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Copper-related defects in silicon: Electron-paramagnetic-resonance identification

P. N. Hai
Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstraat 65-67, NL-1018 XE Amsterdam, The Netherlands
and Faculty of Physics, National University of Hanoi, 90 Nguyen Trai Street, Hanoi, Vietnam

T. Gregorkiewicz and C. A. J. Ammerlaan
Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstraat 65-67, NL-1018 XE Amsterdam, The Netherlands

D. T. Don
Faculty of Physics, National University of Hanoi, 90 Nguyen Trai Street, Hanoi, Vietnam

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In this paper the observation of two electron-paramagnetic-resonance spectra, both present in p-type silicon samples after doping with silver, is reported. The two centers show a symmetry lower than cubic and have an effective electron spin $S=1/2$. In view of the detected hyperfine interaction with nuclear spins $I=3/2$, the spectra are shown to be related to a contaminant introduced into the samples during the diffusion process. By analysis of the features of the spectrum and the defect formation, a spectrum of the tetragonal symmetry, labeled Si-NL58, is identified as a copper-copper pair in a negatively charged state. The second spectrum, labeled Si-NL59, is attributed to a complex containing one copper atom. [S0163-1829(97)01832-8]

I. INTRODUCTION

Copper, silver, and gold in the group 1B of the periodic table receive much interest as deep-level dopants in silicon. All elements have high diffusivity and solubility, especially copper. The available data revealed that diffusion of copper in silicon is enhanced by application of an electric field, indicating diffusion of a positively charged interstitial copper ion Cu^{+},[1] in agreement with solubility results.[2] It was also shown that the diffusing Cu^{+} vanishes during quenching, partly due to the formation of precipitates.[3]

Whereas silver and gold have been used as active elements in the manufacturing of some special silicon-based devices, copper is considered to be a feared and unavoidable contaminant in silicon. It follows from the fact that copper is easily introduced into silicon, especially into p type, by high-temperature heat-treatment processes,[4] chemomechanical polishing,[5,6] etc. Deep energy levels introduced in the band gap of silicon due to the presence of copper may act as traps for carriers or as recombination centers and thus degrade electrical properties of p-n junction devices. Also the precipitation of copper reduces production yields of silicon-integrated circuits. In addition to these effects it has been established that copper can passivate shallow acceptors in silicon. Using a combination of capacitance-voltage (C-V), secondary-ion mass spectroscopy and deep-level transient spectroscopy (DLTS) measurements Aboelfotoh and Svensson[7] have found that passivation of the boron acceptors occurs after copper deposition, and suggested that the fast-diffusing interstitial Cu^{+} passivates the electrical activity of boron by the formation of neutral complexes, in agreement with theoretical predictions.[8] Possibly, this mechanism can be extended to the case of other shallow acceptors (Al, Ga, In), since their passivation by copper has also been reported.[5] Such a passivation process affects the electrical parameters of silicon devices considerably, and some copper gettering procedures have been proposed in order to improve device performance.[9] Therefore understanding of the properties of copper and copper-related defects plays an important role in both applied and fundamental materials science.

Due to its low activation energy for migration [$Q=0.43$ eV (Ref. 10)], copper is mobile even at room temperature and is readily involved in reactions with native defects and impurities to create pairs and complexes. This fact is reflected via a variety of copper-related centers in silicon established so far by Hall, DLTS, photoluminescence (PL) and electron-paramagnetic-resonance (EPR) measurements.

