. Essentially, electron scattering by neutral impurities can be discussed in terms of atomic scattering models. Another important aspect of impurity scattering is that of ionized impurities. In cyclotron resonance, free carriers are usually produced by band-gap photoexcitation. The free carriers necessarily tend to neutralize the existing ionized impurities. Once neutralized, the impurities are seldom reionized under the photoexcitation. Thus the contribution of ionized impurity scattering can be observed only under a special experimental condition; namely, free carriers are produced by extrinsic light, far less in energy than the band-gap light. The neutralized impurities are then ionized and scatter electrons ejected from the impurities in the case of an n-type material. The scatterers are point charges, or positive ions. The scattering is like Rutherford scattering. Based on this model, the first impurity scattering formula has been derived by Conwell and Weisskopf [2]. Further complication in impurity scattering arises when the impurities, either neutral or ionized, capture excitons [1]. The scattering centers will naturally have large form factors. But they remain nonpolar centers neutral, or point charge-like monopoles.

II. POSSIBILITY OF DIPOLE SCATTERING

An independent ionized donor or an independent acceptor renders a monopole scattering center for an incident electron. If they are combined together, however, one encounters a dipole center, or D^+A^- . If one can control such dipole centers, one can make a study of dipole scattering. Theoretically dipole-scattering is treated from time to time [3-5] but no experimental back-up has been reported at least from the cyclotron resonance point of view. The difficulty in making dipole centers lies in the stable nature of substitutional impurities. Impurities, either donors or acceptors, once introduced in a semiconductor, remain stable at fixed sites. There exists, however, possibly one exceptional case. That is lithium compensation of

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boron-doped silicon. Boron is an acceptor in silicon stable enough. Lithium, on the other hand, is an interstitial donor impurity considerably mobile in the silicon lattice. After migration, the mobile lithium impurities are expected to arrive eventually at the boron impurities. With this expectation, lithium impurities were introduced, by means of diffusion process, into the FZ (floating-zone processed) boron-doped Si. The electron scattering time in the original boron-doped Si was predetermined by cyclotron resonance linewidth measurement. If the compensation, or to be more crucial, the pair formation between positive donor and negative impurities is realized, a substantial decrease in linewidth after the introduction of lithium impurities should be expected, since the dipole scattering cross section would considerably be smaller than the cross section by an isolated acceptor impurity. Contrary to our expectation, however, the linewidth simply increased, almost completely reflecting the nature of isolated donors and impurities. What is actually happening would be such that the lithium impurity is to find a more stable niche in the lattice than the site next to the boron impurity. The identity of the niche is uncertain. It could be something connected with an oxygen impurity even in the FZ material. The content of oxygen atoms in an FZ material is expected to be of the order of 10^{15} cm^{-3} , that is larger than the boron impurity concentration of the order of 10^{14} cm^{-3} . Though apparently active in pinning lithium, the oxygen atom itself does not seem to render a large electron scattering cross section. Through a separate investigation, however, oxygen is found to make a thermal donor after hours of heat treatment at 440 C.

After the failure of Li^+B^- pair formation in Si, we have planned a similar trial in Ge. In Ge, oxygen does not exist so much in quantity as in Si, and lithium is even more mobile. The Li-doped Ge is very popular as a solid state detector (SSD) in nuclear as well as in particle physics. The detector device, however, has a shortcoming. It should be kept in cold refrigerant, say in liquid nitrogen, since the lithium dopant tends to run away to the surface owing to the high diffusion coefficient. Doping lithium into the Ge crystal and keeping the doped crystal in a refrigerant is a necessary but easy procedure in order to secure an SSD. But to produce samples containing stable Li^+B^- pairs for cyclotron resonance experimental use is next to impossible. In the process of preparing a small piece of sample to be mounted in the microwave cavity, the matrix containing both acceptors and lithium dopants has to be exposed to room temperature, which expels the lithium dopants out of the crystal. Thinking this way and that way in preparing a stable piece of Li-doped sample for cyclotron resonance experiment, we had finally to give up the trial.

