Materials Science Forum Vols. 258-263 (1997) pp. 491-496 © 1997 Trans Tech Publications, Switzerland

ISOLATED SUBSTITUTIONAL SILVER AND SILVER-INDUCED DEFECTS IN SILICON: AN ELECTRON PARAMAGNETIC RESONANCE INVESTIGATION

P.N. Hai^{1,2}, T. Gregorkiewicz¹, C.A.J. Ammerlaan¹ and D.T. Don²

¹Van der Waals–Zeeman Institute, University of Amsterdam, Valckenierstraat 65-67, NL-1018 XE Amsterdam, The Netherlands

²Faculty of Physics, National University of Hanoi, 90 Nguyen Trai Street, Hanoi, Vietnam

Keywords: silver, silicon, electron paramagnetic resonance, hyperfine interaction.

Abstract Two new electron paramagnetic resonance spectra in silicon doped with silver in a water vapor atmosphere are reported. The observed centers, labeled Si-NL56 and Si-NL57, show a symmetry lower than cubic and an effective electron spin S=1/2. Based on studies with enriched silver isotopes and analysis of the observed two-fold hyperfine splitting, the participation of one silver atom is established for two centers. The Si-NL56 center of the orthorhombic-I symmetry is identified as an isolated substitutional silver atom, and its electronic structure is shown to conform to the vacancy model. Due to the presence of an additional hyperfine interaction with a nuclear spin I=5/2 the Si-NL57 spectrum of the trigonal symmetry is assigned to a complex of silver with another impurity introduced during the diffusion process. Taking into account the sample preparation procedure, the Si-NL57 center is attributed to an Al_s-Ag_i pair in a negative charge state. This observation also indicates the diffusion enhancement of aluminum in silicon treated in the water vapor atmosphere.

Introduction

Silver receives considerable interest as a deep-level dopant in silicon. This is due to its interesting role in silicon processing. From a more fundamental point of view, the Ag dopant constitutes a particularly interesting case of a transition element with a complete d^{10} electron shell, and is directly comparable to such centers as Au and Pt whose electronic structure is intensively investigated.

Some information on electrical and optical properties of the silver impurity in silicon has been established in the past. Electrical measurements [1] revealed its amphoteric character. Using optical spectroscopies Olajos *et al.* [2] investigated the excitation spectra of electronic excited states in Agdoped silicon and identified those as arising from the deep state of the, probably substitutional, Ag donor. However, the microscopic structure of the Ag-induced centers, which is often revealed by means of electron paramagnetic resonance (EPR) spectroscopy, is not clear. In EPR measurements on Ag-doped silicon [3,4] a number of Ag-related centers has been found. One of the spectra, Si-NL42, has been attributed to a single Ag atom in a neutral charge state on a tetrahedral, probably interstitial, site. The issue of the existence of the isolated substitutional silver center in silicon, as postulated from optical and electrical studies, remains therefore open.

In this contribution we present results of an EPR investigation of silicon samples doped with silver in water vapor environment; the high temperature annealing in water vapor was shown to be an effective manner to hydrogenate silicon [5]. In the frame of the study two new EPR spectra have been detected. While their generation was evidently related to the presence of the (heavy) water vapor, no evidence of a direct hydrogen involvement in the microscopic structure of these centers has been found.

Experimental procedures

The samples used in this study were made from B- and P-doped, dislocation-free, float-zone silicon crystals with a room-temperature resistivity in the range of 1000 Ω cm. The dimensions of samples were typically $1 \times 1 \times 15$ mm³ with the length along the [011] crystal direction. The samples were diffused with silver. In this procedure small amounts of natural high-purity silver (99.999%) or monoisotopically enriched (but not high-purity) silver ¹⁰⁷Ag (99.5%) or ¹⁰⁹Ag (99.4%) were deposited on both sides of the sample by scratching. The crystals were then sealed in quartz ampoules

containing argon atmosphere and a few milligrams of water. The diffusion treatment was performed in a tube furnace at a temperature of 1250 °C for a duration of several hours, and then abruptly terminated by quenching to room temperature.