DLTS measurements revealed several Cu-related deep levels. However, a considerable discrepancy still exists among the published data as to the number of Cu-related deep centers and their energy levels.[11–13] Also, no energy level could so far be assigned to an isolated copper center. It seems that the data reported in each study depend very much on conditions of sample preparation, e.g., the details of cooling procedure. The most commonly reported levels in copper-doped silicon are a deep donor at $E_v+0.23$ eV, a deep acceptor level at $E_v+0.42$ eV and another deep donor level at $E_v+0.1$ eV, usually associated with a Cu-Cu pair.[13] PL measurements on silicon contaminated or intentionally doped with copper revealed some luminescent bands with intense zero-phonon lines at 1014.7 meV (Refs. 12,14) and 943.7 meV.[4] Just recently a PL band has been observed in copper-doped p-type silicon.[15] Through extensive studies[14,16] the PL band with the zero-phonon line at 1014.7 meV was attributed to a $\langle 111\rangle$-axial Cu-Cu pair. It makes the pair very interesting for further investigations. EPR studies identified copper in various Cu-related complexes in silicon, for example Mn-Cu, Cr-Cu and Zn-Cu centers.[17–20] These results support the notion that copper can easily involve itself in complex formation. Structural information about copper in the silicon lattice can be obtained from these studies. However, until now, no EPR fingerprints of an isolated copper or of an interesting PL-detected Cu-Cu pair have been found. In this sense the structural picture of copper in silicon is still incomplete. In contrast, clear information on the isolated silver, which has a very similar electron configuration to copper, has been recently acquired.[21,22]

In this paper we present the EPR results obtained in samples doped with silver at high temperature. Besides the interstitial iron Fe_i^0 and the Ag-related Si-NL56 center,[22] two other EPR spectra have been observed. On the basis of the spectral features the relevant defects are attributed to the copper contaminant.

II. EXPERIMENTAL CONDITIONS

The starting materials used in this study were boron-doped, dislocation-free, float-zone silicon crystals with a room-temperature resistivity in the range from 1 to 1000 Ω cm. The dimensions of samples were typically $1\times1\times15$ mm^3 with the length along the $[0\bar{1}1]$ crystal direction. The samples were diffused with natural or monoisotopically enriched silver in a closed ampoule in a dry or wet argon atmosphere. Details of the diffusion and annealing processes can be found elsewhere.[22] In the current case the fast quenching to room temperature was performed by rapidly dropping the closed ampoule containing the sample in water.

The EPR measurements were performed with a superheterodyne spectrometer at the microwave frequency of about 22.9 GHz (K band) and tuned to dispersion. The sample was mounted with the $[0\bar{1}1]$ direction perpendicular to the plane of rotation of the magnetic field. Most measurements were taken at liquid-helium or lower temperature.

III. RESULTS AND DISCUSSION

In the fast-quenched high-resistivity p-type silicon samples doped with silver, besides the interstitial iron Fe_i^0 and the Si-NL56 center,[22] two other paramagnetic spectra were observed. The typical spectra are depicted in Fig. 1(a). One of them, named Si-NL58, gives a spectrum consisting of seven nearly equally spaced components with a small anisotropy. The other, labeled as Si-NL59, contains four also almost equidistant components. The intensity of the Si-NL59 spectrum in this case is smaller than that of the Si-NL58. Further, the presence of both spectra in samples is independent: in a very rapidly quenched sample no Si-NL58 spectrum was observed, besides the Si-NL56, Si-NL59, and Fe_i^0 spectra, as shown in Fig. 2. These facts show that the two spectra belong to different defect centers. In what follows both new spectra will be discussed separately.

A. Si-NL58 center

The identical spectrum appears in samples doped with either monoisotopically enriched $^{107}\mathrm{Ag}$ and $^{109}\mathrm{Ag}$ silver, as shown in Figs. 1(a) and 1(b), respectively, or with natural silver. The spectral intensity is bigger if the ambient of (heavy) water vapor was used during the diffusion process, but the formation of the Si-NL58 center does not require its presence. Therefore silver and hydrogen (deuterium) can be excluded from the structure of this center.

