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Self-interstitial shallow-donor complexes in silicon: An electron-paramagnetic-resonance study

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An electron-paramagnetic-resonance (EPR) study on silicon samples quenched after diffusion of gold (or platinum) from a metallic layer on the surface results in the presence of two types of paramagnetic centers replacing the donor P center. According to the analysis these centers consist of a P donor with a self-interstitial in either the nearest-neighbor (NN) or next-nearest-neighbor (NNN) position. This result supports the early assumption that large amounts of self-interstitials are produced by such a treatment. P (or As) impurities act as stabilizing entities. This is verified by a modified donor hyperfine interaction which exhibits a strong temperature dependence. The results are explained by strain fields and a chemical shift caused by a self-interstitial neighboring a phosphorus atom. Two configurations of this complex differ only slightly in energy. [S0163-1829(98)04516-0]

I. INTRODUCTION

High mobility of self-interstitials and their low concentration in thermal equilibrium near room temperature and at a few hundred °C provide rather low concentrations of untrapped intrinsic defects even in quenched silicon if before quenching the defects were in thermal equilibrium.[1,2] On the other hand, it is known that oxidation and formation of metal silicides at the surface introduce nonequilibrium concentrations of self-interstitials into the bulk which exceed the equilibrium values by orders of magnitude. Corresponding results have been reviewed.[3,4]

The detection of self-interstitials is difficult. It was done for example by transmission electron microscopy (TEM) investigation of extended defects formed near 800 or 900 °C in Si doped with gold[5,6] or nickel[7] in a corresponding manner. Another hint at a supersaturation with self-interstitials emerged from electron-paramagnetic-resonance (EPR) measurements on Si doped with Pt.[8] A Fermi level shift was observed after a suitable annealing of the samples, and preliminary experiments indicated a modified hyperfine structure of shallow donors. The present work is concerned with a thorough investigation of the latter phenomenon.

The stability of intrinsic radiation defects is observed when they are trapped at extrinsic defects. One should mention as examples the EPR detection of interstitial carbon[9] and aluminum[10] and spreading resistance measurements which suggest a deactivation of P donors by ion-generated self-interstitials.[11]

Phosphorus is one of the most important shallow donors in silicon device processing technology. EPR properties of phosphorus have been extensively studied.[12–16] A good theoretical description is obtained by using the effective mass approximation[17] under consideration of the valley orbit splitting.[18,19]

The EPR detection of shallow donors depends on the position of the Fermi level and consequently on the content of deep levels which are introduced by doping with platinum or gold.

Platinum is a suitable dopant to achieve fast carrier recombination. Pt usually occupies substitutional lattice sites in Si and has three levels in the band gap: $\mathrm{Pt}_s(-/0)$ with $E_c-0.243$ eV, $\mathrm{Pt}_s(0/+)$ with $E_v+0.330$ eV, and $\mathrm{Pt}_s(+/++)$ with $E_v+0.067$ eV.[20,21] The only charge state which can be observed by EPR is Pt^-.[22–24] The microscopic structure of this defect can be described by the vacancy model.[25]

Gold as platinum is a lifetime limiter. Substitutional Au has two levels in the band gap: $\mathrm{Au}_s(-/0)$ with $E_v+0.62$ eV and $\mathrm{Au}_s(0/+)$ at $E_v+0.35$ eV.[26–28] The microscopic structure of isolated Au is still under discussion. The reason for this is the missing of clear EPR data of the isolated substitutional Au defect. In a recent paper a vacancy-model for substitutional Au was developed.[29]

The aims of this paper are the following. First, further arguments are offered for the assumption that doping with gold or platinum from the surface introduces a strong supersaturation of self-interstitials homogeneously into the bulk of a Si sample. Up to now the assumption has not been generally accepted. Secondly, it is shown that one way of trapping self-interstitials is the formation of shallow donor–self-interstitial complexes. These defects have been stable at room temperature for years.

II. EXPERIMENT

A. Sample preparation

The usual starting materials were both Czochralski- (Cz) and float zone- (FZ) silicon doped with phosphorus or arsenic. Typical donor concentrations were 1×10^{15} cm^{-3}–3×10^{16} cm^{-3}. All materials had a negligible degree of compensation.