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

Experimental results and discussion

Following the quenching several new spectra were observed. Figures 1(a) and (b) show typical EPR spectra recorded for ¹⁰⁷ Ag- and ¹⁰⁹ Ag-doped samples, respectively. An anisotropic spectrum, labeled Si-NL56, reproducible for doping with natural or monoisotopically enriched silver, consists of two groups of intense EPR lines corresponding to a two-fold hyperfine (hf) splitting. In addition to this signal, another anisotropic spectrum, labeled Si-NL57, was also detected in samples for which monoisotopically enriched silver was used as a dopant source. These two spectra have different angular and temperature dependencies: the Si-NL56 spectrum remains unchanged whereas the other one vanishes when measuring at temperature of 8 K or higher, as depicted in Figs. 1(c) and (d). These facts indicate that these spectra belong to different centers.



Fig. 1: Anisotropic EPR spectra observed at an angle of approximately 2.5° away from the [011] direction in the (011) plane at temperature T=4.2 K for a sample doped with (**a**) ¹⁰⁷Ag (microwave frequency ν =22.7838 GHz) and (**b**) ¹⁰⁹Ag (ν =22.8697 GHz) silver isotope. The EPR spectra recorded 32° away from the [011] at T=8 K for samples doped with (**c**) ¹⁰⁷Ag (ν =22.9412 GHz) and (**d**) ¹⁰⁹Ag (ν =22.8935 GHz).

A. Si-NL56 center

Taking into account the fact that the anisotropic spectrum could only be produced when diffusing Ag in the water vapor ambient at high temperature, we consider Ag or/and H as the possible candidate(s) responsible for the two-fold splitting. To examine the role of Ag and H in the defect structure, two

additional sets of different samples were prepared: the first set of samples was doped with natural (high-purity) or monoisotopically enriched silver in the atmosphere of Ar gas only; the second set was heated without Ag in the ambient of water vapor. The heat-treatment parameters were kept identical in both cases. No Si-NL56 EPR spectrum for the two sets of samples was detected. From these observations we conclude that both Ag and H are needed in the formation process of this center. Another set of samples was prepared with the use of Ag and heavy water vapor (D₂O, with nuclear spin I=1 for deuterium). No differences between samples doped with Ag in the atmosphere of water and heavy water vapor have been found. This leaves Ag as the prominent candidate for the explanation of the hf structure. A similar sample doped with the enriched silver isotope 109 Ag was prepared. The Si-NL56 spectrum could be detected again with the distinct difference in the hf splitting, as shown in Fig. 1(b). The ratio between the splittings observed in the experiment is equal to 0.87, and perfectly matches the ratio of the nuclear magnetic moments of the two isotopes [6]. On the basis of these isotope effects on the spectra we conclude that the anisotropic Si-NL56 center involves a single Ag atom. While H is not observed as a structural component of the Si-NL56 center, it takes part in its formation process. If further confirmed, this would be the first observation of the H-related enhancement of diffusion for a transition metal impurity in silicon.

The spectrum could be fitted with the spin Hamiltonian

$$\mathcal{H}_{S} = \mu_{\mu} \vec{B} \cdot \mathbf{g} \cdot \vec{S} + \vec{S} \cdot \mathbf{A} \cdot \vec{I}, \tag{1}$$

where **g** and **A** represent the Zeeman splitting and the hf interaction tensors, respectively, with the electron spin S=1/2 and nuclear spin I=1/2. Full angular dependence of the spectrum, showing the orthorhombic-I (C_{2v}) symmetry, was obtained when rotating the external magnetic field in the (011) crystal plane, with the result as given in Fig. 2. The results of the computer fit for the Si-NL56 center, are summarized in Table 1.



