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Spin–lattice relaxation of conduction electrons in silicon

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Abstract. The width of the spin resonance of conduction electrons in n-type silicon, which is related to the spin–lattice relaxation time, has been measured at microwave frequencies, between helium and room temperature.

There are two temperature regions of interest: (i) above about 50 °K scattering by lattice vibrations is the dominant relaxation mechanism, and the results are compared with existing theories due to Elliott and Yafet, and (ii) at lower temperatures the results are considered in the light of existing theories of scattering from ionized donor impurities.

1. Introduction

Electron spin resonance in a group IV semiconductor was first detected by Portis *et al.* (1953), using a spectrometer operating at 9·5 Gc/s. In a powdered sample of n-type silicon (donor impurity concentration $N_d \sim 2\times 10^{18}\ \mathrm{cm}^{-3}$) they observed a single resonance line over a wide range of temperature which they attributed to conduction electrons.

Early work by Lancaster and Schneider (1960), also at 9·5 Gc/s, appeared to confirm the theory of Elliott (1954) for the temperature dependence of the linewidth of the conduction electron resonance. However, the close proximity of a resonance associated with surface states created difficulties in the accurate measurement of the width and *g* value of the line and no account was taken of the residual linewidth at low temperatures. For these reasons the present results are felt to be more reliable. The present paper is concerned with measurements, at temperatures between 4 °K and 300 °K, of the width of the conduction electron resonance in silicon samples containing a wide range of donor impurity concentrations. Most experiments have been carried out at 36 Gc/s, which leads to a clear separation of the conduction electron and surface state resonances. The results are compared with the predictions of existing theories relating to the spin–lattice relaxation times of conduction electrons (Elliott 1954, Yafet 1963).

2. Experimental

The 36 Gc/s electron spin resonance spectrometers employed both reflection and transmission cavities together with high frequency magnetic field modulation (100 kc/s or 26·5 kc/s) and 'lock-in' detector systems. Silver-coated Araldite cavities were used with the 100 kc/s system and thin-walled copper cavities with the 26·5 kc/s system, thus allowing the modulation coils to be placed outside the cavities in both systems.

The refrigerants used were liquid helium, liquid hydrogen, liquid nitrogen, alcohol/'dry-ice' (solid CO_2) mixture (203 °K) and chloro-benzene/'dry-ice' mixture (−235 °K).

A few measurements were made at temperatures between the above fixed points by allowing the cryostat to warm up slowly after evaporation of the refrigerant.

Temperatures were measured by thermocouples attached to the microwave cavities at the position of the silicon samples after allowing time for the inside of the cavity to attain the same temperature as the outside. Copper–constantan thermocouples were used down to 78 °K and carbon resistance thermometers below that.

Because of eddy current losses which reduce the cavity Q factor, single crystal specimens could be used only at low temperatures. For example, it was found that single crystals of phosphorus-doped silicon, with $N_d \sim 6 \times 10^{17}$ cm^{-3} could be used up to 77 °K and specimens with $N_d \sim 10^{19}$ cm^{-3} up to 20 °K.

Thus powdered samples were used in a large part of the work. It is a simple matter, using standard meshes, to make powdered samples in which losses are reduced to a tolerable level. Microscopic observations confirmed that in such samples the size of the particles was much less than 100 micrometres. They show, however, a strong spin resonance line which is attributed to a surface effect produced by the mechanical treatment in the powdering process (Feher 1959, Lancaster and Schneider 1960, Walters 1960).

This surface state resonance has a g factor of 2·0061 and a linewidth of about 9 gauss and overlaps the conduction electron resonance line in the spectrum observed at 9·5 Gc/s, since the splitting between the lines is only about 9 gauss.

By using a suitable etching solution (50 parts conc. HNO_3, 30 parts 40% HF, 30 parts CH_3COOH, 1 part Br_2) the surface state resonance line can be removed to a large extent, but the process is difficult to control. Usually a residual surface state resonance remains which interferes with the accurate measurements of linewidth and g factor for the conduction electron resonance.