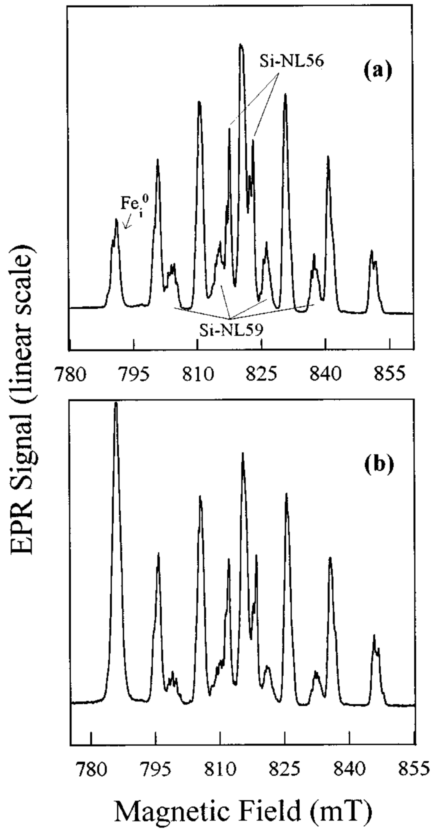

FIG. 1. EPR spectra observed with magnetic field in the $(0\bar{1}1)$ plane at an angle of 40° away from the [100] crystal direction for a sample doped with (a) $^{107}\mathrm{Ag}$ (microwave frequency $\nu=22.9224$ GHz); (b) $^{109}\mathrm{Ag}$ ($\nu=22.7818$ GHz) silver isotopes. Temperature $T=4.2$ K.

The relative intensity of individual components of the Si-NL58 spectrum is roughly equal to 1:2:3:4:3:2:1 (the simultaneous presence of Fe_i^0 gives an additional intensity to the outermost component in the low magnetic field). The observed structure is characteristic for a pair of two equivalent impurity atoms which have a nuclear spin $I=3/2$. A contamination impurity must be responsible for the observed hyper-

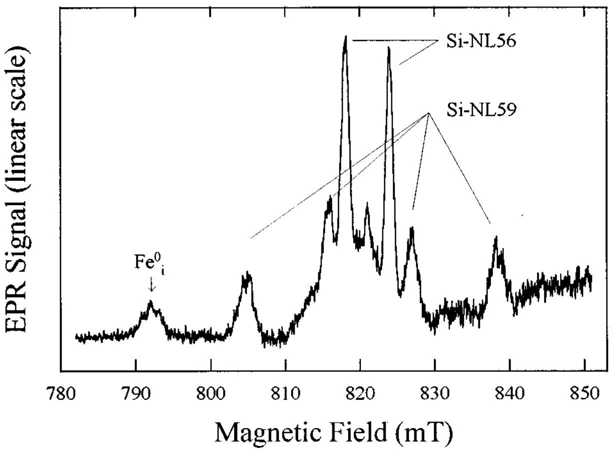

FIG. 2. EPR spectra observed at an angle of 40° away from the [100] crystal direction for a sample doped with natural silver (microwave frequency $\nu=22.9441$ GHz). Temperature $T=4.2$ K.

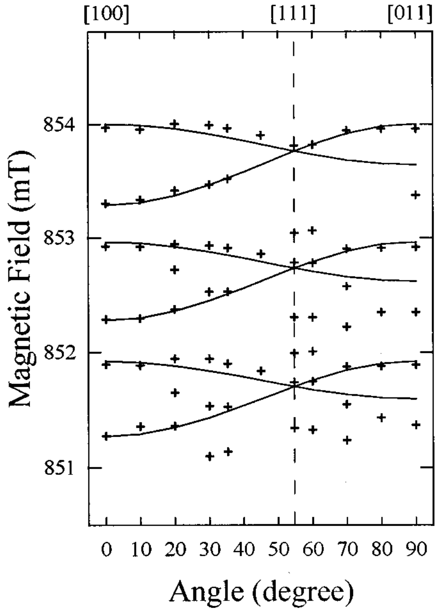

FIG. 3. Angular dependence for rotation of magnetic field in the $(0\bar{1}1)$ plane of the outermost component on the high magnetic-field side of the Si-NL58 spectrum at the microwave frequency $\nu = 22.9484$ GHz. Temperature $T = 1.7$ K.

