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Complexes of gold and platinum with hydrogen in silicon

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Abstract

Three centers that involve gold or platinum and hydrogen have been observed in n-type hydrogenated silicon by electron paramagnetic resonance. The first two centers, labeled Si-NL63 and Si-NL64, were detected in the gold-doped samples revealing hyperfine interaction with two gold atoms for the Si-NL63 center and one gold and two hydrogen atoms for the Si-NL64 center. The third spectrum, labeled Si-NL65, observed in the platinum-doped samples showed hyperfine interaction with one platinum and three equivalent hydrogen atoms that results in the hyperfine structure intensity ratio of $1:3:3:1 \approx 4:12:12:4 \approx 1:3:3:1$. The angular dependencies of the spectra have been measured and show monoclinic-I, triclinic and trigonal symmetry for the Si-NL63, Si-NL64 and Si-NL65 centers, respectively. Based on an analysis of the spin-Hamiltonian parameters, similarities of the hydrogen- and transition-metal hyperfine interactions of the centers are established. Microscopic models are proposed and, for Si-NL64, compared to the model of the well-known PtH₂ center. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Interaction between hydrogen and transition metals in crystalline silicon is known to not only passivate electrically active centers, but also to create new defect levels in the band gap. Results in the past were mostly obtained from electronic and optical spectroscopy, such as deep-level transient spectroscopy (DLTS) and infrared absorption.

Using DLTS, electronic levels related to transition-metal–hydrogen complexes were observed and could be assigned to complexes of hydrogen, one or several atoms, with gold, silver, cobalt, platinum, palladium, nickel or copper [1–8]. Structural information on these centers is not obtained from these measurements. Magnetic resonance, capable of providing detailed insight into the atomic and electronic structure of centers, has so far only been reported for the orthorhombic PtH₂ center and for the trigonal complex [PtH₂]₃ (spectrum Si-NL53) [9,10]. In the present study, by introducing hydrogen at high temperature in an atmosphere of water vapor (H₂O or D₂O), three centers identified as the hydrogenated transition

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metals Au or Pt have been detected by electron paramagnetic resonance. The atomic composition and geometrical structure of the centers was characterized and the quantitative spin-Hamiltonian analysis was performed. Microscopic models will be proposed.

2. Sample preparation and spectrometer

The material used in this experiment is silicon, n-type Czochralski-grown phosphorus-doped single crystal, which has a room-temperature resistivity of 0.75–1.25 Ω cm. The crystal was oriented and cut into bars with typical dimensions of $1.5 \times 1.5 \times 15$ mm³, and with the longest side parallel to a $\langle 011 \rangle$ crystallographic direction. Transition metals (Au, Pt) and hydrogen were separately diffused into the samples. Firstly, gold/platinum was in-diffused by thermal diffusion at temperatures from 1200°C to 1300°C for a duration of 1–72 h from a thin layer covering the surface of the samples, in argon gas atmosphere, followed by a fast quench to water at room temperature. The hydrogenation/deuteration process has been done following a similar procedure. The samples were again put into quartz ampoules filled with argon gas and a few milligrams of pure water/heavy water, and then heated to 1300°C for about half an hour. More details about the sample preparation may be found in Refs. [11,12].

Magnetic resonance experiments were carried out using a superheterodyne spectrometer operated in the K band with the frequency near 23 GHz. Signals were observed with the spectrometer tuned to dispersion under conditions of adiabatic fast passage. The magnetic field was modulated with an amplitude of approximately 0.1 mT and a frequency of 477 Hz. For a more complete description of the equipment and the experimental techniques, see, e.g., Ref. [13].

3. Experimental results

Two EPR spectra, labeled Si-NL63 and Si-NL64, have been found in Au-doped samples after