Samples of $3\times3\times10$ mm^3 size were covered with Pt or Au and annealed at 1200–1300 °C in Ar atmosphere or in vacuum. During the long time of diffusion (from several hours up to three days in the case of Pt) the samples were protected from contamination by keeping them in a double-walled quartz tube with a chlorine-containing gas flow in the outer tube. After quenching to room temperature and careful removing a 100 μm thick surface layer EPR spectra were recorded. We will label such samples in the following as quenched after diffusion from a covered surface. For comparison, the same investigation was performed after once more annealing for a few days at 1200–1300 °C in vacuum, now without a metallic or reaction layer on the surface. We will refer to such samples as quenched after diffusion from an uncovered surface.

In some cases it was necessary to check the homogeneity or a possible local distribution of paramagnetic defects. This was performed by cutting the sample or by stepwise mechanical or/and chemical removing of layers. We carefully avoided to influence the defect distribution by the mechanical or chemical procedures.

B. EPR measurement

For the EPR experiments a Bruker spectrometer ESP 300 operating at 9 GHz was used together with a continuous flow cryostat of Oxford Instruments. In photo-EPR experiments the sample positioned inside the quartz walls of the cryostat was illuminated by intense band-gap light or nearly monochromatic light through a quartz lens and the grid of the Bruker universal rectangular resonator. The measurements were carried out in the temperature range of 15–30 K.

III. RESULTS

We shall further present the results of EPR measurements of the phosphorus signal as a function of the sample preparation.

A. As-grown silicon: The donor P centers

We investigated as-grown silicon for comparison with the $5d^n$ doped material. The results agree well with those known from the literature.[14] Essential relations are summarized in this subsection for use in the discussion of Sec. IV B. At low temperatures the phosphorus donor electron is bound to the nucleus. In this neutral charge state the P defect is paramagnetic. The EPR spectrum of shallow donors is characterized by isotropic Zeemann and hyperfine interactions according to the spin Hamiltonian

$$\mathcal{H}=g\mu_B\mathbf{BS}+A\mathbf{SI}. \tag{1}$$

Here μ_B is the Bohr magneton and $\mathbf{B}$ the magnetic field. The g value of P donors is $g=1.9985$.[12] The EPR spectrum exhibits two lines due to the hyperfine interaction $A\mathbf{SI}$ between the nuclear spin $\mathbf{I}$ ($I=1/2$) of the phosphorus nucleus and the electron spin $\mathbf{S}$. At 1.3 K the hyperfine parameter A is $A_0=39.2\times10^{-4}\ \mathrm{cm}^{-1}$. The hyperfine splitting K, i.e., the distance between the two lines, is

$$K=\frac{hc}{g\mu_B}A, \tag{2}$$

where h is Planck's constant and c the light velocity. In as-grown materials and at temperatures $\lesssim 15$ K the hyperfine splitting is

$$K_0=\frac{hc}{g\mu_B}A_0=4.2\ \mathrm{mT}. \tag{3}$$

The line shape is Gaussian due to hyperfine coupling of the donor electron with the ^{29}Si nuclei randomly distributed on the lattice. Increasing the temperature results in a smaller hyperfine interaction with the P nucleus (Fig. 1). This effect is attributed to the excitation of electrons from the donor ground state to excited states.[14]

