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Ultrasonic spectroscopy in p-type silicon (*)

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Résumé. — On a déterminé la distribution des séparations en énergie des niveaux de l'état fondamental de l'accepteur dans des cristaux Si(B) très purs en mesurant l'absorption résonnante ultrasonore dans une gamme importante de fréquences. Les distributions mesurées se comparent bien avec les distributions attendues des champs électriques des $\approx 10^{12} \text{ cm}^{-3}$ donneurs résiduels. On a mesuré l'intensité critique pour saturer l'atténuation résonnante dans des cristaux avec différentes concentrations d'accepteurs et en fonction de la température. Bien que la distance moyenne des accepteurs soit beaucoup plus grande que le rayon de Bohr des trous liés on trouve que les temps de relaxation sont raccourcis par l'interaction accepteur-accepteur.

Abstract. — From ultrasonic resonant absorption over a wide frequency range we have determined the distribution of the energy splittings of the acceptor ground state in very pure Si(B) crystals. The measured distributions with maxima of the order of 10 μeV fit well to the expected electric field distribution from the $\approx 10^{12} \text{ cm}^{-3}$ residual donors. The critical intensity for saturating the resonance attenuation has been measured in crystals of various acceptor concentrations and as a function of temperature. Although the average distance of acceptor atoms is much greater than the Bohr-radius of the bound defect-electrons, relaxation times are found to be shortened by the acceptor-acceptor interaction.

1. Introduction. — The ground state of a hole bound to an acceptor in cubic semiconductors at low temperatures is a fourfold degenerate I_8 state which may be split into a doublet by elastic or electric fields. Thus, random internal fields of the crystal originating from defects give rise to a distribution of splittings which in turn may be regarded as an indicator of residual defects. Furthermore, such a distribution of two-level systems (T.L.S.) is quite analogous to that in glasses, and the same questions arise as to the relaxation times and the possibility of a long range interaction between the T.L.S. [1].

Information on these questions can be obtained from measuring the ultrasonic resonant attenuation over a wide frequency range. Since the attenuation is proportional to the spectral density of the splittings at a certain frequency, the distribution is thus probed in the corresponding energy range. From measuring the critical intensity for saturating the resonance attenuation one obtains the product $\tau_1 \cdot \tau_2$ of the longitudinal and transverse relaxation times. We report here measurements of the ultrasonic attenuation

at frequencies between 0.4 to 4 GHz in various silicon crystals doped with boron and indium acceptors of concentrations between 9×10^{15} and $5 \times 10^{17} \text{ cm}^{-3}$ with the aim (i) of correlating the measured distributions to the residual crystal defects, (ii) of determining the temperature dependence of the critical intensity; i.e., of $\tau_1(T) \cdot \tau_2(T)$; and (iii) of seeing how the critical intensity depends on acceptor concentration; i.e., on the mean acceptor-acceptor distance.

2. Determination of the distribution of the splittings.

— The resonance attenuation is given by

$$\alpha_{res} = \frac{\pi^2 \hbar}{\rho v^3 k_B} D_{res}^2 N(E) \frac{v^2}{T} \quad (1)$$

where $N(E)$ is the spectral density of those splittings E of the distribution that are in resonance $h\nu = E$ with the ultrasonic wave of frequency ν ; D_{res} is an effective deformation potential constant; ρ is the mass density; and v is the sound velocity. To separate α_{res} from other attenuation mechanisms (relaxation, geometrical effects) we make use of the saturation of α_{res} at high acoustic intensities to obtain the residual attenuation to be subtracted. Figure 1 shows a typical

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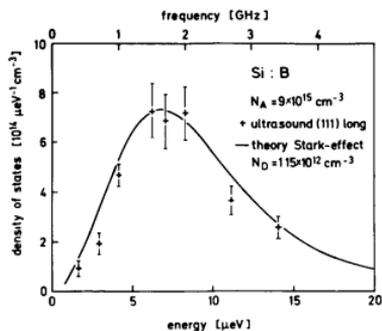


Fig. 1. — Distribution of splittings of the acceptor ground state in Si(B); curve fitted for splittings due to electric fields between residual ionized donors and acceptors.

distribution obtained in this way. We have assumed D_{res} to be independent of E , which seems plausible if the symmetry of the random field does not vary strongly with the field strength. In contrast to our earlier findings in GaAs [2] and Ge [3], where the distribution function was constant in the measuring range, the spectral density falls off at low energies for all the silicon crystals we have measured. Furthermore, for three very pure crystals from the same supplier [4], but with different boron concentrations $N_A = 0.9, 5.5, 8.5 \times 10^{16} \text{cm}^{-3}$, the observed maxima lie between 1.5 and 2 GHz, whilst for indium doped crystals and for a less pure boron doped crystal the maxima lie at higher energies. If we try now to correlate the measured distribution to internal random fields, we find that elastic fields are of no importance and can be ruled out, since the crystals are dislocation-free, of low oxygen content ($< 10^{14} \text{cm}^{-3}$), and the misfit of the boron atom in the silicon lattice is too small at our concentrations to have an effect. Carbon and oxygen impurities cause splittings of the acceptor ground state which are significant only in concentrations above 10^{16}cm^{-3} , as seen in ESR by Neubrand [9]. At small impurity concentrations a residual ESR linewidth is observed. We suppose that these residual splittings are of the same nature as the splittings observed by ultrasonic spectroscopy. It should be mentioned, however, that etching of the sample side walls was necessary to avoid strain field effects from the surface perturbed by grinding [9]. Another possibility is the electric fields of the residual $\approx 10^{12} \text{cm}^{-3}$ donors (as seen by luminescence), which are ionized by giving their extra electron to some neighbouring acceptors. Larsen [5] has calculated the expected electric field distribution assuming random distribution of ionized donors and acceptors. (At low temperatures nearest neighbour pairs should be more probable [6].) Taking into account linear and

