

Temperature dependence of the hyperfine interactions of ^{111}Cd in silicon

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^{111}In was implanted into intrinsic silicon. After annealing of the samples to remove radiation damage caused by the implantation process the hyperfine interaction of the daughter nucleus, ^{111}Cd was studied as a function of temperature by means of the time-differential perturbed-angular-correlation technique. The spectra show that dynamical and static hyperfine interactions were superimposed. This fact is explained in terms of two sites for probe atoms in the silicon matrix, the substitutional and the tetrahedral interstitial sites. In both sites the electron-capture decay of ^{111}In has a different effect on the angular correlation. The static component is a distribution of electric quadrupole interactions with the frequency centroid increasing linearly with $1/T$ between 24 and 100 K. These interactions are assigned to cadmium in substitutional sites. The possibility that these interactions are produced by holes bound to the cadmium-acceptor ions is discussed.

I. INTRODUCTION

In recent years the time-differential perturbed-angular-correlation (TDPAC) technique has been applied to study local properties of semiconductors and insulators.¹ Several experiments were carried out using ^{111}Cd produced by the electron-capture decay of ^{111}In as probe.

In some cases the measured spectra showed either widely distributed quadrupole interactions or time-dependent interactions. These observations were attributed to "aftereffects" (AE's) of the electron-capture decay of the ^{111}In which produces holes in the electronic shells of the Cd probe, thus leading to fluctuating fields at the nucleus. Recently, experiments have been carried out to study the dependence of AE's on temperature in Fe_2O_3 (Ref. 2) and In_2O_3 (Ref. 1). In both cases the attenuation present at room temperature disappeared at elevated temperatures, an effect which was attributed to a shorter lifetime of trapped holes.

In the case of indium oxide it was possible to determine the position of the cadmium acceptor level in the band gap from the temperature dependence of the attenuation. Despite all these advances, it is still difficult to predict whether the angular correlation measured in a given system will be perturbed by AE's or not, although it seems that a necessary condition is that the daughter ion must be a nonisovalent impurity in the host crystal.¹ A further requirement also seems to be the predominant ionic character of the bonds³ between the probe ion and the host crystal.

Semiconductors such as Si, Ge, and III-V compounds can serve as appropriate systems to investigate the above-mentioned points. They are all covalent crystals with cubic symmetries, the III-V compounds with a touch of ionic bonding also. Hence no electric field gradients (EFG's) are to be expected at regular lattice sites in the absence of AE's.

We have begun with such a systematic study and we report here on the results of hyperfine interactions in indium-implanted silicon. The implantation method was chosen because attempts to introduce ^{111}In in silicon by

diffusion^{4,5} or melting⁶ were not successful to obtain probe atoms in cubic environments.

On the other hand the system InSi has been studied by several techniques,^{7,8} the interest being in the location of indium atoms and redistribution on annealing. Also several TDPAC (Refs. 9–12) experiments have been carried out to investigate the annealing behavior. In all these experiments TDPAC measurements at room temperature show high fractions of probe atoms on sites with cubic symmetry. But, it is not possible to correlate these fractions with the lattice location of the probe atoms because both the regular interstitial and the substitutional sites have cubic symmetry. However, if AE's play a role at some temperature this fact could be used to distinguish between both sites, because the electronic environment is expected to be different for probe atoms in both positions.

Recently, low-temperature measurements of the hyperfine interaction of ^{111}In implanted in P-doped silicon have been reported.¹³ It was observed that at low temperatures an important fraction of probe atoms were subjected to static quadrupole interactions, while at room temperature all probes occupied sites of cubic symmetry. The existence of perturbations was attributed to AE's, and its removal with temperature to the increase of the free-electron concentration in the conduction band due to ionization of P-donor dopants. In the present work we report on the observation of a strong temperature dependence of hyperfine interactions in intrinsic silicon and the detection of time-dependent fields beside a distribution of electric fields gradients. The type of effect observed is different from the one reported for oxide semiconductors. In the present case there is a strong temperature dependence of the static parameters: the quadrupole frequency depending linearly on $1/T$.

