Ultrasonic Investigation of the Acceptor Ground State of Si(B)

I. The Longitudinal and Transverse Relaxation Rates of the Strain-Split Two-Level System

By

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The "spin"-lattice relaxation of the two-level system of the strain-split acceptor ground state of Si(B) is determined from the temperature dependence of the ultrasonic relaxation attenuation, around 10 K. It is found that Raman relaxation alone does not fit the results but that, in addition, an Arrhenius-type of relaxation, possibly due to a Jahn-Teller effect, is involved. The transverse relaxation is obtained from intensity-dependent and hole-burning measurements of the resonant attenuation. At small acceptor concentrations it is determined by "spin"-lattice relaxation alone; for higher concentrations an additional temperature-independent interaction term is found much smaller than expected for elastic dipole or exchange interaction.


1. Introduction

The partially orbital degeneracy of the \( \Gamma_8 \) ground state of effective mass acceptors in semiconductors and the fact that the wave function is extended over many lattice sites have some important consequences for the dynamics of the non-magnetic two-level systems which are the result of the splitting of the \( \Gamma_8 \) state by random internal elastic or electric fields: The energy relaxation rate for interaction with short-wavelength phonons will not show a simple \( T^n \)-dependence, as calculated for the Raman relaxation of a \( \Gamma_8 \) point defect, but will be modified due to the extent of the wave function which quenches the interaction, and to the Jahn-Teller resonance. This resonance, again because of the extended wave function, should be well within the acoustic band. The relative importance of both types of relaxation should depend on the acceptor species. Whereas for deep effective mass acceptors the rate is determined by the Jahn-Teller resonance alone, the shallower acceptor boron in silicon is expected to show also the influence of Raman relaxation.

A long-range dynamic interaction between these non-magnetic two-level systems is possible via dipolar electric or elastic fields or by exchange because of the extended wave function and should show up as a dependence of the transverse relaxation rate.
on acceptor concentration. In the following we report the determination of the longitudinal and transverse relaxation rates for various concentrations of the acceptor boron in silicon by measurement of the ultrasonic relaxation attenuation and by saturation and hole-burning of the resonance attenuation.

2. A Call for Theory

2.1 Ultrasonic attenuation by acceptors

Resonance and relaxation attenuation of ultrasound by the acceptor ground state which is split by a static elastic field, has been derived by Isawa et al. [1] using a perturbation approach. For a continuous distribution $N_g(E)$ of splittings $E$ from random internal fields, their result can be brought into the form given by Jäckle et al. [2] for the two-level systems in glasses, assuming that $N_g(E)$ varies slowly over the homogeneous linewidth of the resonance $E = h\nu$. For $E \ll kT$ the resonance attenuation is

$$\alpha_{\text{res}} = -\frac{\frac{dI}{dx}}{2I} = \frac{h\nu^2\tau_2^2D_1^2(E)N_g(E)}{2\rho c^3kT(1 + I/I_C)^{1/2}}, \quad (1)$$

where $\rho$ is the density, $c$ the sound velocity, $D_1(E)$ the average coupling constant, and $I$ the sound intensity. Normalization: $\int_0^\infty N_g(E)\,dE = n_s$. From the critical intensity $I_C$ for saturation of the resonance the product of the longitudinal and transverse relaxation rates $W_1$ and $W_2$ can be obtained,

$$I_C = \frac{\hbar^2\rho c^3W_1W_2}{2D_1^2} \quad (2)$$

$I_C$ can be determined from a fit to

$$\alpha(I) = \alpha_{\text{res}}(I) + \alpha_r, \quad (1a)$$

where $\alpha_r$ is some nonsaturable residual or apparent attenuation.