III. PERMANENT DIPOLE FORMATION IN CZ-GROWN SILICON

Oxygen atoms are unexpected players in Si, sometimes trouble-makers and sometimes acting the other way. Their features are much more strongly displayed in Czochralski-grown Si. The usage of a silica crucible naturally introduces oxygen impurities into the crystal. The displayed characters of an oxygen impurity is not unfold. The most standard one, in which we are primarily interested, is a single interstitial oxygen atom. The reason of our interest is the stable permanent dipole formation with the help of nearest Si atoms. Another less standard aspect is production of the so-called thermal donors. As already mentioned before, this production is achieved only after heat treatment, typically at 440 C. The identity of the thermal donor is considered to be a double donor, say group VI, in association with an isolated oxygen atom. Difficulty in precise identification exists because of the relatively small percentage of oxygen impurities committing in the association with thermal donors. Be that as it may, we are not interested in thermal donors for the moment. Since the thermal donors are produced after heat treatment, we shall employ only as-grown CZ crystals, which contain primarily isolated interstitial oxygen atoms. The role of an interstitial oxygen is to make a permanent dipole with two neighboring Si atoms. As indicated in Fig. 1, an oxygen atom is located in the middle of the Si-O-Si line with a bond angle of 162° . The ionicity of the Si-O bonding, $\alpha_{\text{Si-O}}$, can be expressed [6] by

$$\alpha_{\text{Si-O}} = 1 - \exp [- (X_{\text{Si}} - X_{\text{O}})^2 / 4] , \quad (1)$$

where X_{Si} and X_O are the electronegativities for Si and O atoms, respectively. Introducing the available values $X_{Si} = 1.7$ and $X_O = 3.5$, we obtain $\alpha_{SiO} = 0.51$. This means that the nature of the chemical bond between Si and O is half ionic and half covalent. Thus a permanent dipole moment for the diatomic molecule Si-O is expressed:

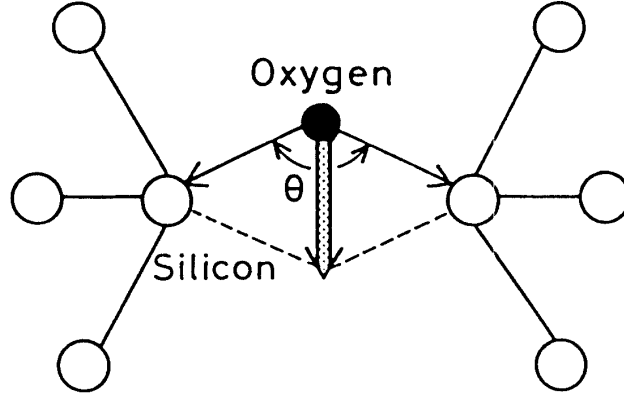


Fig. 1. A permanent dipole formation around an interstitial oxygen atom in Si crystal.

$$D_{Si-O} = \alpha_{Si-O} eL, \quad (2)$$

where e is the electronic charge and L the bond length, which is equal to 1.2 Å. The calculated dipole moment is found:

$$D_{Si-O} = 2.9 \text{ D.U.}, \quad (3)$$

where D.U. is the so-called Debye unit, which is equal to 10^{-18} cgs.esu.cm. The total dipole moment for the triatomic complex Si-O-Si is given by the sum of two vectors at a cross angle of 162°, yielding

$$D_{Si-O-Si} = 0.91 \text{ D.U.} \quad (4)$$

There exists one-to-one correspondence between isolated oxygen atoms and permanent dipoles. The concentration of dipoles can be determined from FTIR measurement, since the typical absorption line at 1105 cm^{-1} ($9.05 \text{ }\mu\text{m}$) is known to originate from interstitial oxygen atoms. A typical comparison in FTIR absorption between CZ and FZ samples is given in Fig. 2 [7]. With the help of an appropriate calibration in determining the oxygen concentration, we can find the dependence of the electron-dipole scattering rate as a function of dipole concentration. Of course one has to subtract the linewidths due to electron-phonon scattering and electron-impurity scattering, if any. In Fig. 3, we plot the contribution of interstitial oxygen atoms (dipoles) to the linewidth expressed in terms of inverse collision time $1/\tau_{ox}$. The cyclotron resonance has been carried out with a microwave frequency of 35 GHz at a fixed temperature of 4.2 K, for five CZ-Si and an FZ-Si samples. The impurity characteristics of the employed samples are given in Table I.