At 36 Gc/s the separation of the two lines is increased to about 36 gauss and there is no overlap.

In the case of a single-crystal specimen the surface state line is insignificant as the surface-to-volume ratio is small.

According to the theory by Dyson (1955) for the shape of the resonance lines from conduction electrons in plate-like specimens, the line shape will be undistorted for

$$\theta \leqslant 4\delta. \tag{1}$$

Here θ is the thickness of the specimen, and $\delta = (2/\mu_0\omega\sigma)^{1/2}$ is the skin depth for the microwave radiation used, where ω is the angular frequency of the radiation and σ is the conductivity of the specimen.

For a silicon specimen with $N_d \sim 6 \times 10^{17}$ cm^{-3} ($\sigma \sim 20$ mho cm^{-1}) and a microwave frequency of 36 Gc/s, $4\delta \sim 200$ μm.

The single-crystal specimens used were less than this in thickness and no significant distortion of line shapes was observed.

3. Measurement of the spin–lattice relaxation time

In this work the spin–lattice relaxation times T_1 encountered were of the order of 10^{-8} sec. In an isotropic solid T_1 is the characteristic time associated with the decay of the total component of magnetization M_z parallel to the large magnetic field to its equilibrium value M_0

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1}. \tag{2}$$

A 'lifetime' broadened resonance line has a Lorentzian shape and, following the treatment of the resonance phenomenon by Bloch (1946),

$$\Delta\omega_{1/2} = 2/T_2 \tag{3}$$

where $\Delta\omega_{1/2}$ is the linewidth at half maximum in angular frequency units and T_2 is the 'transverse' relaxation time.

The relation between T_1 and T_2 has been investigated by Pines and Slichter (1955). If the frequency characteristic of the vibrations of the lattice and hence the reciprocal of the correlation time τ_c is large compared with the Larmor frequency, then Pines and Slichter (1955) and Wangness and Bloch (1953) find $T_1 = T_2$ and

$$\Delta\omega_{1/2} = 2/T_1 \tag{4}$$

for an isotropic lattice structure.

The observed conduction electron resonances have a Lorentzian line shape and the relaxation time was calculated from the first derivative of the absorption line

$$1/T_1 = \sqrt{3}g\beta\Delta B/2\hbar \tag{5}$$

where ΔB is the width between points of maximum slope of the absorption line. The amplitude of the 100 kc/s or 26·5 kc/s field modulation was kept at a sufficiently low value to avoid modulation broadening.

4. Theoretical evaluation of T_1 for conduction electrons

In an early theory Elliott (1954) calculated the ratio of the matrix elements for electron–lattice 'collisions', with and without a spin-flip, and obtained the following relation for T_1:

$$\tau/T_1 \sim (\Delta g)^2. \tag{6}$$

Here Δg is the difference between the observed and free electron g factors and τ the relaxation time associated with the electrical resistivity. Since for scattering from lattice vibrations $\tau \propto T^{-3/2}$, equation (6) predicts that $T_1 \propto T^{-3/2}$ at least at high temperatures.

Yafet (1963) has considered the modulation of the spin–orbit coupling by lattice vibrations as a time-dependent perturbation which can cause spin–lattice relaxation. He finds for a semiconductor in which the conduction band edge is not at $k = 0$

$$\frac{1}{T_1} = \frac{2}{\pi^{3/2}\hbar}\frac{D^2}{\rho u^2}\frac{2m^*kT^{5/2}}{\hbar^2}. \tag{7}$$

Here ρ is the density of the material, u the velocity of sound and $D \sim Ca\Delta g$, where a is a length of the order of the lattice constant, or larger, and C is the deformation potential.

5. Results

The experiments were carried out with silicon samples doped with phosphorus having concentrations N_d, as quoted by the suppliers, from 2×10^{17} cm^{-3} to 10^{19} cm^{-3} and one sample doped with arsenic (10^{17} cm^{-3}).