The energy relaxation rate $W_1$ alone may be determined by analysis of the relaxation attenuation. For our experimental situation [3] we may write

$$\alpha_{\text{rel}} = \frac{\omega n_sD_2^2}{\rho c^3kT} \frac{x}{1 + x^2}, \quad (3)$$

where $x = \omega/W_1(T)$, $\omega = 2\pi v$, and $D_2$ is the average coupling constant for relaxation attenuation. The correlation of $D_1$ and $D_2$ to the deformation potential constants $d'$ and $b'$ of the acceptor ground state in the case random splittings by strains from point defects will be discussed in a following paper. $D_2$ can be determined at the temperature where $T\alpha_{\text{res}}(T)$ is maximum, i.e. where $\omega = W_1(T)$. $W_1(T)$ may be determined from this maximum condition at various frequencies or by analysis of $\alpha(T)$ at one single frequency. It should be noted, however, that the validity of (3) is ascertained only for $\omega \ll W_1(1) \quad (a) \quad \text{ although, at least in the case of Si(In), the experimental curve can be fitted also for } \omega \geq W_1(T) \quad (4).$

A direct determination of the phase memory rate $W_2(T)$ in the case of inhomogeneous broadening is possible with a hole-burning experiment [5]: The resonance absorption is partially saturated at a fixed frequency $v_3$ by a saturating pulse of high intensity $I_S \geq I_C$. With a test pulse of low intensity $I_m \ll I_C$ and variable frequency $v_m$ the saturation around $v_3$ is probed. An analysis based on Bloch equations has been given by Bachellerie et al. [6].
If $I_r$ and $N_E(E)$ are independent of frequency around $\nu_s$, their result for stationary conditions can be written as

$$\chi_m = \chi_0 \left\{ 1 - \frac{I_s}{I_C} \Gamma W_2 \frac{1}{\sqrt{1 + I_s/I_C}} \left[ (\omega_m - \omega_0)^2 + \Gamma^2 \right]^{-1} \right\},$$

where $\chi_0$ and $\chi_m$ are the values of the attenuation of the test pulse with the saturating pulse switched off and on, respectively, and

$$\Gamma = W_2 \left( 1 + \left( 1 + \frac{I_s}{I_C} \right)^{1/2} \right).$$

Thus, the reduction in attenuation is a Lorentzian of linewidth $\Gamma$ and depth $\chi_{\min} = \chi_0 \sqrt{1 + \frac{I_s}{I_C}}$, and

$$\frac{\Gamma}{1 + \chi_0/\chi_{\min}}.$$  \hspace{1cm} (6)

Note that an absolute determination of $I$ is not necessary in these experiments.

### 2.2 The longitudinal relaxation rate

Thermal equilibrium of the isolated strain-split $\Gamma_8$ state modulated by the ultrasonic wave is attained by interaction with the thermal phonon bath. Direct and Raman processes have been discussed by Yafet [7] and by Suzuki and Mikoshiba [8] on the basis of first- and second-order perturbation theory. (The latter authors included the reduction in interaction for phonons having a wavelength shorter than the Bohr radius.) However, scattering of high-frequency phonons may be modified by a Jahn-Teller effect [9].

The experiments [3, 4] show that for the deeper acceptors Mn in GaAs and In in Si neither the temperature dependence nor the absolute value of the predicted Raman relaxation fits the results. Instead an Arrhenius type of relaxation is adequate for $W_1(T)$. The corresponding activation energies were suggested to be connected to the Jahn-Teller effect. They have been confirmed by thermal conductivity [10] and phonon spectroscopy with superconducting tunnel junctions [11]. For shallow acceptors in Ge a relaxation attenuation peak could not be observed, in accordance with the fact that Jahn-Teller effect should be weak in this case and Raman relaxation should be difficult to be measured, since it should appear as a broad shallow peak at higher temperatures where it is masked by attenuation due to phonon-phonon interaction.

Boron in silicon should be an intermediate case in the sense that Raman as well as activated relaxation may be effective in the same temperature range. However, to our knowledge, there is no theory for the relaxation of the $\Gamma_8$ state considering the Jahn-Teller effect. One possibility for the analysis of the experiments may be to regard Raman and Arrhenius-Orbach relaxations as two independent processes; i.e. to add the relaxation rates $W_{1\text{R}}$ and $W_{1\text{A}}$.