II. EXPERIMENTAL

A. Sample preparation

The samples were prepared by implanting ^{111}In ions of 80 keV into intrinsic Si single crystals with a dose of

about 10^{13} ions/cm². The direction of implantation was parallel to a $\langle 110 \rangle$ axis. The projected range of ions was 40 nm with a depth distribution of 16 nm,⁷ leading to a concentration of impurities of about 10^{19} at./cm³. The samples were encapsulated in quartz tubes and annealed in vacuum ($p < 10^{-5}$ kPa) in a two-step annealing process (45 min at 873 K and 10 min at 1200 K) as suggested by Csepregi *et al.*¹⁴ in order to remove amorphization and isolated radiation damage. During the annealing redistribution and segregation occurred and the concentration of implanted impurities decreased by about 2 orders of magnitude.

B. Technique

The hyperfine interaction of ¹¹¹Cd was observed by means of the γ - γ TDPAC technique. The decay of ¹¹¹In to the 417-keV level of ¹¹¹Cd occurs by electron capture. The half-life of this level is 120 psec. It decays to an intermediate level (84-ns half-life) by emitting a 171-keV γ ray and then to the ground state of ¹¹¹Cd by emitting a 245-keV γ ray. Due to the conservation of angular momentum there exists a directional correlation between these two γ rays. This correlation can be perturbed by external fields interacting with the magnetic dipole moment (μ) or electric quadrupole moment (Q) of the intermediate Cd nuclear state. TDPAC experiments reduce to a determination of the perturbation factor $G_2(t)$, where t is the time spent by the nucleus in the intermediate state. To this end we have used a standard four NaI(Tl) detector system.¹⁵ The detectors are placed in a plane at 90° angular intervals. Eight spectra of coincidences between both γ rays $C_{ij}(t)$ were simultaneously recorded. $C_{ij}(t)$ is the number of events in which the first γ ray enters in detector i and after a time t the second enters in detector j . After correction for accidental coincidences the eight spectra were combined:

$$C(90^\circ, t) = [C_{12}(t) + C_{21}(t)]^{1/2} [C_{34}(t) + C_{43}(t)]^{1/2} \quad (1)$$

and

$$C(180^\circ, t) = [C_{13}(t) + C_{31}(t)]^{1/2} [C_{24}(t) + C_{42}(t)]^{1/2}$$

and from these spectra the following ratio was obtained:

$$R(t) = \frac{C(180^\circ, t) - C(90^\circ, t)}{2C(90^\circ, t) + C(180^\circ, t)} \quad (2)$$

which is related to the perturbation factor $G_2(t)$, which will be described below, by

$$R(t) = A_2 G_2(t). \quad (3)$$

The factor A_2 depends on the involved geometry source-detectors and on the anisotropy of the gamma cascade. The experimental ratio $R(t)$ was fitted with theoretical expressions for $G_2(t)$ folded with the measured time resolution curves.

C. Analytic expressions for perturbation factors

The form of the perturbation factor depends on the kind of interactions the probe atoms are subjected to. We show here analytic expressions that were utilized in the fitting procedure.

1. Electric quadrupole interactions

If the perturbation is produced by a static EFG acting on the probe nucleus of quadrupole moment Q and the EFG tensor is described by its main component V_{zz} and the asymmetry parameter η , then the perturbation factor is

$$G_2^s(t) = \sum_{n=0}^3 s_n \cos(2\pi\nu_n t) \exp(-2\pi^2\delta^2\nu_n^2 t^2). \quad (4)$$

The frequencies ν_n are related to the quadrupole interaction frequency $\nu_Q = eQV_{zz}/h$ by the relation $\nu_n = F_n(\eta)\nu_Q$. The coefficients s_n and F_n are known functions of η .¹⁶

The exponential functions account for a normal distribution of relative width δ around ν_n . In case of wide distributions and low frequencies it is convenient to take the limit $\nu_Q \rightarrow 0$ in (4) to obtain

$$G_2^s(t) = \sum_{n=0}^3 s_n \exp(-\sigma^2 n^2 t^2 / 2), \quad (5)$$

where σ is the absolute width of the distribution.