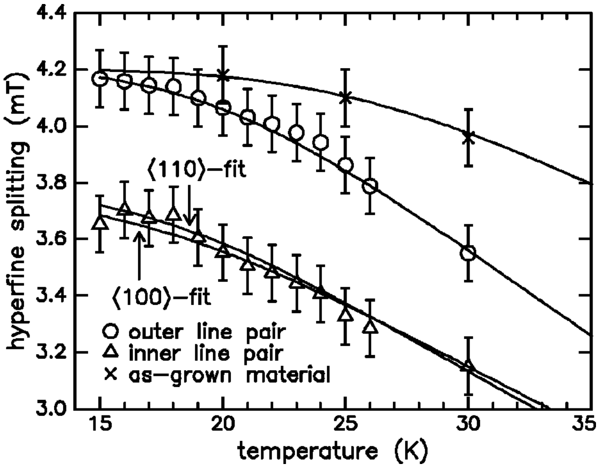

FIG. 1. Temperature dependence of the phosphorus hyperfine splitting. Crosses represent the results of experiments with as-grown material. The solid line through these points is calculated from Eq. (6) with $K_0=4.2$ mT and an average valley-orbit splitting of $6\Delta E=11.6$ meV obtained from the work of Lépine (Ref. 14). Circles and triangles represent the results of experiments with Au doped Si. The solid lines through these points are obtained by a calculation using the values given in Sec. IV B.

In the effective-mass theory one obtains a sixfold degenerate phosphorus ground state with $1s$ hydrogenlike properties. When one takes the tetrahedral symmetry of the true impurity potential into consideration, then these states are split into a singlet A_1, a doublet E, and a triplet T_2.[18,19] Doublet and triplet states are very close to one another. The level of the doublet state is $\Delta E_{E,T_2}=-2\delta\Delta=1.35$ meV above that of the triplet state. These doublet states are separated from the A_1 ground state by the valley-orbit interaction of $6\Delta=13.05$ meV.[14,30] The parameter δ describes the splitting of doublet and triplet in energy values of 2Δ.

In the system under consideration the Fermi-Segrè interaction is dominant. Electrons in the excited states E and T_2 have zero density at the donor nucleus and consequently show no hyperfine interaction. Electrons in the ground state A_1 exhibit a hyperfine splitting of $K_0=4.2$ mT. At elevated temperatures the ground state A_1 and the excited states E, T_2 are populated by electrons. Other excited states lie well above these $1s$ states and can be neglected. We call the number of donors in the ground state n_0, the numbers in an excited state n_j $(j=1–5)$. If the splitting between the triplet level and the doublet level is neglected one obtains according to the Boltzmann distribution

$$\frac{n_j}{n_0}=\exp\left(-\frac{6\Delta}{kT}\right) \tag{4}$$

with the valley-orbit splitting of 6Δ and the Boltzmann constant k. Therefore, the probability w_0 to find a donor in the ground state is

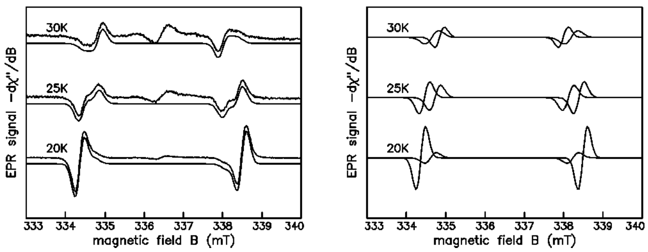

FIG. 2. EPR spectra of the P-type centers in a Au-doped sample at three different temperatures. In the left part of the figure the upper spectrum of each pair is the measured spectrum. The lower spectrum was calculated by adding two pairs of Gaussian shaped lines, represented in the right part of the figure separately.

$$w_0(T)=\left[1+\sum_{j=1}^{5}\exp\left(-\frac{6\Delta}{kT}\right)\right]^{-1}=\left[1+5\exp\left(-\frac{6\Delta}{kT}\right)\right]^{-1}. \tag{5}$$

If the transition rates between the ground state and excited states are sufficiently large, the resonance frequency detected in the EPR measurement is the average value of the frequencies in the occupied levels weighted by the relative populations in these levels.[14] Therefore, the hyperfine splitting of P donors in as-grown Si at temperature T is

$$K(T)=K_0 w_0(T). \tag{6}$$

In Fig. 1 the theoretical dependence of the hyperfine splitting in as-grown material Eq. (6) is compared with the experimental values.