### 2.3 The transverse relaxation rate

The analysis leading to the expression for the burnt hole [4] assumes that transverse relaxation can be described by a relaxation rate $W_2$, though this may not be the case. In general, one may define $W_2$ by the homogeneous linewidth and make the ansatz

$$W_2 = \frac{1}{3} W_1 + W_{\text{int}},$$

where the first term is due to energy relaxation and the second to a secular interaction with fluctuating fields. In our case, these may be the changing elastic or electric fields around a flipping neighboring acceptor or exchange interaction by overlap.
of the extended wave functions. In compensated material also the hopping fluctuation of the electric fields may be effective. Since the strain-split \( \Gamma_0 \) state has no magnetic moment, magnetic dipolar interaction can be excluded. \( W_2 \) has been calculated for elastic interaction by Black and Halperin [12] in the case of two-level systems (TLS) in glasses. They assumed that the fluctuation rate is determined by the energy relaxation of the neighboring TLS (\( W_1 \) model) and that the elastic field of a TLS is dipolar. If the pulse length is larger than \( l/W \), and if for all splittings of the distribution \( kT > E \), then \( W_{\text{int}} \) is temperature independent and may be written as

\[
W_{\text{int}} \sim n_a J / h ,
\]

where the proportionality factor should be of the order of one to ten and \( n_a J \) is an average interaction energy which is a complicated average over all crystal directions. If no cancelling effects occur, formula (A 14) of [12] (an exponent \( 1/2 \) is missing in (A 14)), as calculated for the two-level systems in amorphous materials, should be useful as an estimate, if we replace \( \gamma_1 \) and \( \gamma_1 \) by the deformation potential constants \( d' \) and \( b' \), respectively, and the sound velocities by their angular means of the crystal [13]. The linear dependence on \( n_a \) results from the \( 1/r^3 \) dependence of the dipolar fields.

Electric dipolar interaction has a similar structure, however, the coupling constants of the linear Stark effect are not known. According to the estimates of Bir et al. [14], the electric dipolar interaction may be comparable to the elastic one for Si(B) and may even be stronger for Si(In).

For exchange interaction, Tokumoto et al. [15] have proposed a \( W_1 \) model, where \( W_{\text{int}} \) is given by the exchange integral of the \( H_2 \) molecule at some average distance. Because of the exponential dependence \( W_{\text{int}} \) depends sensibly on the way of averaging. Tokumoto et al. take \( W_{\text{int}} \) at the most probable pair distance. We arrive at somewhat smaller effective distances and much larger values for \( W_{\text{int}} \) following the procedure applied by Hu and Hartmann [20] to dipolar interaction.

\( W_{\text{int}} \), as calculated for both types of interaction, turns out to be too large by one to two orders of magnitude compared with our experimental results. One reason for this discrepancy may be that correlation times shorter than \( 1/W \) may be effective for the fluctuations, thus leading to a narrowing (fast motion case).

### 3. Experimental Procedure

The ultrasonic attenuation was measured by the pulse-echo method. The end faces of the crystals were polished flat to about 50 nm and parallel to within 5'' of arc over a diameter of \( \approx 10 \) mm. Care was taken to minimize mechanical damage of the surfaces by polishing long enough with the smaller grain to remove the damage by the larger one. A 1 \( \mu \)m Al film was evaporated onto one side as a counterelectrode for the 1 to 2 \( \mu \)m thick CdS transducer deposited on the top of it. Top electrode was the inner conductor of a coaxial cavity, ending in a 2 mm diameter soft bellows to avoid strains in the sample. The cavity was tunable between 0.3 and 4.4 GHz by an anodically oxidized capacitive aluminum slug (Kinder [16]). The length of the ultrasonic pulse train (2 \( \mu \)s) corresponds to nearly one round trip. Electrical power varied up to 20 W, repetition rate from 1 to 10 ms. The echoes were detected by a superhet receiver, including a logarithmic IF amplifier followed by a boxcar integrator and an \( xy \) recorder. The attenuation was determined from the amplitudes of two echoes keeping the signal height of the reference echo constant, using a calibrated attenuator at the receiver input.

The determination of the critical acoustic intensity \( I_c \) is more problematic. We assume that the conditions for acousto-electric reciprocity are fulfilled [17, 18], that the intensity is constant over the cross-section of the sound beam, and that the signal
heights of the acoustic echoes are not significantly altered by geometrical effects. By evaluation of the insertion loss of the cavity including tuners and switches and by measurement of the transmitter power, the absolute value of $I_c$ is then determined from a fit of $a(l)$ to (1a). Depending on frequency and resonator geometry, insertion loss varied between 30 and 80 dB. The experimental error is difficult to be estimated. It may be larger than 3 dB.