Fig. 2: Angular dependence of the Si-NL56 and Si-NL57 spectra measured in the ¹⁰⁹Ag-doped sample. The bold and thin solid lines represent a fit to the experimental points (+) according to equation (1) for spectrum Si-NL56 and equation (2) for Si-NL57, respectively. The microwave frequency is ν =22.8697 GHz

Cu, Ag and Au atoms have similar free-atom electronic configurations in vacuum $(n-1)d^{10}ns^1$ (n=4, 5 and 6, respectively). The same applies to Pt in the negative charge state Pt⁻, which is isoelectronic to Au⁰. Therefore the similar kind of symmetry in the isolated sites could be expected for all of them. In fact several experimental results were shown to support the idea. The EPR data for the isolated substitutional platinum Pt_s⁻ [7] revealed the C_{2v} symmetry. Also for Au in silicon a C_{2v} spectrum (Si-NL50 [8]) has been reported, although its relation to an isolated neutral gold atom is under dispute and requires further confirmation. In the IR absorption measurements for Ag-doped

Table 1: Spin-Hamiltonian parameters of the Si-NL56 center. Respective values for the oxygen-vacancy defect are also given for comparison. The hf components are given in MHz.

Center	Tensor	Principal values			Ref.
		[100]	[011]	[011]	
Si-NL56	g	1.9954	1.9960	1.9980	This
(¹⁰⁷ Ag)	A	160.0	155.5	159.4	work
(¹⁰⁹ Ag)	A	184.3	179.2	183.7	
Si:OV-	g	2.0033	2.0025	2.0093	[12]
(¹⁷ O)	A	4.363	-0.997	5.593	

silicon [2] the observation of four lines for the $1s(E+T_2)$ multiplet indicates that the center has C_{2v} symmetry (or lower). Based on the vacancy model [9] this spectrum was then postulated to arise from a neutral substitutional silver dopant. From these findings, it seems reasonable to conclude that the common trend for the symmetry of these impurities in the isolated substitutional site in silicon is the orthorhombic-I. Following the observation of the isotope effects, we concluded on the participation of a single Ag atom in the structure of the C_{2v} Si-NL56 center reported here. At the same time the isotope effects on the spectra do not support the possibility that the center consists of a pair of Ag and H atoms. Also a pair of Ag and an impurity with zero nuclear magnetic moment seems improbable, although such a possibility cannot be ruled out experimentally. Therefore we suggest that the Si-NL56 spectrum of the C_{2v} symmetry arises from an isolated substitutional Ag atom. With the current findings the microscopic picture of an isolated Ag impurity in silicon becomes complete. It bears also a close similarity to the behavior of nickel in silicon: the isolated interstitial nickel Ni⁺_i in the high-symmetry site [10] and the isolated substitutional nickel Ni⁺_a of the C_{2v} symmetry [11].

The Si-NL56 spectrum, with the orthorhombic-I symmetry, the electron spin S=1/2, the principal g values close to the spin-only value $g_c=2.00232$, and the nearly [011] axial hf interaction, (i.e. similar to the case for the isolated vacancy V^- in silicon [12]), is in good agreement with the vacancy model proposed by Watkins [9]. Following this model, the substitutional Ag atom in its neutral charge state has a completely filled 4d shell accommodating 10 electrons $(4d^{10})$. The unpaired 5s electron, responsible for the paramagnetism of the center, occupies the b_1 orbital of the vacancy t_2 gap manifold state, which is split due to a Jahn-Teller distortion. Applying the treatment proposed by Anderson *et al.* [13] with the anisotropic term of the hf interaction P=-176.4 MHz for a ¹⁰⁷Ag 4d orbital [14], we find that the experimental value of $A_{[0\bar{1}1]} - (A_{[100]} + A_{[011]})/2 = +1.65$ MHz corresponds to the $N^2 \approx 1.2\%$ percentage of d character in the orbital. This value is in good agreement with the spin density value of 2.8% for 4d orbital on the Ag atom found alternatively in the numerical analysis of the experimental hf interaction based on the conventional one-electron linear-combination of atomic-orbitals (LCAO) approximation. Such a localization value is reasonable within the vacancy model.

