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Paramagnetic State of the Isolated Gold Impurity in Silicon

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The paper reports on the observation of the electron paramagnetic resonance spectrum of the isolated substitutional gold impurity in silicon. The spectrum has orthorhombic I (C_{2v}) symmetry and an effective spin $S=\frac{1}{2}$. It has been detected in silver-doped silicon samples with gold being introduced as contamination of the isotope used for diffusion. Parameters of the spectrum are given and an electronic model is proposed. With the results of the current study the puzzling question concerning paramagnetism of the isolated gold impurity in silicon appears to be clarified.

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Because of its application in device manufacturing and interesting physical properties, gold is among the most extensively studied impurities in silicon. On the basis of combined results of Hall effect, deep level transient spectroscopy (DLTS), and resistivity measurements, it has been established that the gold impurity in silicon has amphoteric character, introducing a deep donor and a deep acceptor level at $E_V+0.35$ eV and $E_V+0.62$ eV, respectively; for a review see Ref. [1]. This conclusion has further been supported by photoluminescence study, as an emission band was detected in gold-doped silicon and postulated to originate from the free-to-bound transition of the substitutional gold donor center [2].

Although the electrical properties of gold in silicon seem to be well established, its electronic structure could only be speculated upon. Information leading to the defect model is often provided by electron paramagnetic resonance (EPR). However, in the EPR studies of gold in silicon a variety of gold-related defect clusters has been identified [3,4]. The EPR results appear in considerable contrast to the aforementioned studies, which predict basically one defect (substitutional gold impurity) with three charge states possible within the band gap of silicon. This apparent contradiction is indicative of the resolving power of magnetic resonance and its unique ability to reveal structural information of truly microscopic character.

The gold-related defects as identified by EPR thus far are clearly secondary to the isolated gold impurity, whose properties constitute a key to the understanding of their structure. However, in spite of prolonged attempts, no EPR signal of the isolated gold impurity has ever been obtained. A somewhat similar situation exists also for other elements of group I-B, i.e., copper and silver. Several copper-related EPR spectra were observed but all were identified as copper-impurity pairs or complexes. For silver, with a somewhat lower diffusivity, an EPR spectrum of an isolated interstitial Ag atom was reported only very recently [5], its generation obviously being hindered by the simultaneous creation of numerous larger silver-related complexes. The difficulties in tracing isolated group I-B impurities appear rather unique in the broad field of EPR spectroscopy of transition metals, as spectra related to many of these in isolated substitutional sites have been identified [3]. The apparent lack of a paramagnetic state of substitutional gold is particularly strange since the negatively charged isolated platinum Pt^-, which is isoelectronic to Au^0, has been observed by EPR and, consequently, its structure is well understood [6,7]. In this situation several explanations have been put forward to explain the absence of the EPR of isolated gold in silicon. The most convincing one has been offered recently by Anderson [8]. In this work the electronic structure of $Si:Au^0$ is assumed to be generally similar to that of the $Si:Pt^-$ center, i.e., it is based on the vacancy model. Further, the existence of the Jahn-Teller effect is postulated and the defect is believed to tunnel between two trigonally distorted configurations. The rapid tunneling leads to the vanishing of the perpendicular g value of the tetragonal center. With $g_\perp \approx 0$, the transition probability becomes very low and consequently the EPR spectrum is difficult to observe. This theoretical explanation was supported more recently by Watkins *et al.* on the basis of Zeeman studies of gold excitation spectra in silicon [9]. Following the magnetic field dependence of 793-meV and 611-meV photoluminescence (PL) bands the g tensor of the relevant center could (roughly) be determined and indeed its $g_\perp$ value was found to be close to zero. This spectacular confirmation of the theoretical prediction by an experiment, however, has to be treated with caution in view of the aforementioned limited number of gold-related PL emission bands [2,10] and problems with their precise microscopic identification. In particular, one has to realize that the microscopic identification of the 793-meV line with the isolated gold center is based on sample preparation conditions and correlation with DLTS [2,11], and as such appears especially weak when compared to the multiplicity of gold-related EPR spectra observed in similarly prepared material.

In this Letter we report the observation of a new gold-related EPR center which has a different g tensor from that measured in Ref. [9]. We will argue that it can be identified with the isolated substitutional gold impurity, thus bypassing the theoretical description as offered by

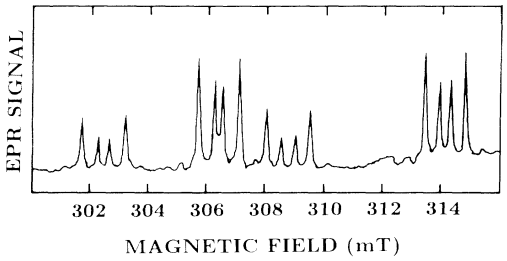

FIG. 1. EPR spectrum of the Si-NL50 center as measured at the angle 50° away from [100] showing the hyperfine structure due to one gold nucleus with nuclear spin $I=\frac{3}{2}$. The microwave frequency is $\nu=9.1773$ GHz.