In the hole-burning experiment, the test pulse and the saturation pulse were generated at the opposite faces of the crystals with individually tunable coaxial cavities. The frequency selectivity, which determines the lower limit of measurable values of $W$, was about 30 MHz.

For temperatures above 4.2 K the sample was contained in a double-walled metal can which in the lower part could be thermally isolated against the helium bath. In the upper part there was good thermal contact to the evaporating helium gas. By pumping the bath and regulating the heat given to the resonator, temperatures between 4 and 50 K were stabilized to 1%. To avoid thermal fluctuations of the exchange gas its pressure had to be kept at roughly 10 mb and some streaming resistances had to be inserted into the can. Temperatures were measured with carbon resistors calibrated to 2% of temperature.

The samples were high-quality FZ silicon single crystals from Wacker Chemitronic (Burghausen, FRG) with boron concentrations between $2 \times 10^{20}$ and $8.5 \times 10^{22}$ m$^{-3}$ at low compensation. Concentrations of other defects are given in Table 1.

4. Experimental Results and Discussion

The general features of the temperature dependence of the attenuation in Si(B) are analogous to those in GaAs(Mn) [3] and Si(In) [4]: There is a relaxation peak around 10 K and a saturable rise of the attenuation proportional to $1/T$ below about 4 K.

4.1 Relaxation attenuation

Intensity-dependent measurements are necessary for a correct determination of the relaxation attenuation to ensure that either the intensity is high enough to minimize resonance attenuation by saturation or that the intensity is low enough, so that the full resonance can be taken into account by its $1/T$-dependence. Fig. 1 shows the

Table 1

Data of the Si:B crystal samples

<table>
<thead>
<tr>
<th>crystal No.</th>
<th>impurity concentrations</th>
<th>etch pit density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>boron ($10^{22}$ m$^{-3}$)</td>
<td>carbon ($10^{22}$ m$^{-3}$)</td>
</tr>
<tr>
<td>78</td>
<td>0.02</td>
<td>$\leq 0.5$</td>
</tr>
<tr>
<td>83</td>
<td>0.098</td>
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<td>91</td>
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<td>0.12</td>
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<td>87</td>
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</tr>
<tr>
<td>86</td>
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<td>7.5</td>
</tr>
<tr>
<td>55</td>
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</tr>
<tr>
<td>54</td>
<td>8.5</td>
<td></td>
</tr>
</tbody>
</table>

2) The neglect of this together with using a wrong formula for analysis (see [1]) may have led to erroneous results in former ultrasonic investigations on Si(B) [19].
result for a crystal with higher doping. The intensity of 1 W/m² was high enough to saturate the resonance attenuation completely. (Surprisingly, for the higher intensity there is a rise in attenuation to low temperatures independent of pulse length and pulse repetition.) The curve is the best fit by trial and error adding the Raman rate $W_{1R}$ (assuming the effective coupling constant to thermal phonons, as calculated in [8], to be frequency-, i.e. temperature independent), and the Arrhenius-Orbach rate $W_{1A}$ (fit parameters: attempt frequency $W_0$ and activation energy $\Delta$) with the values $D_4 = 4.5 \times 10^{-10}$ J, $W_0 = 2 \times 10^{10}$ Hz, and $\Delta = 3.5 \times 10^{22}$ J. No good fit could be obtained with $W_{1R}$ or $W_{1A}$ alone. Though the procedure of adding $W_{1R}$ and $W_{1A}$ may not be justified by a complete theory including the Jahn-Teller effect, it is clear that also for Si(B) Raman relaxation alone does not describe our results. At low temperatures, where according to our fit $W_{1R}$ should dominate, the experimental points correspond to $W_1 \sim T^n$ ($n \approx 3$), whereas the fit shows a steeper dependence. Direct relaxation can be excluded at these temperatures since the splittings $E$ are small. Essentially the same results were obtained with a crystal of high acceptor concentration ($n_a = 8.5 \times 10^{12}$ m⁻³). Since a specific orientation dependence is predicted [7], a more detailed study at different frequencies in the magnetic field is prepared.