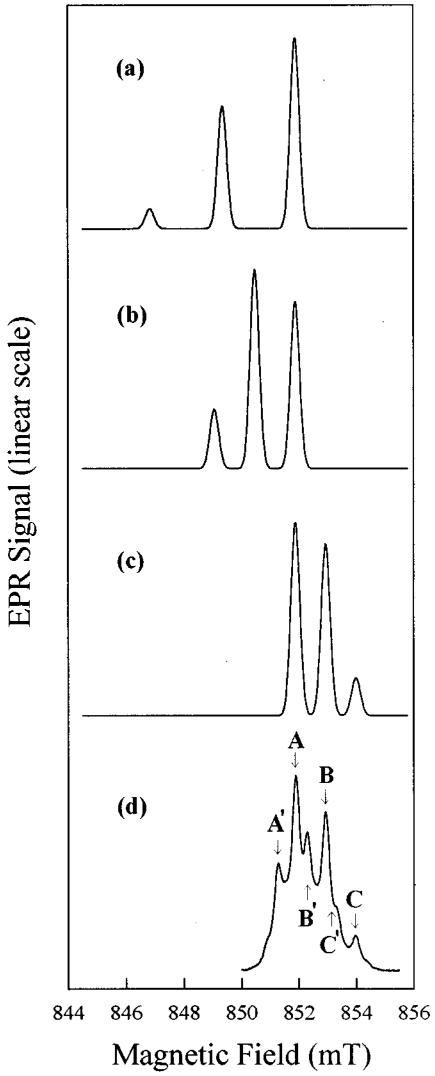

FIG. 4. Simulated EPR spectrum for the outermost component in the high magnetic field of the Cl-Cl pair (a), Ir-Ir pair (b) and the Cu-Cu pair (c) at the microwave frequency of 22.9484 GHz, calculated by superposing Gaussian lines of a width of 0.3 mT. The experimental spectrum at the [100] crystal direction is also included (d), where A, B, and C denote EPR lines in orientation 1; and A', B', and C' are for orientation 3.

fine splitting. The spectrum broadened and its intensity decreased remarkably when raising the temperature from $T = 1.7$ K to higher temperatures. The intensity of the spectrum is smaller around the [111] crystal direction. Except for the outermost ones, the components are not well resolved due to overlap of the hyperfine structure with the small anisotropy of the whole spectrum. Thus the full angular dependence of the outermost component in the high magnetic field was carefully recorded at $T = 1.7$ K, as given in Fig. 3. Although there is a partial overlap between EPR peaks within the component, the tetragonal symmetry could be established as the most probable. Generally speaking, a paramagnetic center of the tetragonal symmetry will form three distinguishable EPR orientations; however, the resonance of two of them coincides when the magnetic field is in the $(0\bar{1}1)$ plane, leading to the typical EPR intensity ratio of 2:1, associated with the orientations regularly denoted as 1 and 3. For the outermost component in the EPR orientation 1 the hyperfine lines are labeled A, B, and C for the three distinct pairs with a different isotope composition, whereas for the orientation 3 they are labeled A', B', and C'. By considering the hyperfine lines in the orientation 1, i.e., A, B, and C, whose intensity is less affected by the line overlap than that in orientation 3, the experiment revealed that their intensity ratio is $A{:}B{:}C \approx 5.5{:}4.5{:}1$, as depicted in Fig. 4(d). The rather well-resolved features in this component and the whole spectral configuration reflect the fact that the responsible impurity element must naturally contain two isotopes only where both have the same nuclear spin $I = 3/2$, their abundance ratio is in the range of 2 and their magnetic moments, which naturally relate to the hyperfine splittings, should not be very different. Taking into account the aforementioned requirements, in principle, several elements could be considered: chlorine with ^{35}Cl and ^{37}Cl, copper with ^{63}Cu and ^{65}Cu and iridium with ^{191}Ir and ^{193}Ir. One can note from the literature that copper is the major unavoidable contaminant, while the other candidates have to be purposefully introduced into silicon during the diffusion process. For a pair of two identical atoms the line intensities depend only on the abundance of the isotopes and the line positions relate naturally to the nuclear magnetic moments of the isotopes. Therefore a theoretical calculation of the line intensities and positions of the pairs by superposing the EPR line with a Gaussian shape of a width of 0.3 mT as observed was performed for all three cases using the nuclear magnetic moment values for these elements from Fuller's table.[23] The calculated intensity composition for three lines of the orientation 1 in the outermost component together with the parameters of three elements are shown in Table I. The corresponding simulated outermost component, including only three lines in orientation 1 in each case, and the experimental one in the [100] direction are depicted in Fig. 4. The excellent agreement in the copper

TABLE I. Calculated intensity ratios of three hyperfine structure EPR lines of orientation 1 for the outermost component for Cl-Cl, Ir-Ir, and Cu-Cu pairs. The experimental ratio between observed lines is also included.