Table 1. Sample characteristics of all the as-grown materials.

Sample No.	Growth method	Oxygen concentration	Dopant concentration
1	FZ	$\sim 10^{16} \text{ cm}^{-3}$	$\sim 10^{12} \text{ cm}^{-3}$
2	CZ	9.6×10^{17}	$\sim 10^{12}$
3	CZ	4.1×10^{17}	$\sim 10^{12}$
4	CZ	1.3×10^{18}	[P] = 7.5×10^{14}
5	CZ	6.7×10^{17}	[P] = 1.3×10^{14}
6	CZ	7.3×10^{17}	[P] = 3.7×10^{14}

[P] signifies phosphorus concentration.

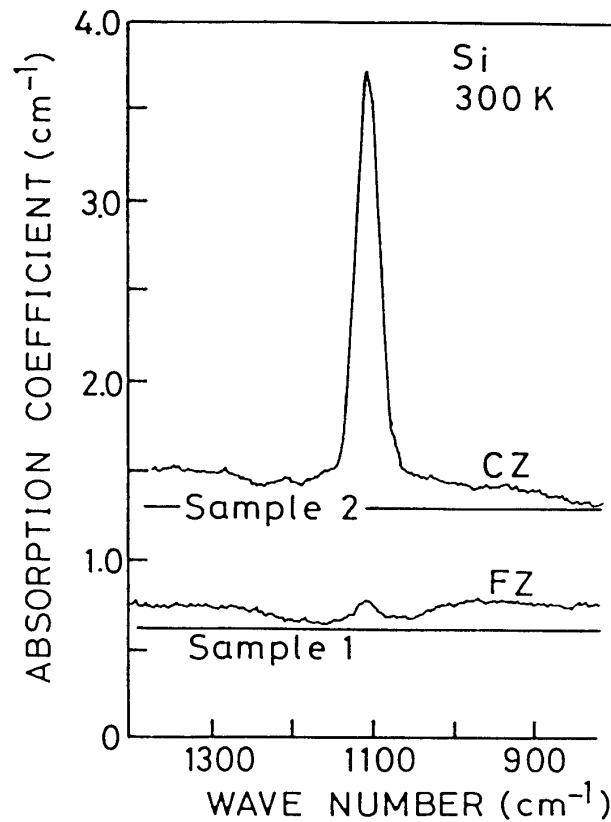


Fig. 2. FTIR absorption signals obtained at 300 K for sample 1 (FZ) and sample 2 (CZ). The baseline for each trace is also shown.

Stratton has calculated the inverse relaxation time both for screened and unscreened dipoles [3]. For unscreened dipoles, applicable to the present case, it is given by

$$1 / \tau_d = (2\pi N_d k h) / 3m^* (2kL)^2 (e^2 m^* / \epsilon k^2 h^2)^2, \quad (4)$$

where N_d is the concentration of dipoles, k the wave number of the incident electron, ϵ the dielectric constant of Si and m^* the effective mass of the conduction electron. After taking the Boltzmann average over all possible k , and replacing eL by D , we have a rearranged form:

$$1 / \tau_d = [\pi^{3/2} m^{*1/2} e^2 D^2 / 2^{1/2} h^2 (k_B T)^{1/2} e^2] N_d . \quad (5)$$