2. Time-dependent interactions

If there are fluctuations in the fields acting on the nucleus during the time that the nucleus spends in the intermediate level the perturbation factor could be an exponential function. If the hyperfine field fluctuates randomly with a correlation time τ that is short with respect to the inverse of the average interaction frequency ω , then $G_2(t)$ is given by the Abragam-Pound motional-narrowing approximation:¹⁷

$$G_2(t) = \exp(-\lambda_r t) \quad (6)$$

and

$$\lambda_r = \langle \omega^2 \rangle \tau.$$

When aftereffects are involved it is important to take into account that the fluctuations introduced by the decay cease after some time and then the hyperfine interactions become static. If the average probability (per unit of time) that the fluctuations stop is λ_g , then the perturbation factor is given by¹⁸

$$G_2(t) = \left[\frac{\lambda_g}{\lambda_g + \lambda_r} + \frac{\lambda_r}{\lambda_g + \lambda_r} \exp[-(\lambda_r + \lambda_g)t] \right] G_2^s(t), \quad (7)$$

where λ_r and $G_2^s(t)$ are as defined in (4) and (6), respectively.

III. RESULTS AND ANALYSIS

Figure 1 shows a TDPAC spectrum taken after implantation. This kind of spectrum is typical for implantations in silicon. It corresponds to a wide distribution of large quadrupole frequencies that can be associated with the radiation damage produced by the implantation process. These perturbations on the angular correlation are partially removed by annealing at high temperatures as is shown in Fig. 2(a) (after annealing for 45 min at 873 K and 10

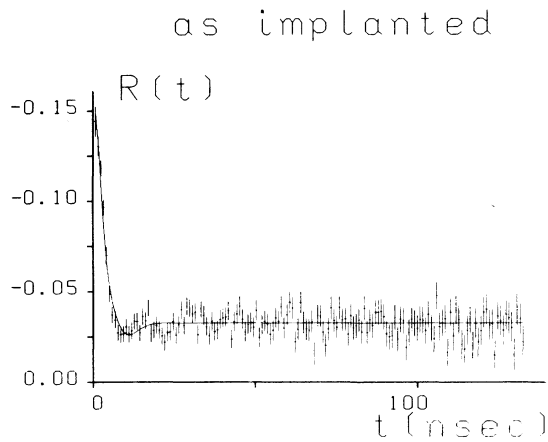


FIG. 1. Typical TDPAC spectrum obtained before annealing.

min at 1200 K). In this spectrum exists still a component with a large distribution that can be described with expression (5) ($\sigma_1=290$ MHz), but an important fraction of probe atoms ($f=71\%$) is now in sites of low EFG's. The large distribution can be associated with probe atoms either in precipitates or near the surface. The value for σ_1 agrees with the results reported for indium in *n*- (Ref. 9) and *p*- (Ref. 10) type silicon.

The fraction of probe atoms subjected to low EFG's can be associated with probe atoms on substitutional or tetrahedral interstitial sites, both of cubic symmetry. The presence of small EFG's in these sites will be discussed in