	Isotope	Abundance (%)	μ (μ_N)	Intensity ratio $A{:}B{:}C$
Cl	^{35}Cl	75.77	0.82181	1 : 6.3 : 9.8
	^{37}Cl	24.23	0.68407	
Ir	^{191}Ir	37.30	0.1454	1 : 3.4 : 2.8
	^{193}Ir	62.70	0.1583	
Cu	^{63}Cu	69.20	2.2228	5.0 : 4.5 : 1
	^{65}Cu	30.80	2.3812	
Experiment				5.5 : 4.5 : 1

case (calculated $A{:}B{:}C \approx 5.0{:}4.5{:}1$) and the noticeable mismatch in the two other cases between the experimental and the calculated values provide the extremely significant evidence to identify the Si-NL58 center as a Cu-Cu pair. In this way the chemical identity of the involved impurity is completely based on the analysis of the hyperfine structure of the observed spectrum.

The experimental data could be fitted using the spin Hamiltonians

$$\mathcal{H}_S = \mu_B \vec{B} \cdot \mathbf{g} \cdot \vec{S} + \sum_{i=1}^{2} \vec{S} \cdot \mathbf{A}_i^{^{63}\mathrm{Cu}} \cdot \vec{I}_i , \tag{1}$$

$$\mathcal{H}_S = \mu_B \vec{B} \cdot \mathbf{g} \cdot \vec{S} + \sum_{i=1}^{2} \vec{S} \cdot \mathbf{A}_i^{^{65}\mathrm{Cu}} \cdot \vec{I}_i , \tag{2}$$

$$\mathcal{H}_S = \mu_B \vec{B} \cdot \mathbf{g} \cdot \vec{S} + \vec{S} \cdot \mathbf{A}^{^{63}\mathrm{Cu}} \cdot \vec{I} + \vec{S} \cdot \mathbf{A}^{^{65}\mathrm{Cu}} \cdot \vec{I}, \tag{3}$$

where $\mathbf{g}$ and $\mathbf{A}^{\mathrm{Cu}}$ represent the Zeeman splitting and the hyperfine interaction tensors of the tetragonal symmetry, respectively, for ^{63}Cu and ^{65}Cu, and the electron spin is $S = 1/2$. The results of the computer fit, as determined for the Si-NL58 center, are summarized in Table II. One can see that the ratio of the principal values of the hyperfine interaction tensor determined for the isotopes is equal to 0.93, which matches exactly the ratio of the nuclear magnetic moments $\mu = 2.2228\mu_N$ for ^{63}Cu and $\mu = 2.3812\mu_N$ for ^{65}Cu.[23] This serves as solid proof to confirm the identification as a Cu-Cu pair for the Si-NL58 spectrum. Since copper has a large nuclear quadrupole moment for both isotopes,[23] an attempt to improve the fit to the experimental data with the additional nuclear quadrupole interaction term $\vec{I} \cdot \mathbf{Q} \cdot \vec{I}$ in the spin Hamiltonian has been made. The $\mathbf{Q}$-tensor values obtained from the computer fit were very small and the quality of the fit was not improved. It means that the nuclear quadrupole effect is negligible with respect to the observed hyperfine interaction as expected for a center with nearly isotropic structure. Besides, quadrupole interactions manifest themselves in EPR as a second-order effect only. The true value of the quadrupole nuclear interaction may be derived from an electron-nuclear double-resonance (ENDOR) study of the Si-NL58 spectrum. However, because of the large hyperfine interaction observed (≈ 280 MHz) such a measurement was not experimentally accessible at present.

TABLE II. Spin-Hamiltonian parameters of the Si-NL58 center corresponding to Si:(Cu-Cu)$^-$. Respective values for the related chalcogen pairs are also given for comparison. The hyperfine components are expressed in MHz.

