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IDENTIFICATION OF PARAMAGNETIC SILVER CENTRES IN SILICON

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In silver-doped silicon several new spectra were observed by electron paramagnetic resonance (EPR). In the paper the spin-Hamiltonian analysis of six prominent spectra, labelled Si-NL42 through Si-NL47, is presented. Confirmation of the presence of one silver atom in the centres was achieved by intentional doping with silver impurity enriched in one of its isotopes, ^{107}Ag or ^{109}Ag. Spectrum Si-NL42, the one isotropic centre, is identified with neutral interstitial silver. All other spectra reveal trigonal symmetry of the associated centres. The atomic models related to the EPR spectra are discussed.

Transition element impurities are important dopants of semiconductors [1]. In device material, they are frequently added intentionally to control carrier lifetimes. This property is associated with the deep-bandgap electronic levels. The understanding of their electronic structure is a challenging task for fundamental semiconductor physics as it involves the local interaction between electrons in the d shell of the transition element with the s and p electrons of the host semiconductor [2]. Up to the present time, the study of transition elements has focused on elements from the iron group [3]. Relatively little attention was given to elements with 5d electronic structure, in the group of gold and platinum, and even less to the 4d transition element group. In the latter group silver is a prominent example. This paper reports on the, to our knowledge, first, observation, by electron paramagnetic resonance (EPR), of spectra related to silver impurity in silicon. The production and properties of the centres will be described. By the controlled doping with silver enriched in one of its isotopes with nuclear magnetic moment, ^{107}Ag or ^{109}Ag, the presence of one silver atom in several of the centres is unambiguously demonstrated. The parameters of the spin-Hamiltonian analysis of the observed spectra, labelled Si-NL42 to Si-NL47, are summarized in table I.

For the present study samples were prepared by diffusion of high-purity silver for times varying from 24 to 40 hours at the temperature of 1250 °C into silicon. Either silver of the natural isotopic composition was used, i.e. 51% of ^{107}Ag and 49% of ^{109}Ag, or silver enriched in one of its isotopes; available monoisotopic silver was 99.5% ^{107}Ag and 99.4% ^{109}Ag. Diffusions were carried out in both n- and p-type, float-zone, dislocation-free silicon. Diffusion was followed by quenching of the sample, within a quartz ampoule, into water, with subsequent storage of samples at liquid-nitrogen temperature. Paramagnetic resonance was performed on X-band (microwave frequency $\approx$9 GHz) and K-band ($\approx$23 GHz) superheterodyne spectrometers. Samples, of typical dimensions $1.5\times1.5\times15$ mm^3, were mounted with their long edge along the axis of the TE_{011} microwave cavity. Their [0$\bar{1}$1] crystal direction is then perpendicular to the plane of rotation of the static magnetic field. All EPR measurements were performed at 4.2 K sample temperature.

Spectrum Si-NL42. In figure 1 the evidence is presented for the correlation of the Si-NL42 spectrum with a centre having one silver atom. In samples doped with silver enriched with one of the silver isotopes a twofold hyperfine splitting is observed, as shown in figures 1(b) and 1(c). This corresponds naturally to the nuclear spin $I=1/2$ of both isotopes. A small but significant difference in hyperfine splitting is observable. The ratio of the splitting observed in the experiments, equal to 0.87, is in exact agreement with the ratio of the nuclear magnetic moments of the isotopes, $\mu=-0.1135\ \mu_N$ for

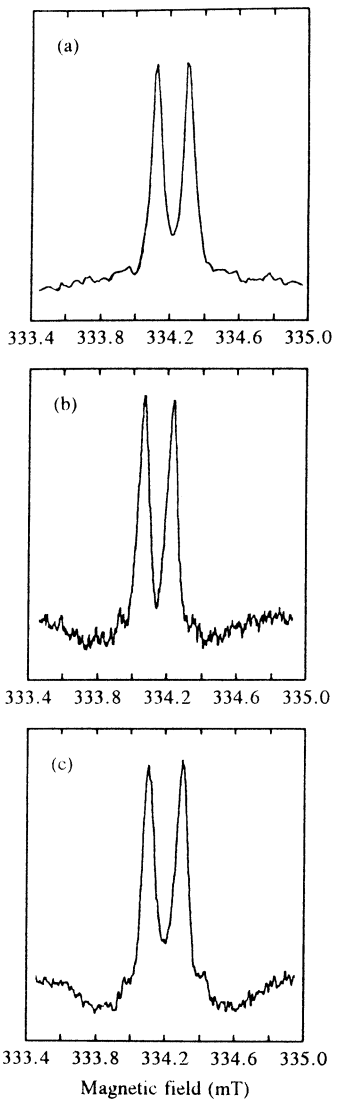

Figure 1. Silver-related hyperfine splitting in spectrum Si-NL42 in X-band measurement for (a) silver of natural isotopic composition, (b) enriched ^{107}Ag isotope (99.5%), (c) enriched ^{109}Ag isotope (99.4%).