B. Si-NL57 center

The trigonal symmetry of this center is evident from its angular dependence in the $(0\overline{1}1)$ crystal plane depicted in Fig. 2. The observed spectrum is not very well resolved, and overlaps partially with the Si-NL56. It contains six groups of EPR lines consistent with the six-fold hf splitting due to an interaction of an effective electron spin S=1/2 with a nuclear spin I=5/2 with an abundance of 100%. Further two-fold splitting within a line group can be explained by the hf interaction with a nuclear spin I=1/2 with an abundance of 100%. This spectral structure indicates a complex consisting of two different impurity atoms. Using the isotope effects, the two-fold hf splitting could be explained by Ag since the ratio of the doublet splittings observed for the samples doped with enriched ¹⁰⁷ Ag and ¹⁰⁹ Ag is consistent with the ratio of the nuclear magnetic moments of the two isotopes, and the identical spectra are obtained regardless of whether water or heavy water vapor atmosphere is used.

We therefore conclude to the involvement of one Ag atom in the defect structure of this center. With the nuclear spin I=5/2, the other component of the complex has to be considered as a contaminant introduced by diffusion. One can note that the Si-NL57 spectrum was not present in samples doped with high-purity natural silver. There are several elements with I=5/2 and a 100% natural abundance: ²⁷Al, ⁵⁵Mn, ¹²⁷I, ¹⁴¹Pr, Re (with two isotopes having roughly identical nuclear magnetic moments). Out of these, I, Pr and Re can be excluded as rare contaminants of silicon. Several samples were prepared under the same conditions and with a very small amount of Mn. The Si-NL57 spectrum could not be observed in such cases. In this way Mn has been ruled out as a possible constituent of the Si-NL57 center. On the other hand, the Si-NL57 spectrum could be readily seen in samples prepared under the same conditions and co-doped with natural high-purity Ag (99.999%) and Al. We note further that the isotopically enriched Ag used in our experiments was indicated to have a considerable Al contamination. In view of the above facts we assume that Al is involved in the defect composition and propose to assign the Si-NL57 spectrum to an Al-Ag pair.

The experimental data could be fitted using the spin Hamiltonian

$$\mathcal{H}_{S} = \mu_{B}\vec{B} \cdot \mathbf{g} \cdot \vec{S} + \vec{S} \cdot \mathbf{A}_{Al} \cdot \vec{I}_{Al} + \vec{S} \cdot \mathbf{A}_{Ag} \cdot \vec{I}_{Ag}, \qquad (2)$$

where g, A_{Al} and A_{Ag} represent the Zeeman splitting tensor and the hf interaction tensors for Al and Ag, respectively, with the effective electron spin S=1/2. The results of the computer fit are listed in Table 2. Applying the LCAO treatment to analyze the experimentally determined hf interaction components, the spin densities $\eta^2 \alpha^2$ and $\eta^2 \beta^2$ in the 3s and 3p orbitals on the Al atom are then determined as 1.6% and 0.8%, respectively. For the Ag atom only the isotropic part of the hf interaction is detected resulting in the spin density $\eta^2 \alpha^2$ in the 5s orbital of 1.6%.

Based on the observed hf interactions we propose to identify the Si-NL57 center as an Al-Ag pair. Obviously, the trigonal symmetry of the pair requires two atoms located along $\langle 111 \rangle$, possibly on the nearest-neighbor sites. In nonirradiated silicon, Al is known to occupy substitutional sites and acts as a shallow acceptor, spin S=0. Therefore the observed electron spin S=1/2 of the Si-NL57 center has to arise from the Ag component. From the analysis of the experimental results, one can

Table 2: Spin-Hamiltonian parameters of the center Si-NL57. The hf components are given in MHz.

Element	¹⁰⁷ Ag	¹⁰⁹ Ag	²⁷ Al
gli		1.9971	
g⊥	2.0127		
A _{ll}	21.4	24.7	61.4
A	21.4	24.7	59.2

that the hf interaction with the Ag atom is isotropic and, as such, results from the localization of the unpaired spin predominantly in the 5s orbital. This situation corresponds to the $4d^{10}5s^1$ electronic configuration of a Ag atom, in which a 5s electron gives rise to the electron spin S=1/2. As discussed for the Si-NL56 spectrum, both Ag_i^0 and Ag_s^0 isolated silver centers have the required electronic configuration. However, in view of the results obtained for the Si-NL56 center and the general trend of $(n-1)d^{10}ns^1$ type impurities outlined earlier, a neutral Ag atom on a substitutional site is likely to undergo a tetragonal Jahn-Teller and a weaker trigonal distortion, so that the overall symmetry of the hypothetical $Al_s^- Ag_s^0$ pair would be C_{2v} , or lower. Since the observed symmetry of the Si-NL57 center is trigonal, the $Al_s^- Ag_s^0$ pair is not a good candidate for the microscopic model of this defect. On the other hand, the $Al_s^- Ag_s^0$ pair will be trigonal and therefore in agreement with the experimental findings. Based on this reasoning, we attribute the Si-NL57 spectrum to the $Al_s^- Ag_i^0$ pair in the negative charge state.