Ref. [8].

In our recent EPR investigations of silver-doped silicon, the isolated interstitial silver and several silver-related complexes were observed and identified [5]. Here, we present details of an orthorhombic I (C_{2v}) spectrum detected in the same material. Details of the measurement and the material preparation are given in Ref. [5]. In the sample intentionally doped with silver, in addition to the signals of Fe_i^0, Ti_i^+, Ag_i^0 (Si-NL42 center) and some other silver-related spectra, another spectrum, labeled Si-NL50, was observed. The spectrum, which was found to be stable at room temperature, shows hyperfine structure with fourfold splitting. It is illustrated in Fig. 1. The orthorhombic I symmetry of the center is deduced from its angular dependence as depicted in Fig. 2. The spectrum appears to have more complexity due to a strong angular dependence of line intensities and the occurrence of "forbidden" transitions.

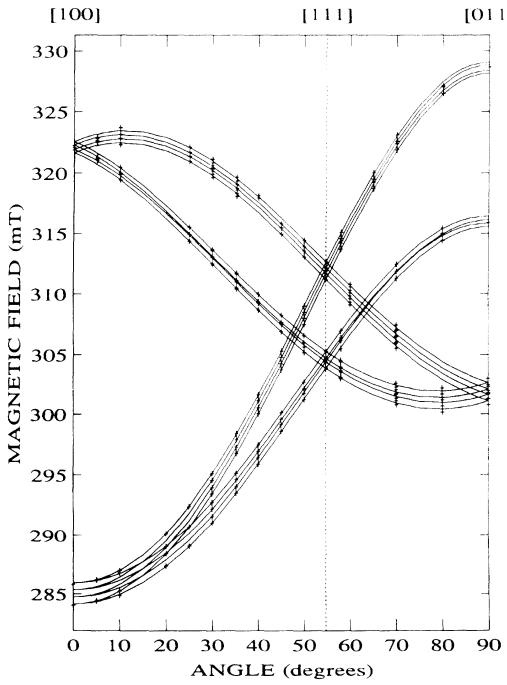

FIG. 2. Angular dependence of the Si-NL50 EPR spectrum. The magnetic field is rotated in the $(0\bar{1}1)$ plane. Solid curves represent fits to the experimental points with Hamiltonian (1) and parameters as given in Table I. The microwave frequency is $\nu=9.1773$ GHz.

The observed fourfold hyperfine structure is characteristic for a center containing one nucleus with a nuclear spin $I=\frac{3}{2}$ and an abundance of 100%. In principle several elements fulfill these conditions: ^{9}Be, ^{23}Na, ^{35}Cl and ^{37}Cl, ^{39}K and ^{41}K, ^{63}Cu and ^{65}Cu, ^{69}Ga and ^{71}Ga, ^{75}As, ^{79}Br and ^{81}Br, ^{159}Tb, ^{191}Ir and ^{193}Ir, and ^{197}Au. However, taking into account the already identified impurity centers, sample preparation conditions, diffusivity values, the observed small hyperfine splitting and, finally, the symmetric line shape and equal linewidth which are indicative of the presence of one isotope only, most of these nuclei can be rather safely excluded, leaving gold as the only reasonable candidate.

The experimental data could be fitted by the spin Hamiltonian

$$\mathcal{H}=\mu_B \mathbf{B}\cdot\vec{\mathbf{g}}\cdot\mathbf{S}+\mathbf{S}\cdot\vec{\mathbf{A}}\cdot\mathbf{I}+\mathbf{I}\cdot\vec{\mathbf{Q}}\cdot\mathbf{I}, \quad (1)$$

with electron spin $S=\frac{1}{2}$, nuclear spin $I=\frac{3}{2}$, and hyperfine and quadrupole tensors $\vec{\mathbf{A}}$ and $\vec{\mathbf{Q}}$ constrained to the orthorhombic I symmetry of the $\vec{\mathbf{g}}$ tensor. A good fit with a maximum deviation of ≈ 80 μT was obtained. Resulting parameters are summarized in Table I. In the simulation with these parameters, transition probabilities of all sixteen EPR transitions were calculated. From the simulation, it was shown that the higher intensities of outer hyperfine lines, as observed in the experiment, are

TABLE I. Principal values of g, hyperfine, and quadrupole tensors as determined for the Si-NL50 spectrum. For comparison data for other analogous orthorhombic I centers in silicon are included. Values of A and Q are given in MHz.