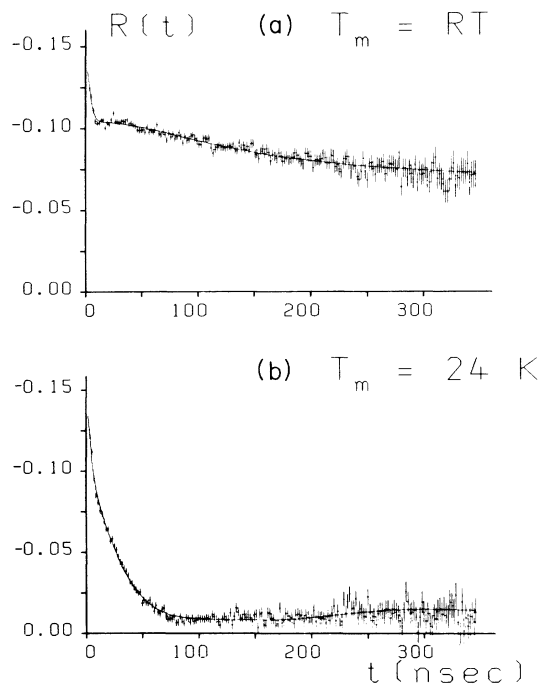


FIG. 2. TDPAC spectra obtained after annealing: (a) measured at room temperature; (b) measured at 24 K.

the next section. Here we may say that until now a complete "unperturbed" situation has never been reported for In in intrinsic silicon independent of temperature and duration of annealings.^{11,13}

In Fig. 2(b) a TDPAC spectrum measured at a sample temperature of $T_m=24$ K is shown. The hyperfine interaction apparently depends strongly on the sample temperature. In order to analyze this dependence we have kept the interaction parameters assigned to probes near the surface or in precipitates in room-temperature (RT) values ($\sigma_1=290$ MHz and $f_1=29\%$) fixed in all the fits. To describe the slow part of the spectra it is important to notice that at high delays t , $G_2(t)$ is lower than the so-called "hard-core" value $0.2A_2$, expected for static interactions with randomly oriented EFG's (e.g., in polycrystalline samples). However, in single crystals different values for the s_n can occur. Therefore we fitted expression (1) to the experimental data with s_n as free parameters. The obtained values were not consistent with a particular direction of the EFG. Also the high-frequency spread ($\delta \geq 50\%$) obtained in these fits is also not consistent with a preferential direction of EFG's. In order to describe the experimental data one has to assume that a time-dependent interaction is present. Now the question arises whether the time-dependent interaction is connected with atoms in the bulk or with those included in the fraction f_1 . We could solve this problem by fitting only the slow part of spectra for $t > 20$ ns with expression (4) plus an additive constant.

This constant is introduced in order to take into account a shift in the hard-core value due to the contribution of the f_1 component as well as a shift due to a contribution of a time-dependent interaction. An example of this fitting procedure is shown in Fig. 3(a). We summarize here the results obtained for the spectra between 24–80 K.

- (a) Below 32 K the constant is negative and it becomes positive as the temperature increases.
- (b) The quadrupole frequency ν_Q varies linearly with $1/T$.
- (c) The distribution δ reaches a minimum between 30 and 40 K.

The negative value obtained for the constant indicates that a time-dependent interaction is present in the slow component of the spectra, associated with atoms in the bulk. The change of sign indicates a change in the dynamical interaction with temperature and it is an additional proof that the measured $G_2(t)$ below the hard-core value is not a result of a preferential direction of EFG's.

We have also attempted to fit all the spectra with the expression (7). Such a fit is shown in Fig. 3(b) and we can summarize the results as follows: It is possible to obtain good fits with expression (7) but only for $T < 32$ K; for large T , χ^2 increases rapidly. The quadrupole frequency ν_Q as well as the relaxation parameter λ_r increases with $1/T$. However, in the range 20–80 K, where the change in the spectra is very pronounced, λ_g remains constant and is equal to zero, i.e., the dynamic interaction does not vanish but only the fluctuation rate changes with temperature.