This theoretical evaluation is shown in Fig. 3 by the lower straight line, where we have taken $m^* = 0.33m_0$, $D = D_{ox} = 0.91$ D.U. and $\epsilon = 11.7$. Here we have introduced the notation D_{ox} to denote the oxygen-associated dipole moment. In numerical form, the expression (5) can be written:

$$1 / \tau_d = 1.7 \times 10^{-9} T^{1/2} N_d \quad [s^{-1}] . \quad (6)$$

The upper solid line in Fig. 3 is for better fitting with the experimental points [7], which we denote $1 / \tau_{ox}$ to distinguish from theoretical $1 / \tau_d$. The fitting requires $D = 1.1$ D.U. instead of $D_{ox} = 0.9$ D.U. Perhaps the value 1.1 D.U. could be taken as an experimentally determined one for the dipole moment of the complex Si-O-Si. With the replacing value of 1.1 D.U., the empirical formula (6) should be multiplied by a factor of $(1.1/0.91)^2$ to yield

$$1 / \tau_d = 5 \times 10^{-9} N_d \quad [s^{-1}] , \quad (6a)$$

at 4.2 K, corresponding to the upper solid line in Fig. 3.

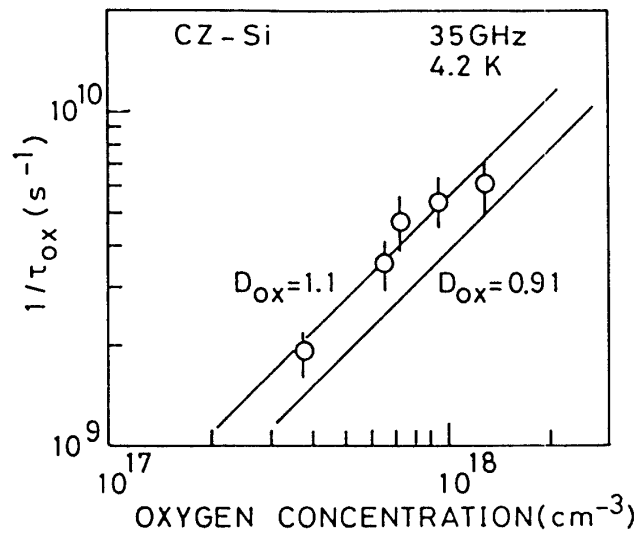


Fig.3. Contribution of interstitial oxygen atoms to the cyclotron resonance linewidth as a function of oxygen concentration. Both theoretical and empirical solid lines are shown in parallel with the experimental points.

IV. COMPARISON WITH NEUTRAL IMPURITY SCATTERING

It would be of interest to compare dipole scattering magnitude with neutral donor or acceptor scattering magnitude. We have relevant cyclotron resonance data at 4.2 K for phosphorus and boron impurities [1]; namely,

$$1 / \tau_p = 2.8 \times 10^{-5} N_p \quad (7a)$$

and

$$1 / \tau_B = 7.7 \times 10^{-7} N_B, \quad (7b)$$

respectively. We thus find that the Si-O-Si dipole scattering is nearly by four orders of magnitude weaker than neutral phosphorus scattering and two orders of magnitude weaker than the neutral boron scattering. Our original expectation that the dipole scattering should be much weaker than the neutral impurity scattering is all the more verified experimentally. For details of neutral impurity scattering, readers are referred to reference [1].

A fundamental difference between neutral impurity scattering and dipole scattering is that while practically no temperature dependence is reported for the former, a $T^{1/2}$ dependence is predicted for the latter. The $T^{1/2}$ dependence is similar to the electron scattering by piezoelectric phonons in polar crystals. There exists something in common between the two types of scattering, since both are connected with displaced ionicity.

CONCLUSION

We have introduced for the first time the cyclotron resonance approach in observing the electron scattering by permanent dipoles in a semiconductor, CZ-grown silicon crystal. The dipole consists of an interstitial oxygen atom, bonded with neighboring silicon atoms. There is no fear of moving-out of the centers like in the case of Li-compensated p-type materials. The observed dipole scattering rate is found to be by 10^2 to 10^4 orders of magnitude smaller than the scattering rates by neutral donors or acceptors in silicon.

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