B. Silicon doped with Au or Pt

Samples were quenched after diffusion of Au or Pt from a covered surface (see Sec. II A). For example, we consider a sample of 1×10^{16} P/cm^3 starting material doped with Au. Due to the Au saturation concentration of $\sim10^{17}$ cm^{-3} the samples contain more Au than P. Consequently at the temperature of the EPR measurement the P donor electrons are transferred to the Au acceptors. The P donors are in the positive charge state and cannot be detected by EPR in the dark. Illumination with band gap light produces electron hole pairs. The electrons can be captured by positive P donors. Therefore, a small part of the P donors become paramagnetic under illumination.

The phosphorus centers show modified EPR properties in contrast to the measurements described in Sec. III A. First, two pairs of EPR lines were detected: an inner line pair and an outer one. Secondly, increasing the temperature results in a strong decrease of the hyperfine splittings for both line pairs.

The outer pair of lines [label (a)] as well as the inner one [label (b)] will be attributed to a self-interstitial related (SIR) complex containing one P atom. Therefore, they are called SIR-1P(a) and SIR-1P(b), respectively. Figure 2 presents the EPR spectra dependence on the temperature. Each of the line pairs is governed by an isotropic spin Hamiltonian as in Eq. (1) with the corresponding label as a superscript:

$$\mathcal{H}^{(j)}=g^{(j)}\mu_B\mathbf{B}\mathbf{S}^{(j)}+A^{(j)}\mathbf{S}^{(j)}\mathbf{I}^{(j)},\quad j=a,b. \tag{7}$$

Within the margins of error, the g values coincide with that of P in as-grown Si:

$$g^{(a)}=g^{(b)}=1.9985\pm0.00004.$$

The hyperfine splittings $K^{(j)}$ are related to the parameters $A^{(j)}$ as in Eq. (2):

$$K^{(j)}=\frac{hc}{g\mu_B}A^{(j)}. \tag{8}$$

For various temperatures the values of $K^{(j)}$ were obtained by a deconvolution of the measured spectra (Fig. 2). In Fig. 1 the dependencies are compared with that of the P centers in as-grown Si.

At 20 K the SIR-1P(a) lines have a width of ≈0.25 mT, which is comparable to the value of P in as-grown silicon. The linewidth of SIR-1P(b) is with a value of ≈0.3 mT slightly larger.

The change in the EPR properties is not caused by the light illumination. This can be seen from experiments with as-grown material: Light illumination does not change the hyperfine splitting of the P centers in as-grown samples.

Doping with Pt instead of Au produces the same changes in the EPR properties of P centers. They are stable at room temperature. Samples stored for more than one year gave the same results.

C. Quenching after diffusion from an uncovered surface

After the Pt or Au doping procedure and the measurements described in Sec. III B the samples were once more annealed ~90 h at 1200 °C now with an uncovered surface and quenched to room temperature. Because of the position of the Fermi level the EPR spectra of the P donors were detected only under illumination. The P donors show the same properties as in as-grown material (Sec. III A).

D. Quenching after diffusion from a partly covered surface

In this type of experiment the as-grown sample of $3\times3\times10$ mm^3 size was doped from only one of the large faces while the other five faces were uncovered. After 3 days of diffusion the result was the same as in the case of a completely covered surface. The sample showed a homogeneous distribution of modified P donors.

E. Other shallow donors

The experiments described in Secs. III A and III B were also performed on silicon doped with As instead of P. The arsenic doped silicon quenched after diffusion from a Au or Pt covered surface shows similar changes in the EPR properties as in the case of P. In contrast to the P centers the substructure of the lines due to As was unresolved at all temperatures. Due to difficulties in separating the lines by deconvolution an exact evaluation was not performed.

IV. DISCUSSION

A. Self-interstitial injection by Pt or Au doping from the surface

In this section we shall present arguments that the changes in the EPR properties of the shallow donors described in Sec. III are due to the introduction of self-interstitials into the crystal.

Only after doping with Pt or Au from a covered surface a modified shallow donor signal is observed (Secs. III B, III D, and III E). The fact that the P hyperfine structure and its temperature dependence are equal for doping with Pt or Au suggests that in both cases the P donors are influenced by the same defect. Previous results, mentioned in the beginning of Sec. I, suggested that the doping treatment described above produces a high degree of supersaturation with self-interstitials.[5,6,31] This assumption is supported by the experiments reported in Sec. III C. After subsequent annealing of an uncovered sample at 1200 °C and quenching to room temperature the usual behavior of P is observed. Contaminants such as iron or chromium would not leave the sample in the second annealing step. Therefore, one can conclude that intrinsic defects are responsible for the change of the P properties.