Although detailed measurements of the Hall coefficient for determining N_d more accurately were only made for sample C, inspection of the electron spin resonance spectrum at 20 °K or below reveals whether the donor impurity levels are discrete or form an 'impurity' band (Feher 1959).

The results of the linewidth measurements at 36 Gc/s are shown in figures 1 and 2. Some preliminary measurements at 300 Mc/s† with single-crystal specimens (sample C) are included in figure 1. Except at temperatures below 77 °K, for specimens C, D and E, the linewidth decreases with decreasing temperature.

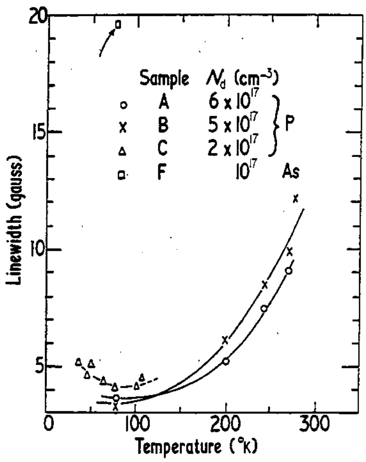

Figure 1. Linewidth of the conduction electron resonance in lightly doped silicon (phosphorus in samples A, B, C; arsenic in sample F).

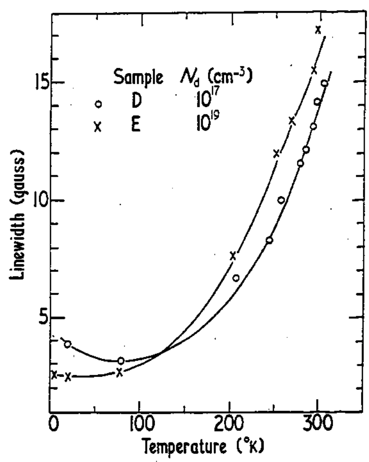

Figure 2. Linewidth of the conduction electron resonance in heavily doped silicon (phosphorus).

The g values of the conduction electron resonance in samples D and E, measured at 77 °K in single crystals, were observed to be isotropic with values $1{\cdot}9987 \pm 0{\cdot}001$ and $1{\cdot}9988 \pm 0{\cdot}001$ respectively, in agreement with Feher's (1959) measurements.

6. Discussion of results

6.1. *Phonon-dependent relaxation mechanism*

With the values $C = 8{\cdot}0$ ev (Castner 1962), $a = 5{\cdot}4$ Å, $\Delta g = 3{\cdot}5 \times 10^{-3}$, $\rho = 2{\cdot}4 \times 10^3$ kg m^{-3}, $u = 5{\cdot}4 \times 10^3$ m sec^{-1}, $m^* = 0{\cdot}35\, m$ and $D = Ca\Delta g$, equations (7) and (5) yield, for $T = 273$ °K, $T_1 = 5 \times 10^{-8}$ sec, $\Delta B = 1{\cdot}3$ gauss and, for $T = 77$ °K, $\Delta B = 0{\cdot}06$ gauss.

The value for ΔB at 273 °K is in order of magnitude agreement with the observed value but at 77 °K the observed linewidths are between 2·5 and 3·5 gauss.

The possible causes of the observed linewidths at low temperatures will be considered later; for the moment let it be assumed that the relevant interaction is independent of temperature.

† W. Duncan, Physics Department, University of Newcastle upon Tyne, made these measurements with a sensitive 300 Mc/s superheterodyne spectrometer.

Thus, if temperature-independent contributions are subtracted from the experimentally observed values, then the remaining values should represent the width arising from the phonon-induced relaxation mechanism.

The results of such a subtraction are shown for sample B in figure 3. Although equation (7) agrees fairly well with the magnitude of the observed linewidth at temperatures in the region of 300 °K, the observed temperature dependence of the 'phonon contribution' to the linewidth appears to be somewhat greater than $T^{5/2}$.