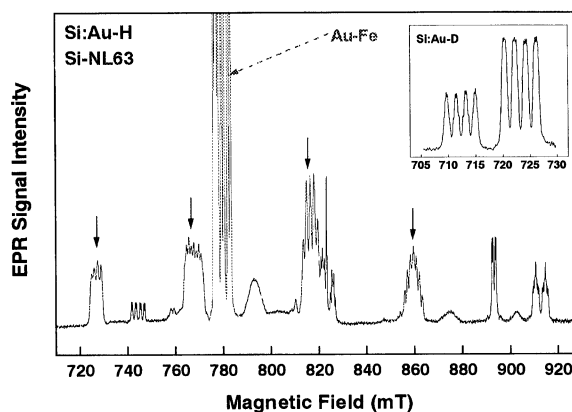


Fig. 1. A typical EPR spectrum of the Si-NL63 center observed in the gold-doped hydrogenated samples for magnetic field \mathbf{B} about 1° away from a $\langle 011 \rangle$ crystallographic direction, temperature $T = 4.2$ K and microwave frequency $f = 23.02168$ GHz. The solid arrows indicate each group of spectral lines. The inset in the upper right corner presents a part of the EPR spectrum observed at $f = 22.8540$ GHz for \mathbf{B} about 25° away from $\langle 011 \rangle$ direction in the deuterated samples revealing extra splitting in each of the spectral lines.

hydrogen in-diffusion. The first spectrum, the Si-NL63, is observed under normal measurement conditions, i.e., at 4.2 K and in darkness, presenting a mixed hyperfine structure of fourfold 4:4:4:4, sevenfold 1:2:3:4:3:2:1, and other arbitrary mixed structures due to the hyperfine interaction with one, two equivalent or two non-equivalent nuclei with spin $I = \frac{3}{2}$ and 100% natural abundance, respectively. A typical spectrum is shown in Fig. 1 for the magnetic field \mathbf{B} about 1° away from the $\langle 011 \rangle$ crystallographic direction. The angular dependence of the spectrum was measured and shows that the center has monoclinic-I symmetry with large anisotropy of the \mathbf{g} tensor. The measurements were also carried out in the deuterated samples, which were prepared under similar conditions as the hydrogenated ones. A part of the Si-NL63 spectrum observed in the deuterated samples is depicted in the inset of Fig. 1 for a magnetic field \mathbf{B} about 25° away from the $\langle 011 \rangle$ direction revealing extra splitting in each of the spectral lines.

The Si-NL64 spectrum is observed under visible-light illumination. The typical spectrum, as shown in Fig. 2, reveals hyperfine structure of

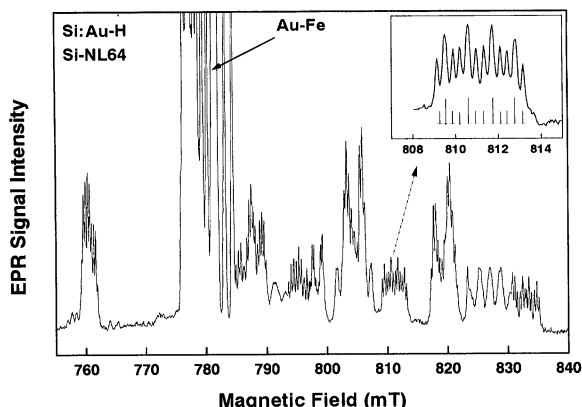


Fig. 2. EPR spectrum of the Si-NL64 center observed under visible-light illumination for the full range of the magnetic field from 750 to 840 mT for \mathbf{B} about 10° away from a $\langle 011 \rangle$ crystallographic direction, a microwave frequency $f = 23.02168$ GHz and temperature $T = 4.2$ K. A closer view of the hyperfine structure of 1:2:1:1:2:1:1:2:1 is shown in the inset.

1:2:1:1:2:1:1:2:1 due to hyperfine interaction with one gold atom ($I = \frac{3}{2}$, 100%) and two hydrogen atoms ($I = \frac{1}{2}$, 100%). The spectrum has the rare low triclinic symmetry with spin-Hamiltonian parameters as listed in Table 1. In the deuterated samples, due to the hyperfine interaction with deuterium ($I = 1$, 99.5%) the expected hyperfine structure would be 1:2:3:2:1:1:2:3:2:1:1:2:3:2:1:1:2:3:2:1. However, due to the smaller nuclear magnetic moment and due to the quadrupole interaction, the observed spectrum becomes very complicated and unresolved for almost all directions of applied magnetic field.

The third spectrum, labeled Si-NL65, is observed in the platinum-doped hydrogenated samples simultaneously with the PtH₂ center. The center has very low formation probability, presenting hyperfine interaction with one platinum atom ($I = \frac{1}{2}$, 33.8%) and three equivalent hydrogen atoms that results in the observed hyperfine structure with a relative intensity of $1:3:3:1 \approx 4:12:12:4 \approx 1:3:3:1$ of spectral lines, as depicted in Fig. 3. The angular dependence of the Si-NL65 spectrum was measured and shows trigonal symmetry for the center with $g_{\parallel} = 1.9673$ and $g_{\perp} = 2.1569$.