^{107}Ag and $\mu = -0.1305\ \mu_N$ for ^{109}Ag. For the sample doped with natural silver the average splitting is observed. The individual lines are broader due to the composite character of the spectrum consisting of two components of nearly equal amplitude. Similar observations were made on K band. The spectrum is isotropic, both in its fine and hyperfine structure. It implies that the silver impurity must occupy an unperturbed high-symmetry site. Candidates are the substitutional site and the tetrahedral interstitial site. On the former site four electrons of the silver will be engaged in forming covalent bonds, leaving a $4d^7$ core configuration. On this basis spin $S = 3/2$ is expected, at variance with observation. For the interstitial site, neutral silver has configuration $4d^{10}5s$ in a natural agreement with the observed spin $S = 1/2$. Following these arguments, spectrum Si-NL42 is identified with neutral interstitial silver. From the intensity of the spectrum the concentration of the centre is estimated as 10^{13} cm^{-3}. Comparison with the solubility data indicates that the Si-NL42 centre represents a small fraction of the total amount of silver expected to be present.

Spectrum Si-NL43. The observed angular dependence reveals trigonal symmetry of the corresponding centre. In figure 2(a) measured data points are shown for a ^{109}Ag-doped sample, together with the results of the analysis based on the appropriate spin Hamiltonian. The lower symmetry suggests an impurity-pair structure. Indeed, codoping with iron resulted in additional hyperfine splitting when using the isotope ^{57}Fe, with nuclear spin $I = 1/2$. The pair may be of the familiar donor-acceptor type. In the ionised state, the substitutional acceptor silver will have $4d^8$ electronic configuration with $S_{Ag} = 1$. The ionised donor Fe^+ on the usual interstitial site has $3d^7$ structure with $S_{Fe} = 3/2$. An antiparallel coupling between the spins leads to $S = 1/2$ for the pair, in agreement with the measured result. The model is analogous to the one proposed for the AuFe pair [4].

Table I. Spin-Hamiltonian parameters of the EPR spectra Si-NL42 to Si-NL47.

Spectrum	Symmetry	Spin	g Tensor		D Tensor	A Tensor		
			$g_{//}$	$g_{\perp}$	(GHz)	nucleus	$A_{//}$ (MHz)	$A_{\perp}$
Si-NL42	cubic	1/2	1.9744			^{107}Ag	4.76	
						^{109}Ag	5.47	
Si-NL43	trigonal	1/2	2.0680	2.0986		^{107}Ag	42.44	29.41
						^{109}Ag	48.47	33.12
						^{57}Fe	25	19
Si-NL44	trigonal	1/2	2.0028	3.9846		^{107}Ag	9.0	3.9
						^{109}Ag	10.5	4.5
		3/2	2.0004	1.9999	86			
Si-NL45	trigonal	1/2	2.020	6.090				
		5/2	2.020	2.036	95			
Si-NL46	trigonal	1/2	2.019	7.999				
		7/2	2.018	2.036	44			
Si-NL47	trigonal	1/2	5.776	1.096				

Spectrum Si-NL44. As for the preceding two cases, the spectrum Si-NL44 also shows the characteristic doublet splitting into components of equal intensity. Principal values for the hyperfine interaction constants $A_{//}$ and $A_{\perp}$ based on analysis of the experimental data obtained over the full range of angles, are collected in table I. The ratio of the results obtained for the two doping cases, all within the range 0.87 ± 0.02, is in perfect agreement with the ratio of the nuclear magnetic moments of the 107 and 109 silver isotopes. This provides a conclusive proof of the presence of one, and only one, silver atom in the observed centres. The angular dependence of spectrum Si-NL44 can well be analyzed using effective electron spin $S=1/2$ and a simple spin Hamiltonian with Zeeman interaction term only. However, from such an analysis an unphysical value, near 4, is obtained for the principal g value perpendicular to the rotation axis of the centre. This result indicates that actually one is dealing here with a three-electron system, with real spin $S=3/2$. The quartet of levels is split by an axial crystal field into two doublets. The preferred analysis thus uses spin $S=3/2$ and the appropriate Hamiltonian. The result yields a splitting by $2D=172$ GHz, which indeed is larger than the microwave energy quantum. Resonance is only observed in the lower-energy doublet. The second impurity in the Si-NL44 centre is not yet identified. No specific models for atomic structure and spin can therefore be proposed.