### 4.2 Resonance attenuation: critical intensity and hole-burning

As is seen from Fig. 2, the burnt hole is a Lorentzian (drawn lines). It is power broadened (5) and shows a Bloch-Siegert shift (lowering of the center frequency) at high intensities. The intensity dependence of $I$ and $x_{\text{min}}$ is in good agreement with (4), as shown in Fig. 3, so that in fact a transverse relaxation rate $W_2$ can be deduced according to (6). Pulse length (2 µs) is much larger than $1/W_2$, so that we have the stationary situation analyzed in [6]. The temperature dependence of $W_2$ between 2 and 6.5 K for various acceptor concentrations obtained in this way, is shown in Fig. 4.

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2) Calculated from the relation $D_4 = (1 + (b'/d')^2)\lambda^4/(9\pi)$ given in [8] with the deformation potential constants $|b'| = 2D_4/\lambda^4 = 2.58 \times 10^{-19}$ J and $|d'| = 2D_4'/\sqrt{3} = 8.21 \times 10^{-19}$ J according to [21].
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Fig. 3. Determination of $W_1$ from intensity dependence of hole width according to (5). Straight line corresponds to $W_1 = 150$ MHz. Si(B) No. 86, $\nu = 2.0$ GHz, $T = 4.2$ K.

Fig. 4. Temperature dependence of $W_1$ at various acceptor concentrations. $\Delta n_a = 9.5 \times 10^{20}$ m$^{-3}$, $\nu_3 = 1$ GHz; $\circ$ and $\bullet$ $6 \times 10^{21}$ m$^{-3}$ at 2 and 1 GHz, respectively; $+ 5.5 \times 10^{22}$ m$^{-3}$, 1 GHz; $\times 8.5 \times 10^{22}$ m$^{-3}$, 1 GHz.

The results can be interpreted as follows: For $n_a \leq 6 \times 10^{21}$ m$^{-3}$ we have $W_2(T)/$MHz = $2.9(T/K)^{2.7}$ independent of $n_a$. It is interesting that by this method the same unexpected temperature dependence is found as from relaxation attenuation. A comparison of the absolute values gives $W_2 \approx 0.6 W_1$, which is in good accordance with (7) for $W_{int} = 0$; i.e. we are in the regime of isolated TLS, where only $W_1$ is effective for transverse relaxation. For $n_a \geq 5.5 \times 10^{22}$ m$^{-3}$, $W_2$ becomes larger and may be fitted by an additional temperature-independent interaction term according to (7). The lines drawn are fits with $W_{int} = 1.2 \times 10^8$ s$^{-1}$ ($n_a = 5.5 \times 10^{22}$ m$^{-3}$) and $W_{int} = 2.2 \times 10^8$ s$^{-1}$ ($n_a = 8.5 \times 10^{22}$ m$^{-3}$). These values are smaller by two orders of magnitude than those obtained from (8) for elastic dipolar interaction or from the $W_1$ model of exchange interaction. Since the exchange interaction is relatively large, it may have a narrowing effect.

The measurement of $I_c$ as determined from the intensity dependence of the attenuation (Fig. 5), gives qualitatively the same results for the concentration depend-

Fig. 5. Determination of $I_c$ from intensity-dependent attenuation according to (1a). The fit data are $\sigma_{res} (I \approx 0) = 174$ dB/m, $\sigma_t = 98$ dB/m, and $I_c = 2$ W/m$^2$. $T = 4.5$ K, $\nu = 1.25$ GHz. Si(B) No. 87a

Fig. 6. Critical intensity in Si(B) at various acceptor concentrations. $T = 4.2$ K, $\nu = 1$ GHz.
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ence (Fig. 6) of $W_\alpha$. However, the absolute values of $W_\alpha$ from $I_\alpha$ are up to a factor of five smaller than those from hole-burning, which may be due to systematic errors in the determination of $I_\alpha$, as was discussed in Section 3.

Measurements in a wider concentration range and also with other acceptors may help to sort out the importance of the various types of interaction. Since the range of linewidths measurable by the hole-burning method is rather limited, other techniques have to be applied.

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References


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