		Principal directions			
Center	Tensor	[100]	[011]	$[0\bar{1}1]$	Reference
Si:^{61}Ni$^-$	g	2.0163	2.0182	2.0536	[12]
	A	1.01	−39.98	−37.60	
	Q	2.42	2.09	−4.51	
Si:^{105}Pd$^-$	g	2.0551	1.9716	1.9190	[15]
	A	19.28	36.01	35.11	
	Q	−12.80	15.85	−3.05	
Si:^{195}Pt$^-$	g	2.0789	1.3867	1.4266	[6]
	A	379.3	439.5	550.8	
Si:^{197}Au^0	g	2.3015	1.9956	2.0752	This work
	A_{Au}	18.88	6.32	5.36	
	a	10.19	10.19	10.19	
	B	8.69	−3.87	−4.83	
	Q	3.26	−2.67	−0.59	
	Q^{US}	−21.80	9.70	12.10	
	Q^{vc}	25.06	−12.37	−12.69	
	A_{Si}	≈ 31	≈ 31	≈ 31	

caused by two forbidden transitions with $\Delta m_I = \pm 1$ (between levels $+\frac{3}{2} \leftrightarrow +\frac{1}{2}$ and $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$) which coincide with the allowed ones.

Numerical analysis of the experimental hyperfine tensor $\overleftrightarrow{A}$ gives $a = \pm 10.19$ MHz and $b = \pm 4.35$ MHz for its isotropic and anisotropic parts, respectively. The spin density $\eta^2\alpha^2$ in the $6s$ orbital and $\eta^2\beta^2$ in the $5d$ orbital on the gold atom is determined as 0.35% and 11.53%, respectively.

The interaction between the nuclear quadrupole moment and defect-associated electric-field gradient at the site of the nucleus gives rise to the quadrupole energy described by the last term of the Hamiltonian (1). The size of the effect depends on the unbalance of charge density associated with the defect. The most obvious source of an electric field is a distant point charge. For the gold nucleus, such a contribution is small in comparison with the experimental value and therefore can be neglected. The other contribution arises from unbalanced charges at the nucleus itself caused by unpaired electrons in p or d orbitals. Because of the similarity in the mechanism of the hyperfine and quadrupole interactions for an electron with unpaired spin (US) in a d orbital, the quadrupole tensor $\overleftrightarrow{Q}^{US}$ can be derived from the anisotropic hyperfine tensor component $\overleftrightarrow{B}$ ($\overleftrightarrow{A} = a\overleftrightarrow{1} + \overleftrightarrow{B}$) [12]. The principal values of thus determined $\overleftrightarrow{Q}^{US}$ tensor are given in Table I. As can also be concluded these values apparently cannot explain the experimental data and hence the other contribution to the field gradient, $\overleftrightarrow{Q}^{vc}$, resulting from electrons in the bonds, must be present. Subtracting $\overleftrightarrow{Q}^{US}$ from the experimental data one finds the principal values of the $\overleftrightarrow{Q}^{vc}$ tensor as given in Table I. The value $q \approx 12.5$ MHz corresponds in this case to about 13.5% localization of a d electron. At the same time, from the [100] axial symmetry of the $\overleftrightarrow{Q}^{vc}$ tensor, it can be deduced that the relevant d electron occupies an a_1 or a_2 symmetry-type orbital.

In addition to the self-hyperfine structure, an isotropic hyperfine splitting of ≈ 31 MHz due to the interaction with ^{29}Si silicon is observed. This is illustrated in Fig. 3;

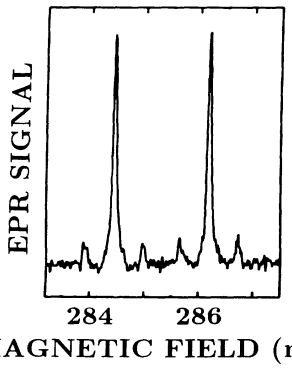

FIG. 3. Part of the Si-NL50 EPR spectrum for $B \| [100]$ showing the hyperfine interaction with four equivalent silicon neighbors.

the relative intensity indicates in this case the interaction with four equivalent silicon neighbors. A silicon hyperfine value of 31 MHz corresponds to localization of about 0.7% of an s electron on each of the silicon atoms.