Spectra Si-NL45 and Si-NL46. These two spectra, simultaneously observed in n-type silicon, have a similar behaviour. Both are unstable at room temperature and, upon their decay, the spectrum Si-NL44 appears. Resolved silver-related hyperfine structure is not observed in the two cases. When analyzing the trigonal resonance patterns with electron spin $S=1/2$, high effective values for the perpendicular g values are obtained. Using the relation $g_{eff}=g_{\perp}(S+1/2)$ with $g_{\perp}=2$, from ref. 3, the real spins of the centres are determined as $S=5/2$ for Si-NL45 and $S=7/2$ for Si-NL46. A spin as high as 7/2 was not earlier reported for a paramagnetic centre in silicon. Possible atomic and electronic

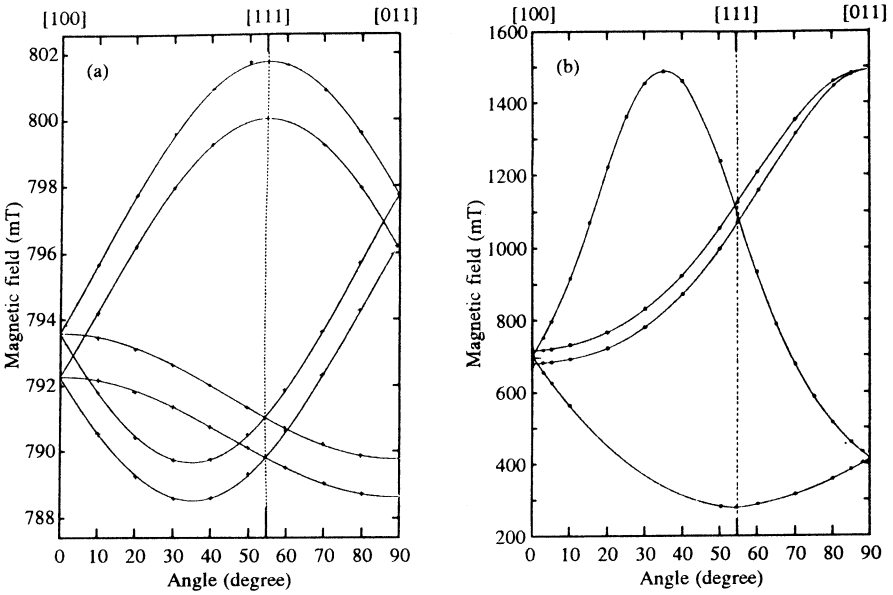

Figure 2. Angular dependence for rotation of the magnetic field in the $(0\bar{1}1)$ plane for (a) the trigonal EPR spectrum Si-NL43, and (b) the trigonal EPR spectrum Si-NL47; measurements at K band.

structure models to account for the spin values are $(Ag_sAg_s)^-$ for Si-NL45 with $S=5/2$ and $(Ag_sAg_s)^+$ for Si-NL46 with $S=7/2$.

Spectrum Si-NL47. The angular dependence of this very anisotropic trigonal spectrum is illustrated in figure 2(b). On the basis of analysis with spin $S=1/2$, both principal values of the g tensor, $g_{//}=5.776$ and $g_\perp=1.096$, are found to deviate substantially from the free-electron g value $g=2$. This result evidences that orbital momentum still contributes to the magnetisation. The more significant analysis of these parameters starts from real spin $S=3/2$ for the centre, orbital momentum $L=1$, and includes crystal field and spin-orbit interaction [5]. No hyperfine structure was resolved for spectrum Si-NL47. The, more tentative, conclusion of silver involvement is based on the presence of non-quenched orbital angular momentum, typical for transition element impurities, a high spin value, reflecting Hund's rule, and the exclusive observation of the spectrum in silver-doped silicon.

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