Samples of as-grown silicon quenched from 1200 °C to room temperature do not exhibit modified EPR spectra of the P donors. That means, the concentration of self-interstitials exceeds the value of thermal equilibrium at room temperature less than in the case of samples doped with Au or Pt; in this sense, the degree of supersaturation with self-interstitials is low.

The mechanism of self-interstitial production by Au or Pt doping is still under discussion. At temperatures above 900 °C the diffusion of Au and Pt is determined by the kick-out mechanism.[3] This means that a Pt as well as a Au atom changes its lattice site from interstitial to substitutional and vice versa by creating or annihilating a self-interstitial according to

$$\mathrm{Pt}_i \rightleftharpoons \mathrm{Pt}_s + \mathrm{Si}_i\,. \tag{9}$$

The corresponding relation is valid for Au. As after diffusion of a $5d^n$ atom from the surface layer finally a substitutional lattice site is occupied by the metal ion, one self-interstitial is generated.

However, some experiments indicate a self-interstitial concentration exceeding that of the $5d^n$ atoms.[5] This phenomenon was attributed to the creation of self-interstitials by a surface reaction.

The experiments mentioned in Sec. III D suggest that the annihilation of self-interstitials at the uncovered surface is a slow process compared to their formation at the reaction layer and their diffusion through the bulk of our samples. Therefore, quenching from a partly covered surface produces a homogeneous distribution of self-interstitials trapped at P.

B. Models of the phosphorus—self-interstitial complexes

In Secs. III B and III D we described a strongly modified P hyperfine structure. In this subsection models will be discussed which are compatible with the experimental data. The deconvolution of the EPR spectra does not yield a contribution of unperturbed P atoms with the properties of donors in as-grown Si. We offer two possible reasons: First, all phosphorus donors are influenced by self-interstitials. We mention the paper which reports a deactivation of P donors attributed to ion-generated self-interstitials.[11] Secondly, due to differences in the capture cross sections only the P donors influenced by self-interstitials are populated by electrons. From our experimental facts it is not possible to decide between these possibilities.

The fact that two narrow lines were detected indicates the existence of two distinct configurations of self-interstitials neighboring the P donors. A random distribution of self-interstitials can be excluded because of the high mobility of untrapped interstitials. Some kind of binding is necessary to explain the stability of the self-interstitials over years. Contrary to these close pairs is the behavior of distant iron—shallow-donor pairs.[32] They are stable only for several days. In that case the interaction is not sufficient for keeping the interstitial iron in the lattice.

In a simple model the modifications in the EPR properties of P can be explained by the assumption of two pair configurations: The self-interstitial bound to the P donor may be in a nearest-neighbor and in a next-nearest-neighbor position. The binding energies differ only slightly, which explains their different intensity ratio at various temperatures. Figure 2 shows on the right that at 30 K both configurations are nearly equally probable, whereas at 20 K the configuration causing the outer line pair is preferred. It will be shown below that the outer line pair is attributed to a strain source in a $\langle 111\rangle$ direction, i.e., to the nearest-neighbor pair. The modified hyperfine splitting and its temperature dependence can be explained by two differences with respect to donors in as-grown Si: The valley orbit splitting is smaller, and there are strain fields caused by neighboring self-interstitials.

The valley orbit or chemical splitting (6Δ) depends on the chemical nature of the defect. Therefore, it is not surprising to find differences in the valley orbit splitting of P in as-grown samples and the P influenced by self-interstitials. The stronger decrease in the hyperfine splitting with increasing temperatures is assumed to result from a smaller 6Δ value for both the inner and the outer line pair.

The second effect of the self-interstitials neighboring the P donors is a strain field. The hyperfine structure of donor EPR spectra in samples subjected to uniaxial stress was thoroughly investigated in the paper of Wilson and Feher.[13] The effect of strain strongly depends on its direction with respect to the crystal axes. Strain in a $\langle 111\rangle$ direction does not change the hyperfine interaction of the P ground and excited states. Strain in other directions causes a mixing of excited states and the ground state and in consequence a modification of the hyperfine interaction.