Better fits can be obtained if it is assumed that there are

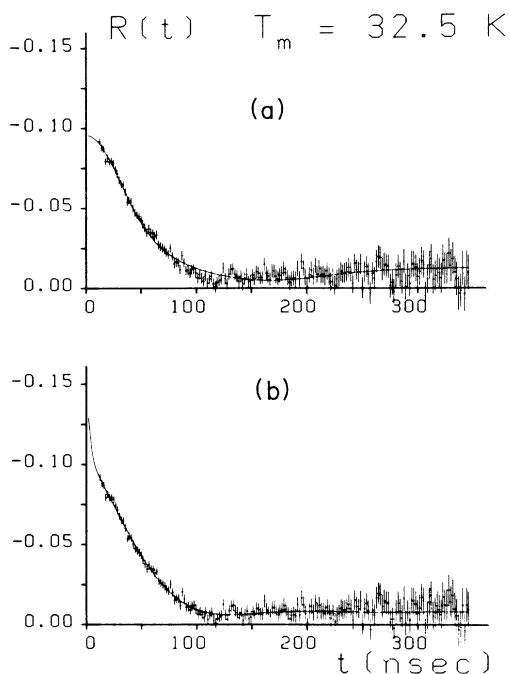


FIG. 3. TDPAC spectrum measured at 32.5 K. Only the slow part is fitted (a) with the theoretical expression (4) for a static quadrupole interaction plus an additive constant and (b) with expression (7).

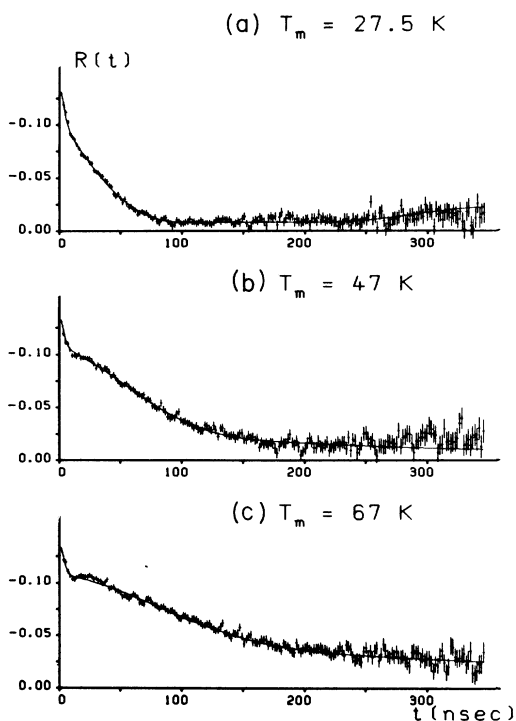


FIG. 4. TDPAC spectra at different temperatures. Solid lines correspond to the following case: 29% of probe atoms near the surface or in precipitates ($\sigma_1=290$ MHz), 39% of probes feeling dynamical interaction and 32% subjected to static quadrupole interactions.

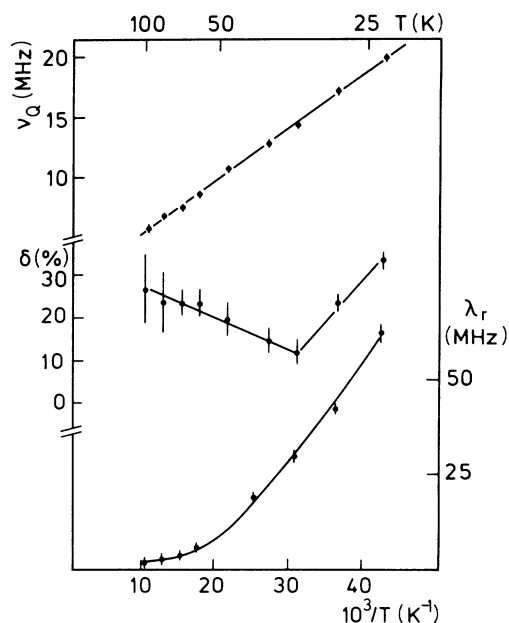


FIG. 5. Interactions parameters are shown as a function of temperature.

two different lattice sites for the probe ions in the bulk. In site *S* the interaction is mainly static and in site *R* the interaction is dynamic. Then we can use a linear combination of the functions (4) and (6) with weights f_s and f_r , respectively. After fitting all spectra taken between room temperature and 24 K, leaving all the involved parameters free in a second series of fits, we fixed the fractions at the average values $f_s=0.32$ and $f_r=0.39$. The results obtained in this way are shown in Fig. 4. The corresponding values of ν_Q , δ , and λ_r are plotted in Fig. 5.