		(Cu-Cu)$^-$		(S-S)$^+$	(Se-Se)$^+$
	^{63}Cu		^{65}Cu	^{33}S	^{77}Se
$g_\parallel$		1.9959		1.99992	2.0020(4)
$g_\perp$		1.9943		2.00115	2.0039(4)
$A_\parallel$	278.9		298.3	114.956	618(9)
$A_\perp$	278.6		298.0	112.323	600(9)
η^2 (%)		10.22		8.28	8.46
Symmetry		D_{2d}		D_{3d}	D_{3d}
Reference		This work		25	26

Information on the electronic distribution in the defect can be derived from the hyperfine structure of the EPR spectrum with the aid of the conventional one-electron linear-combination of atomic-orbitals (LCAO) approximation. Applying this approach with respect to the ^{63}Cu case, the s and d orbitals of the wave function are selected to account for the isotropic and anisotropic parts a and b, respectively, of the hyperfine interaction $\mathbf{A}$. The numerical analysis gives $a = 278.7$ MHz whereas the small anisotropy of the hyperfine tensor is almost equal to that of $\mathbf{g}$ tensor. The spin densities $\eta^2\alpha^2$ and $\eta^2\gamma^2$ in the $4s$ and $3d$ orbitals on each copper atom are then determined as 5.11 and 0%, respectively, resulting in the total localization of the unpaired electron $\eta^2 = 10.22\%$ on the pair with a complete s-like character.

Pairs of two identical atoms with an almost isotropic $\mathbf{g}$ tensor, similar to the Si-NL58 center, are the chalcogen pairs [(S-S)$^+$, (Se-Se)$^+$)] in the positively charged state.[24–26] Especially in the case of (^{33}S-^{33}S)$^+$ with the nuclear spin $I = 3/2$, the EPR spectrum also consists of seven components with intensity ratio of 1:2:3:4:3:2:1. The small anisotropy of $\mathbf{g}$ and hyperfine interaction tensors for (^{33}S-^{33}S)$^+$ could only be determined by the higher resolution of ENDOR measurements.[25] The experimentally published data, which are included in Table II for an easy comparison, have shown the weak anisotropy of the Zeeman splitting $\mathbf{g}$ and the hyperfine interaction tensors for these pairs consistent with their axial atomic structure. As can be seen from Table II the localization of the paramagnetic electron on the copper pair Si-NL58 is bigger than that on chalcogen pairs. One notes that the trigonal symmetry (D_{3d}) was established for the chalcogen pairs, whereas the Si-NL58 pair has most probably the tetragonal symmetry.

The experimentally established tetragonal symmetry of the impurity pair requires the two copper atoms to be both either on substitutional sites, or equivalent interstitial sites along a $\langle 100 \rangle$ cubic crystal direction, corresponding to point group D_{2d} ($\bar{4}2m$). This excludes all Cu$_s$-Cu$_i$ configurations. The similar restriction follows from the observed equivalence of the copper atoms.

As can be concluded from the LCAO analysis of the hyperfine interaction $\mathbf{A}$ the unpaired electron localization η^2 with no d orbitals for the wave function in the ground state indicates that the interaction mainly arises from contact spin density which can be given by electron(s) in the $4s$ state(s). As a consequence the electronic configuration of this pair is proposed to be formed by two copper ions with the closed $3d^{10}$ shells, and one unpaired electron in the $4s$ shells which gives rise to the observed electron spin $S=1/2$. Therefore the following electronic models, which satisfy this requirement, should be considered for the microscopic structure for the Si-NL58 pair: $(\mathrm{Cu}_s\text{-}\mathrm{Cu}_s)^+$, $(\mathrm{Cu}_s\text{-}\mathrm{Cu}_s)^-$, $(\mathrm{Cu}_i\text{-}\mathrm{Cu}_i)^+$, and $(\mathrm{Cu}_i\text{-}\mathrm{Cu}_i)^-$.