4. Discussion

The chemical composition of the defects is derived from the appearance of hyperfine structure in the EPR spectra. The microscopic model is then proposed based on the spin-Hamiltonian parameters and the observed symmetry of the defect. In our experiment, all spectra reveal the hyperfine interaction with transition-metal atoms, i.e., hyperfine interaction with gold for the Si-NL63 and Si-NL64 spectra and platinum for the Si-NL65 spectrum. The mixed hyperfine structure of fourfold-, sevenfold-splitting and other mixed structure of the Si-NL63 spectrum can be explained if we assume that there is an involvement of two non-equivalent gold atoms. The low symmetry monoclinic-I of the angular dependence of the spectrum and the fact that it can only be observed in the samples with high concentration of gold supports this assumption. The incorporation of hydrogen into the Si-NL63 center is established following the observation of extra small splitting in the samples diffused with deuterium instead of hydrogen, see the inset of Fig. 1. Unfortunately, due to the small hydrogen hyperfine interaction, the exact number of hydrogen atoms involved cannot be determined. Apparently, these results are not sufficient by themselves to establish a detailed model of the defect. Therefore, for simplicity of our calculations, we have ignored the contribution of hydrogen hyperfine interaction and performed the simulation for the simplest case of a defect with two equivalent gold atoms. The calculated results are given in Table 1. A more detailed analysis of the spin-Hamiltonian parameters of the center can be found in Ref. [11].

For the Si-NL64 spectrum, from the observed well-resolved hyperfine structure of 12 components with the relative intensity of 1:2:1:1:2:1:1:2:1:1:2:1 as presented in Fig. 2, one can obviously conclude that the center contains one gold atom and two hydrogen atoms. In a triclinic symmetry configuration, the two hydrogen atoms cannot be strictly on equivalent sites in the defect; they must find themselves on sites with a nearly identical local structure that results in an equal hydrogen hyperfine interaction as observed in the

Table 1

Spin-Hamiltonian parameters for the Si-NL63, Si-NL64 and Si-NL65 centers, calculated by computer fits and simulation of the EPR angular dependencies. The values of the PtH₂ center are also given for comparison

| Parameters | g_1/A_1 | g_2/A_2 | g_3/A_3 | θ | Units |
|-----------------------------------|-------------------------------|-----------------------|-----------|----------|-------|
| Si-NL63 (monoclinic-I) | | | | | |
| g | 1.9138 | 2.2942 | 2.0387 | 21 | |
| A^{Au} | 34.5 | 46.8 | 42.2 | 10 | MHz |
| Si-NL64 (triclinic) | | | | | |
| g | 2.1282 | 2.0689 | 2.0039 | | |
| g_{xy} | -0.0731 | | | | |
| g_{yz} | 0.0394 | | | | |
| g_{zx} | 0.0360 | | | | |
| A^{Au} | 13.8 | 23.5 | 18.1 | | MHz |
| A^{H} | 8.676 | 11.392 | 8.536 | | MHz |
| a^{H} | 9.5 | 9.5 | 9.5 | | MHz |
| b^{H} | 0.95 | 0.95 | 0.95 | | MHz |
| Si-NL65 (trigonal) | | | | | |
| g/A | $g_{\parallel}/A_{\parallel}$ | g_{\perp}/A_{\perp} | | | |
| g | 1.9673 | 2.1569 | | | |
| A^{Pt} | 708.8 | 52.2 | | | MHz |
| A^{H} | 14.5 | 12.7 | | | MHz |
| a^{H} | 13.3 | 13.3 | | | MHz |
| b^{H} | ~0.6 | ~0.6 | | | MHz |
| PtH ₂ (orthorhombic-I) | | | | | |
| g/A | g_1/A_1 | g_2/A_2 | g_3/A_3 | | |
| g | 2.1299 | 2.1683 | 1.9563 | | |
| A^{Pt} | 175.7 | 237.3 | 541.2 | | MHz |
| A^{H} | 9.8 | 8.2 | 7.9 | | MHz |
| a^{H} | 8.6 | 8.6 | 8.6 | | MHz |
| b^{H} | ~0.6 | ~0.6 | ~0.6 | | MHz |

experiment. Having triclinic symmetry, the AuH₂ center cannot be viewed as an exact counterpart of the well-known orthorhombic-I PtH₂ center. However, closer inspection and analysis reveal many similarities between the two centers. Considering first the hyperfine interaction with the transition element it appears that their principal values, as given in Table 1, are very nearly proportional to the respective nuclear g values of the gold and platinum (¹⁹⁵Pt: $g_n = 1.1290$, ¹⁹⁷Au: $g_n = 0.09717$), implying equal spin localization in the core part of the centers. The same conclusion can be deduced for the hydrogen hyperfine interactions. In both cases the isotropic part a is near 9 MHz and the anisotropic part b near 0.6 MHz, resulting in the same values for the