Taking into account these considerations we can describe the outer line pair [SIR-1P(a)] by a self-interstitial neighboring the P donor in a $\langle 111\rangle$ direction. The valley orbit splitting is partly quenched which causes a stronger decrease in the hyperfine interaction with increasing temperature due to the smaller potential barrier between ground and excited states compared to P in as-grown material. On the other hand, at low temperatures $\lesssim 15$ K when the electrons are in the ground state, the hyperfine splitting of the outer line pair is approximately identical to the splitting of noninfluenced P donors. This means that there is no mixing of excited states and ground state, which is true for strain in a ⟨111⟩ direction.

The inner line pair [SIR-1P(b)] can be described by a self-interstitial neighboring the P donor in a ⟨100⟩ or ⟨110⟩ direction. As in the case of the outer line pair, the valley orbit splitting is partly quenched which explains the strong temperature dependence of the hyperfine splitting. At low temperatures $\lesssim$15 K the inner line pair exhibits a smaller hyperfine interaction compared with the outer line pair. This means that states with smaller hyperfine interaction are mixed to the ground state. This mixing of states is caused by the strain field of the self-interstitial.

A quantitative treatment is obtained by using the strain theory of Wilson and Feher.[13] By using the deformation potentials Ξ_u for pure shear and Ξ_d for dilatation it is possible to calculate energy levels and wave functions under the influence of strain in the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions. To measure the strain Wilson and Feher used the dimensionless so called valley strain

$$x=\frac{\Xi_u}{3\Delta}[\epsilon_{zz}-(\epsilon_{xx}+\epsilon_{yy})/2]. \tag{10}$$

ϵ_{xx}, ϵ_{xx}, ϵ_{xx} are components of the strain tensor

$$\epsilon_{ij}=\frac{1}{2}\left(\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right) \tag{11}$$

and **u** is the displacement vector. In the isotropic continuum approximation a self-interstitial at point **r** produces a displacement field at the origin, i.e., at the site of the phosphorus donor

$$\mathbf{u}(\mathbf{r})=-a\frac{\mathbf{r}}{r^3} \tag{12}$$

with a as the elastic strength of the self-interstitial.[33] From Eqs. (10), (11), and (12) we obtain $x=-a\Xi_u/(r^3\Delta)$ for a self-interstitial located at **r** in a ⟨100⟩ direction, $x=a\Xi_u/(2r^3\Delta)$ for a self-interstitial located at **r** in a ⟨110⟩ direction, and $x=0$ for a self-interstitial located in a ⟨111⟩ direction.

The result of our quantitative treatment is the fit represented in Fig. 3. The ground state A_1 and one of the excited E states are mixed under the influence of strain. The corresponding energy levels show a nonlinear dependence on the valley strain x. All other states remain unchanged. The corresponding energy levels show a linear dependence on the valley strain.

We fitted the calculated hyperfine splittings to the experimental data by varying the valley-orbit splitting Δ and the valley strain x. For simplicity we assumed that the ratio δ of the doublet-triplet splitting to the valley-orbit splitting is the same as in as-grown Si. As in Sec. III A, the temperature dependence of the hyperfine splitting for a given value of the valley strain x was determined by averaging the hyperfine splittings of all levels weighted by their thermal populations. Contrary to the case of unstrained donors, not only the ground state but also one of the excited states exhibits a hyperfine splitting. This state is labeled in Fig. 3. The hyperfine splittings of both the ground state and the excited state, calculated for the appropriate value of the valley-orbit splitting, are represented in the upper part of Fig. 3.