Now we will address the problem of microscopic identification of the Si-NL50 spectrum. As discussed before, in view of the observed self-hyperfine interaction, the participation of a single gold atom is evident. At the same time the spectrum is observed only in samples intentionally doped with silver. In this case small amounts of gold have been introduced into the sample as contamination. Following the EPR results described in this Letter the actual traces of gold contaminant in the studied samples (at a level of at least 3 orders of magnitude lower than the Ag contents) were indeed confirmed by photoluminescence spectroscopy [13]. We suggest that the low concentration of gold and the simultaneous presence of silver play an important role in preventing the formation of gold-impurity pairs or gold clusters as usually observed in gold-diffused samples. Gold, together with other impurities of group I-B copper and silver, is characterized by a superfast interstitial diffusion mechanism. Because it also has large electronegativity, gold tends to form pairs with other impurities rather than be trapped on substitutional sites. This explains the variety of gold-related impurity complexes identified in the past and constitutes a likely reason that the isolated form of these dopants is difficult to observe. In the present case, when gold is introduced only as marginal contamination to silver, the fast diffusing interstitial silver could serve as the effective getter of eventual candidates for gold-impurity pair formation. Alternatively it is also possible that the presence of interstitially diffusing silver promotes the substitutional diffusion mechanism of gold. In any case, as a consequence the chances of direct substitutional trapping of isolated gold could be significantly increased.

Having established the gold participation, it can be further concluded on the basis of the orthorhombic I symmetry of the Si-NL50 center that the spectrum is related to either an isolated substitutional gold (similarly to Pt^-) or a gold-impurity pair (in analogy to the iron-acceptor pairs). In the latter case, however, as only self- (and ^{29}Si) hyperfine structure is observed, the other impurity involved would have to be of zero nuclear magnetic moment, thus excluding the majority of the most popular contaminants and practically eliminating the pair model. Further, as known from the literature on impurity pairs, due to their strong spin localization hyperfine interaction with silicon neighbors has never been detected for such centers. By contrast, the ligand hyperfine interaction is always observed for isolated substitutional impurities. In the present case, the observed hyperfine interaction with four equivalent silicon neighbors clearly supports the identification of the Si-NL50 spectrum with the isolated substitutional gold.

Similarly to the case of Pt^-, the presently detected gold center has spin $S = \frac{1}{2}$ and shows the same C_{2v} sym-

metry with rather small orthorhombic component. Both defects are therefore also expected to have similar electronic structure. Recently, developing the vacancy model proposed by Watkins [14], Anderson, Ham, and Watkins have successfully described the anisotropy of the g values as well as the self-hyperfine interaction of the Pt^- defect [7]. In this description the paramagnetic electron is assumed to be in a b_1 singlet state, which results in a hyperfine interaction being roughly axial along $[0\bar{1}1]$, in close resemblance to V^-, and which could explain the observed reduction of $g_\perp$. Applying this approach to gold, a still further reduction with complete annulling of $g_\perp$ is expected. However, as can be concluded from Table I, the hyperfine tensor as measured for the Si-NL50 center is clearly axial along [100]. This resembles the case of substitutional nickel Ni^- [12] and substitutional palladium Pd^- [15] and indicates that the spin must be described mainly by an a_1- or a_2-type orbital. In view of the observed contact and ligand hyperfine interactions, the a_2 orbital with two nodal planes can be excluded. The symmetry of the gold hyperfine tensor thus requires the unpaired-spin electron to be in the a_1 orbital, thus rendering the description as developed in Ref. [8] inappropriate. Although substitutional transition impurities produce similar defects in silicon, their magnetic properties show clear differences and hence it is not possible to use one universal model for the general description of their particular electronic structures. For an easy comparison spectroscopic parameters as obtained by magnetic resonance for several of these substitutional centers are collected in Table I. We therefore conclude that the isolated substitutional gold Au_s^0 in silicon is paramagnetic with an electronic spin $S=\frac{1}{2}$ and orthorhombic I symmetry. The g values of the center deviate significantly from the spin-only $g=2.0023$ value, but not as much as in the case of Pt_s^-. For a spin $S=\frac{1}{2}$ center of the low orthorhombic symmetry no orbital contribution to the magnetic moment is expected, as the orbital states are singlets. The deviation from the free-spin g value is caused by strong spin-orbit interaction, as is typical for a high-Z nucleus.

Finally, the apparent contradiction between the present experimental findings and those reported in Ref. [9] should be addressed. In this context two comments are relevant. First, on the basis of the significantly different g values, it seems evident that the two observed centers are different. Second, one has to note that, while the relation of the presently found Si-NL50 center to the isolated gold impurity is supported by spectroscopic arguments, i.e., clear hyperfine structure and well-resolved symmetry, the assignment of the PL bands to the isolated gold, as assumed in Ref. [9], is based on indirect evidence and does not appear particularly convincing, especially in view of the large variety of gold-related spectra identified by magnetic resonance.

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