In view of the great similarity of the electronic configuration between Cu^0, Ag^0, Au^0, and Pt^- centers, it is expected that these impurities in either an isolated substitutional or an interstitial site would have the same symmetry. Theoretically Fazzio *et al.*[27] have shown that Cu, Ag, and Au in the substitutional site undergo a Jahn-Teller distortion, which splits the vacancylike t_2 level and yields a ground state for Cu_s^0 with electron spin $S=1/2$, and for Cu_s^+ and Cu_s^- with $S=0$. Also, in line with the vacancy model,[28] the symmetry of the isolated Cu_s^0, Ag_s^0, and Au_s^0 is predicted to be lower than cubic, probably orthorhombic-I (C_{2v}), due to such a Jahn-Teller distortion. For Cu_i^0 ($S=1/2$), Cu_i^+ and Cu_i^- ($S=0$) in an interstitial site no Jahn-Teller distortion is expected to occur. Further, the experimentally reported data also support this trend: the electron spin $S=1/2$ and the orthorhombic-I (C_{2v}) symmetry were established for Ag_s^0 (Ref. 22) and Pt_s^-.[29] Following these arguments the hypothetical $(\mathrm{Cu}_s\text{-}\mathrm{Cu}_s)^+$ or $(\mathrm{Cu}_s\text{-}\mathrm{Cu}_s)^-$ pair would have an overall symmetry lower than tetragonal, possibly monoclinic-I. Since the symmetry of the Si-NL58 pair is tetragonal, the $(\mathrm{Cu}_s\text{-}\mathrm{Cu}_s)^+$ or $(\mathrm{Cu}_s\text{-}\mathrm{Cu}_s)^-$ pairs are not good candidates for the microscopic model of this defect. On the other hand, the theoretically predicted cubic symmetry for Ag_i^0 was confirmed in an experiment.[21] Therefore two alternatively possible models $(\mathrm{Cu}_i\text{-}\mathrm{Cu}_i)^+$ or $(\mathrm{Cu}_i\text{-}\mathrm{Cu}_i)^-$ are left for the Si-NL58 center.

For two identical interstitial Cu ions in silicon located close to the tetrahedral site along a $\langle 100\rangle$ axis, their nondegenerate ground states $A_1(T_d)$ will form bonding and antibonding states [$A_1(D_{2d})$ and $A_2(D_{2d})$, respectively]. Since the ground state $A_1(T_d)$ is expected to be positioned in the valence band, the bonding state $A_1(D_{2d})$ will be lying deeper in the valence band than the atomic ground state and will be filled with two electrons. In order to account for the electron spin $S=1/2$, one electron should be accommodated in the antibonding state $A_2(D_{2d})$. We note that the total of three electrons will be present in the $4s$ shells in $(\mathrm{Cu}_i\text{-}\mathrm{Cu}_i)^-$ and only one in $(\mathrm{Cu}_i\text{-}\mathrm{Cu}_i)^+$. Obviously only the electronic model $(\mathrm{Cu}_i\text{-}\mathrm{Cu}_i)^-$ in the singly negative charge state can explain the observed defect structure. Therefore we attribute the Si-NL58 spectrum to the $(\mathrm{Cu}_i\text{-}\mathrm{Cu}_i)^-$ pair in a negatively charged single acceptor state.

It seems to be well established that the most intense PL band at 1014.7 meV is related to copper impurity in silicon introduced intentionally or unintentionally (as a contaminant). Based on the analysis of the uniaxial stress splitting and the Zeeman effect measurements of this Cu_0^0 no-phonon PL line, and the quadratic dependence of its intensity on the copper concentration, Weber *et al.*[14] have established that the 1014.7-meV emission originates from a copper-copper pair in a $\langle 111\rangle$ configuration. Recently, performing DLTS and PL measurements, Erzgräber and Schmalz[13] have shown the correlation between the copper-induced deep donor at $E_v+0.1$ eV (0/+) and the luminescent copper center with Cu_0^0 no-phonon line at 1014.7 meV and suggested that they originate from the same Cu-related center. Thus with the tetragonal symmetry of the **g** tensor and the assignment to the single acceptor as reported in this study, one can conclude that the anisotropic copper pair (Si-NL58) and the luminescent copper pair are not the same center. This conclusion is supported by the PL measurements on all samples containing the Si-NL58 EPR spectrum: the appearances of the EPR spectrum and the PL band at 1014.7 meV do not seem to coincide.