quadratic Stark effects, we can fit Larsen's Holtzmark distribution to our $N(E)$ with reasonable parameters for the residual donor concentration N_D (comparable to the estimate from luminescence experiments), the coefficient β for the quadratic Stark effect (as estimated by Pikus, Bir, and Butikov [7]) and the coefficient χ for the linear Stark effect (three times larger than the estimate [7] for shallow acceptors). To check our hypothesis we are preparing experiments with varying compensation ratios by neutron irradiation which leads to a uniform distribution of phosphorous donors by $\text{Si} \rightarrow \text{P}$ transformation which should result in a corresponding shift of the distribution.

3. Critical intensity and relaxation times. — The critical intensity I_c for saturating the resonance attenuation is obtained by measuring the dependence on the acoustic intensity I

$$\alpha(I) = \alpha_{\text{res}} \sqrt{1 + I/I_c}. \quad (2)$$

We relate I to the applied microwave power by an insertion loss measurement [8]. In a Bloch equation formalism we get from I_c the product $\tau_1 \cdot \tau_2$ of the spin-lattice or energy relaxation time τ_1 and the transverse or dephasing relaxation time τ_2

$$I_c = \hbar^2 \rho v^3 / (2 D_{\text{res}}^2 \tau_1 \tau_2). \quad (3)$$

If only spin-lattice relaxation were effective, one might assume $\tau_1 \cdot \tau_2 = 2 \cdot \tau_1^2$ [1], that is, I_c should not depend on concentration N_A . To see whether an interaction between the acceptors (spin-spin relaxation) plays a role, we have measured I_c for three very pure Si(B) crystals from the same supplier with different acceptor concentrations N_A but otherwise essentially identical. The result is shown in figure 2. The value of a fourth crystal with the lowest concentration N_A but otherwise less pure, shows a leveling-off. This may be due to the

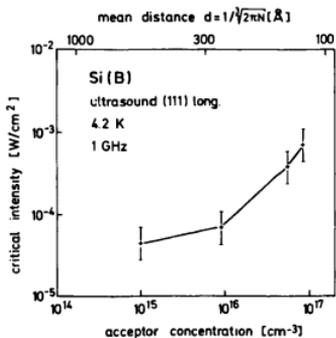


Fig. 2. — Critical intensity for saturating the resonance attenuation in crystals with different acceptor concentrations.

extra impurities or may indicate a tendency to non-interaction. As can be seen from the upper abscissa, the most probable distances are at least 10 times larger than the Bohr-radius, so that direct overlap effects can be excluded. This is in accordance with the fact that we do not see a dependence of the distribution of the splittings on N_A . If we know the temperature dependence of τ_1 , we can deduce $\tau_2(T)$ by measuring the temperature dependence of I_c . This is valid only if the measuring pulse length ($2 \mu\text{s}$) is longer than τ_1 which is true in the case of Si(B) for temperatures higher than 2 K at 1 GHz. For instance, at 4.15 K and 1 GHz for Si(B) we have

$$\tau_1 = 1.3 \times 10^{-8} \text{ s},$$

as extrapolated from an analysis of the relaxation attenuation between 5 K and 20 K. In this case τ_1 is determined by Raman and Orbach processes (relaxation via a Jahn-Teller level of the F_8 state). In this temperature range, in the case of Si(B), we would expect the relaxation time to vary as $\tau_1^{-1} \propto T^5$. However, the measured temperature dependence of the critical intensity varies more slowly than expected and depends on acceptor concentration. We find $I_c \propto T^5$ for the crystal with $N_A = 9 \times 10^{15} \text{ cm}^{-3}$ and $I_c \propto T$ for $N_A = 8.5 \times 10^{16} \text{ cm}^{-3}$. The frequency dependence of I_c is roughly as $\omega^{1.5}$ in the range from 0.5 to 3 GHz at 4.2 K. This would mean $\tau_2 \propto \omega^{-1.5}$, since at 4.2 K Raman and Orbach processes dominate in τ_1 , both being frequency independent.

In the case of Si(In) we find at temperatures between 0.5 and 4.0 K a T^2 dependence of I_c (Fig. 3), as one might expect if direct relaxation were dominant. However, the absolute value I_c is too high by two orders of magnitude, and also at temperatures above

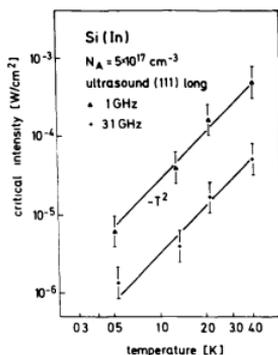


Fig. 3. — Critical intensity for saturating the resonance attenuation versus temperature in the case Si(In).

2 K we estimate the Raman process to be the most important, whilst for temperatures below 3 K, τ_1 is estimated to be longer than the duration of the ultrasonic pulse. This shows that measurements of the critical intensity alone do not give sufficient information on the relaxation processes.

Clearly, a more direct determination of τ_2 is necessary before discussing the possible interaction mechanisms.

In conclusion, we have shown that in very pure silicon crystals the splitting of the acceptor ground state is determined by the random electric fields from residual donors and that there is a dynamical interaction between the acceptors.

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