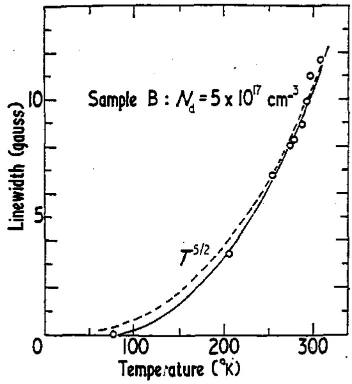

Figure 3. Linewidth of the conduction electron resonance in silicon sample B after subtraction of the temperature-independent contribution.

It has been suggested that this deviation is related to the effect of inter-valley scattering via Umklapp to the opposite valley (Yafet, private communication). Such an interaction would become effective for $T > 160$ °K since the wave vector of the phonon involved is $3{\cdot}5 \times 10^4$ m^{-1} and the velocity of sound in the (100) direction in silicon is approximately $5{\cdot}9 \times 10^3$ m sec^{-1}.

The behaviour of the highly doped material (sample E) is expected to be similar to that of metals (Feher and Kip 1955) since the degeneracy temperature is approximately 60 °K.

6.2. *Relaxation mechanisms at low temperatures*

At low temperatures spin–lattice relaxation via the spin–orbit coupling to the donor impurities was considered as a possible relaxation mechanism.

The 'random walk' model of Pines and Slichter (1955) was used to make an order of magnitude estimate of the relaxation time produced by this interaction W_{SO}. Their expression for T_1 is

$$1/T_1 = \alpha\tau_c(W_{SO})^2\hbar^{-2} \tag{8}$$

where α is the fractional concentration of impurities and $\tau_c = 2a_0/v$ is the correlation time for the interaction in terms of the mean electron velocity v at the temperature concerned and the atomic radius a_0 of the impurity.

The largest contribution to the spin–orbit interaction arises when the electron is near the nucleus, so that one expects the spin–orbit interaction in the solid to be somewhat smaller than that of the free atom allowing for the fact that an electron in the solid spends less time on the atoms than electrons of free atoms.

At 77 °K, $v \sim 6 \times 10^4$ m sec^{-1} and $\tau_c \sim 5 \times 10^{-15}$ sec. Thus, assuming free atom values (Yafet 1963) for W_{SO}, 0·027 ev and 0·31 ev for phosphorus and arsenic in silicon respectively, we obtain from equation (8), with $N_d = 10^{17}$ cm^{-3}, relaxation times

$T_1 \simeq 4\times10^{-9}$ sec for phosphorus-doped silicon and $T_1 \simeq 10^{-10}$ sec for arsenic-doped silicon. The resulting calculated linewidths are approximately 18 gauss and 700 gauss respectively, which is about ten times too large. It should be noted that equation (8) predicts a linewidth increasing with decreasing temperature since $\tau_c = 2a_0/v \propto T^{-1/2}$ This is observed in samples C, D and E.

7. Conclusion

We infer from the analysis of the linewidth of the resonance of conduction electrons that in silicon more lightly doped with phosphorus (samples A, B, C) scattering by lattice vibrations is the dominant interaction determining T_1 down to temperatures between 100 °K and 50 °K.

The measured values of the linewidth are reasonably compatible with Yafet's theory (equation (7)) bearing in mind the uncertainty in the parameter D, and the effect of Umklapp processes.

These conclusions are based mainly on results obtained with powdered samples of silicon. The few results obtained with single-crystal specimens at 36 Gc/s and 300 Mc/s are not significantly different.

Further experiments are being carried out with single crystals in order to determine whether the increase of linewidth with decreasing temperature, at low temperatures, arises from an impurity-dependent relaxation mechanism, as exemplified by equation (8), or from some other cause, such as incomplete motional narrowing of unresolved hyperfine structure.

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