B. Si-NL59 center

The Si-NL59 spectrum was detected only in the very fast-quenched silver-doped p-type silicon samples when the diffusion was conducted in the water vapor ambient. Its spectrum is given in Figs. 1(a) and 1(b), where it appears besides the interstitial iron Fe_i^0, the Si-NL56 and Si-NL58 centers. Its production does not seem to be under control. This spectrum includes four nearly isotropic equally spaced components, which are corresponding to a fourfold hyperfine splitting due to the interaction of an effective electron spin $S=1/2$ and a nuclear spin $I=3/2$. The trace of the Zeeman splitting tensor and the big hyperfine interaction values can be approximately determined as $g\approx 1.9956$ and $A\approx 310$ MHz, respectively. In addition another small and weakly anisotropic splitting, most probably by a hyperfine interaction, within the components was observed. However, this small hyperfine interaction is not completely resolved due to strong overlap of EPR lines in each component. For this reason it is difficult to identify the center, but one can note that such a feature of the spectrum is characteristic for a complex. Already by a superficial analysis of the observed hyperfine splitting a possible combination of two or more identical atoms with nuclear spin $I=3/2$ was not possible. Thus the complex consists of one impurity atom with nuclear spin $I=3/2$ and the atom(s) of another impurity. Apparently silver or hydrogen cannot be the candidate for a nucleus which gives rise to the big fourfold hyperfine splitting, but could still be the prominent candidate producing the small anisotropic hyperfine splitting, because of the required presence of these impurities in the defect formation. The possible constituent responsible for the fourfold hyperfine splitting must come from a contamination impurity. When considering a weakly anisotropic center containing one impurity with a nuclear spin $I=3/2$ and an abundance of 100%, one can expect that the shape of four components should be the same. This is not the case for the observed spectrum: the two outermost components seem to be similar, but broader and smaller than the two inner components which are also similar to each other, as seen in Figs. 1(a) and 2. So this impurity should have at least two isotopes with the same nuclear spin $I=3/2$. Again Cu, Cl, and Ir can be considered as possible candidates. However, taking into account the sample preparation and the fact that the presence of the copper pair (Si-NL58) was already clarified in the same sample as well as the nearly equal values for the Zeeman splitting and the largest hyperfine interaction with those of the Si-

NL58, it is reasonable to conclude on the presence of one copper atom in the Si-NL59 center. The copper atom is located at a high symmetry, probably tetrahedral (T_d), site and makes an interaction with its partner, silver or hydrogen (giving rise to the small anisotropic hyperfine splitting), to form the complex. Since both have the nuclear spin $I=1/2$, in principle EPR cannot distinguish between these two candidates. Due to the weak EPR signal, ENDOR measurements, which could identify either silver or hydrogen involvement in the complex, were not successful. Thus in this stage of the study, the confirmation of silver or hydrogen participation as well as the information of the number of atoms involved in the complex cannot be presented. Further investigations in a higher frequency EPR spectrometer need to be carried out to resolve the small anisotropy of this spectrum.

However, the experimental data could be described using the following spin Hamiltonian:

$$\mathcal{H}_S=\mu_B\vec{B}\cdot\mathbf{g}\cdot\vec{S}+\vec{S}\cdot\mathbf{A}^{\mathrm{Cu}}\cdot\vec{I}^{\mathrm{Cu}}+\sum_{i=1}^{n}\vec{S}\cdot\mathbf{A}_i^X\cdot\vec{I}_i^X, \tag{4}$$

where $\mathbf{g}$, $\mathbf{A}^{\mathrm{Cu}}$ and $\mathbf{A}_i^X$ represent the Zeeman splitting and the hyperfine interaction tensor for the copper and silver or hydrogen (denoted as X) constituent, respectively, with the electron spin $S=1/2$, the nuclear spin $I^{\mathrm{Cu}}=3/2$ and $I^X=1/2$; n is a number of silver or hydrogen atoms involved in the center.

IV. CONCLUSION

In a sample doped with silver the paramagnetic center Si-NL58 was observed using the EPR method. This center was shown to relate to a contamination impurity. Based on the spectrum analysis the Si-NL58 center has been identified as a copper-copper impurity pair occupying interstitial sites along a $\langle 100\rangle$ crystal direction, being observed as $(\mathrm{Cu\text{-}Cu})^-$ in a negatively charged single acceptor state. In addition another copper-related spectrum, Si-NL59, has been observed.

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