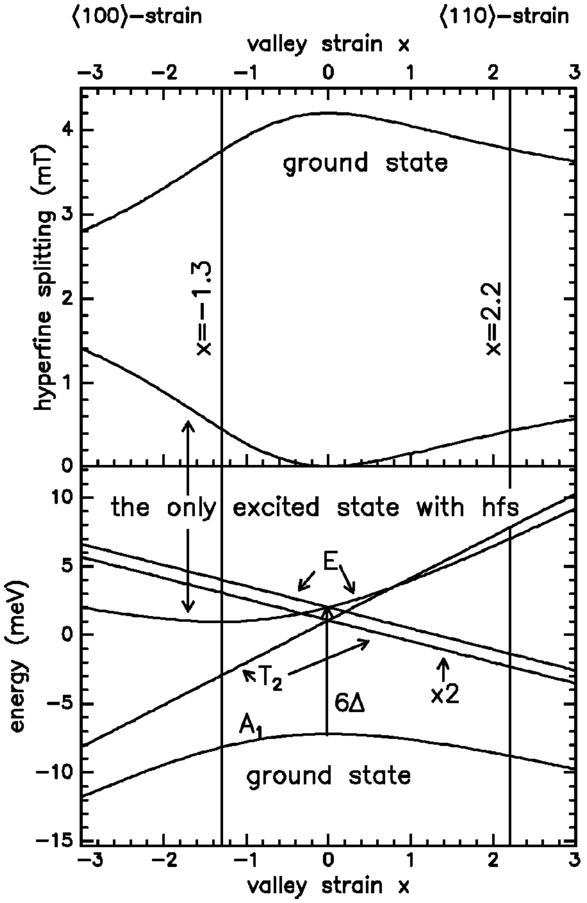

FIG. 3. Energy levels and hyperfine interaction in dependence on the valley strain x calculated from the theory of Wilson and Feher (Ref. 13) with the parameters: $6\Delta=9.2$ meV and $\delta=-0.31$. The lower part of the figure shows the energy levels. The upper part of the figure shows the hyperfine splitting for the ground state and the only excited state with a hyperfine splitting (HFS). All other states have no hyperfine interaction.

One obtains the following fit parameters. Outer line pair [SIR-1P(a)]: The self-interstitial is located in a ⟨111⟩ direction with a valley orbit splitting $6\Delta\approx9.2$ meV. Due to the strain in ⟨111⟩ direction there is no effect on the energy levels and the wave functions. The direction corresponds to a nearest-neighbor position.

Inner line pair [SIR-1P(b)]: One solution is to assume the self-interstitial in a ⟨100⟩ direction with $6\Delta\approx9.2$ meV and $x\approx-1.3$. We assume that the incorporation of a self-interstitial causes compressional strain. For this direction compression is described by negative values of x. This direction corresponds to a next-nearest-neighbor position of the self-interstitial. Another possible solution is obtained with $6\Delta\approx9.5$ meV and $x\approx2.2$. Changing the sign of x means changing the direction of uniaxial stress from ⟨100⟩ to ⟨110⟩.[13] Therefore this solution describes a compression caused by a self-interstitial in a ⟨110⟩ direction.

Theoretical curves using these values are shown in Fig. 1. They agree well with the measured values. This model supports the assumption that it is a self-interstitial which neighbors the P donor because the silicon self-interstitial is known to be sufficiently mobile even at low temperature for changing its lattice site.

V. CONCLUSIONS

As previously inferred from the detection of extended defects by TEM and from Fermi level shifts detected by EPR, quenching after diffusion of gold or platinum from a metallic layer on the surface produces a high degree of supersaturation with self-interstitials. However, at least the mechanism of formation is still in question. The modified EPR hyperfine structure of shallow donors gives another strong argument for the formation of intrinsic defects by this treatment.

A second conclusion concerns the stabilization of self-interstitials. It is known that self-interstitials generated by electron irradiation can be trapped by extrinsic defects such as carbon, boron, or aluminum. It was shown now that also self-interstitials created by doping with Pt or Au from a covered surface are stable in the bulk for a long time in the order of years.

One way of trapping is the formation of complex defects with shallow donors. The EPR hyperfine structure of modified P donors was investigated. Its magnitude and temperature dependence can be explained by the assumption of a self-interstitial–phosphorus pair. The nearest-neighbor configuration is slightly energetically preferred to the next-nearest-neighbor configuration.

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