Since the Si-NL57 spectrum was only observed for the samples doped with isotopically enriched Ag which was contaminated with Al, and not when natural Ag of high purity (99.999%) was used, we conclude that Al ions were introduced into silicon during the heat treatment. At first sight such a conclusion appears unlikely since Al is known to be a very slow diffusant in silicon. We point out, however, that in this case the diffusion process of Al could be influenced by three additional factors: i) a simultaneous presence of Ag, which is known to create vacancies [10], and therefore promotes the substitutional diffusion mechanism; ii) the oxidation of the sample surface, which took place in water vapor atmosphere at 1250 °C temperature, and which also enhances the diffusion [15]; iii) the presence of H atoms which could affect the activation energy for diffusion. In any case, a low concentration of aluminum contamination is consistent with the low intensity of the Si-NL57 spectrum observed in this study.

Conclusions

The isolated substitutional silver atom in silicon has been identified and analyzed by the EPR technique. The experimental data could be satisfactorily explained within the vacancy model. The other new EPR spectrum reported here is associated with the $Al_s^- Ag_i^0$ pair. In the process of sample preparation for the current study also the hydrogen-enhanced diffusion of Al and Ag in silicon has been observed.

Acknowledgements

One of us (P.N.H) acknowledges the Faculty of Mathematics, Informatics, Physics and Astronomy, University of Amsterdam for the study fellowship in the Van der Waals–Zeeman Institute.

References

- 1. N. Baber, H.G. Grimmeiss, M. Kleverman, P. Omling and M.Z. Iqbal, J. Appl. Phys 62, 2853 (1987) and references therein.
- 2. J. Olajos, M. Kleverman and H.G. Grimmeiss, Phys. Rev. B 38, 10633 (1988).
- 3. N.T. Son, V.E. Kustov, T. Gregorkiewicz and C.A.J. Ammerlaan, Phys. Rev. B 46, 4544 (1992).
- 4. N.T. Son, T. Gregorkiewicz and C.A.J. Ammerlaan, J. Appl. Phys. 73, 1797 (1993).
- 5. M. Höhne, U. Juda, Yu.V. Martynov, T. Gregorkiewicz, C.A.J. Ammerlaan and L.S. Vlasenko, Phys. Rev. B 49, 13423 (1994).
- 6. G.H. Fuller, J. Phys. Chem. Ref. Data 5, 835 (1976).
- 7. H.H Woodbury and G.W. Ludwig, Phys. Rev. 126, 466 (1962).
- 8. N.T. Son, T. Gregorkiewicz and C.A.J. Ammerlaan, Phys. Rev. Lett. 69, 3185 (1992).
- 9. G.D. Watkins, Physica 117B & 118B, 9 (1983).
- 10. G.W. Ludwig and H.H. Woodbury, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1962), Vol. **13**, 223.
- 11. L.S. Vlasenko, N.T. Son, A.B. van Oosten, C.A.J. Ammerlaan, A.A Lebedev, E.S. Taptygov and V.A. Khramtsov, Solid State Commun. **73**, 393 (1990).
- 12. M. Sprenger, S.H. Muller, E.G. Sieverts and C.A.J. Ammerlaan, Phys. Rev. B 35, 1566 (1987).
- 13. F.G. Anderson, F.S. Ham and G.D. Watkins, Phys. Rev. B 45, 3287 (1992).
- 14. A.K. Koh and D.J. Miller, At. Data Nucl. Data Tables 33, 235 (1985).
- 15. S. Mizuo and H. Higuchi, Jpn. J. Appl. Phys. 21, 56 (1982).