This method of fitting the experimental data shows the same trends for the interaction parameters as was found with the other two fitting procedures described above. For $T > 100$ K, ν_Q is so small and δ so large that the errors become too large. Therefore these data were not included in Fig. 5.

IV. DISCUSSION AND CONCLUSIONS

From channeling experiments it is known that implantation of In in silicon produces In in substitutional and interstitial sites,^{7,8,19} and this situation can either remain after annealing^{7,8} or the substitutional component decreases in favor of the number of In atoms on the regular tetrahedral interstitial site.²⁰ Also, it could be expected that the population of both sites would be similar as produced by a sort of autocompensation of the semiconductor, because in large-gap semiconductors there exists a force tending to equalize the concentration of donors and acceptors.²¹ Then it is possible to understand the presence of two kinds of hyperfine interactions for indium in intrinsic silicon in terms of substitutional and interstitial sites. For indium in both sites AE's would play a different role because of the different electronic surroundings. While indium in the substitutional site is bound by

the covalent sp^3 , the probable electronic configurations for indium in the tetrahedral interstitial site are the atomic s^2p , the ionized s^2 ,²² or the double ionized s , similar to those that have been reported for interstitial aluminium in silicon.²³ We tentatively assign the dynamic interaction to probe ions in interstitial sites, although it is difficult to say what state of charge the probe ion assumes after the electron-capture decay, and what kind of coupling with the silicon lattice can produce the observed relaxation rate.

We assign the static interaction to probe ions in the substitutional site. In this way, the measured values for the population of both sites are consistent with the auto-compensation effect and with the fact that indium in the interstitial site is a donor impurity. This assumption is also in agreement with the fact that time-dependent interactions were not observed in TDPAC investigation of ¹¹¹In implanted in *n*-type silicon.¹³ In that case it can be anticipated that the interstitial component would be very small since the presence of P donors increases the solubility of acceptors,⁷ i.e., indium in substitutional sites. On the other hand, the static interactions observed in *n*-type silicon agree very well with those reported here. The frequency also varies linearly with T^{-1} (between 20 and 80 K), although the slope is 20% larger, and there is a minimum in the distribution δ although its position is also shifted a little.

To account for the temperature range where changes in the hyperfine parameters occur it is possible to assign an activation energy of a few meV for the removal of the sources of the EFG. Such low activation energies must be related to some electronic effect. A possible source of EFG's at the nuclear site could be holes bound at the acceptor probe ions. If the picture of a pseudo-helium-atom model²⁴ is valid, then the neutral Cd center is composed of two electrons bound to form the sp^3 bonds and two holes at some lattice parameters away. These holes could

produce an EFG and at higher temperatures it would be lower because the holes will be in excited orbits of larger radius.

The ionization energy of cadmium centers in silicon are $E_1 = 550$ meV and $E_2 = 770$ meV,²⁵ and the excited states should have comparable energies. Then in order to account for the low activation energy other charged states must be involved. The ionization energy of Cd^+ has so far not been reported, but it should be small as can be expected for A^+ levels.²⁶ Then it would be possible to understand the static interactions and its temperature dependence as arising from the presence of more than two holes bound to the cadmium acceptor. Holes are produced by electron capture decay. This kind of AE must be distinguished from the one assigned here to indium in interstitial sites. In that case the holes remain in the electronic shell of the probe atom during the lifetime of the intermediate state of the γ - γ cascade. However, in the case of In in substitutional sites the sp^3 bonds are complete and holes several lattice parameters away cause a small EFG.

In order to check this explanation similar experiments in semiconductors with different dielectric properties are required. In that case the cadmium levels should be situated at different energies and the EFG produced by charges in a distance of some lattice parameters should also be different. These experiments are in progress.

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