AuH₂ center on localization of 0.6% and distances of 0.5 nm as reported for PtH₂ in Refs. [9,10]. These similarities allow us to use the well-established PtH₂ model as a starting point for the AuH₂ center. The model is sketched in Fig. 4(a) with the core of the defect containing a substitutional gold atom and two hydrogen atoms at the anti-bonding site to two silicon nearest neighbors. As the neutral gold is iso-electronic to negative platinum, it is reasonable that the Si-NL64 spectrum corresponds to the [Au_s(H_i)₂]⁰ center observed in the neutral paramagnetic state. For reasons yet unknown the AuH₂ center has distorted to lower symmetry.

Observed in the platinum-doped hydrogenated samples simultaneously with the PtH₂ center, the

EPR spectrum of the Si-NL65 center shows many similarities to that of the PtH₂ center. Firstly, the hyperfine structure 1:3:3:1 ≈ 4:12:12:4 ≈ 1:3:3:1 of the Si-NL65 spectrum can be understood as an extended picture of the hyperfine structure of 1:2:1 ≈ 4:8:4 ≈ 1:2:1 of the PtH₂ spectrum in which the hyperfine interaction with a third equivalent hydrogen atom is added. This requires the rearrangement of all nuclei involved on an

atomic scale. The theoretical calculations by Resende et al. [14,15] show that all defects of single transition metals (Pt, Pd, Au, Ag...) with three hydrogen atoms have trigonal symmetry compared to the orthorhombic-I symmetry of the defect with only two hydrogen atoms. Indeed, the symmetry of the Si-NL65 center observed in our experiments is trigonal. The spin-Hamiltonian parameters obtained from computer fits to the experimental data are given in Table 1. Secondly, the hydrogen hyperfine interaction of the Si-NL65 center also shows a slight anisotropy with the isotropic part *a* near 13 MHz and the anisotropic part *b* near 0.6 MHz, implying a localization of 0.9% of electron spin on each of three protons and a distance of 0.5 nm to the core of the defect. The atomic model of the Si-NL65 center is sketched in Fig. 4(b) in which the platinum atom is at the substitutional site and three interstitial hydrogen atoms are anti-bonded to three silicon nearest neighbors. In this axial configuration, the three hydrogen atoms are arranged with trigonal symmetry about a <111> trigonal axis through the platinum atom. Taking into account the fact that the PtH₂ center is paramagnetic in the negative charge state [Pt_s(H_i)₂]⁻, it is quite possible that the Si-NL65 spectrum corresponds to the [Pt_s(H_i)₃]⁰ center observed in the neutral paramagnetic charge state.

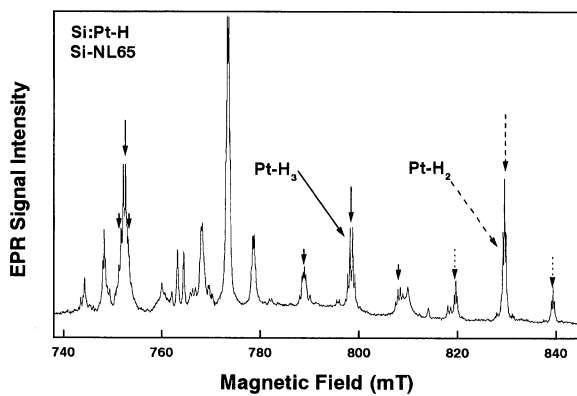


Fig. 3. EPR spectrum of the Si-NL65 center recorded under visible-light illumination for magnetic field $\mathbf{B} \parallel \langle 011 \rangle$ direction, temperature $T = 4.2$ K and microwave frequency $f = 22.713688$ GHz. The spectrum is characterized by a 1:3:3:1 ≈ 4:12:12:4 ≈ 1:3:3:1 hyperfine structure and is indicated by solid arrows. The spectrum PtH₂ is also observable and marked by dashed arrows.

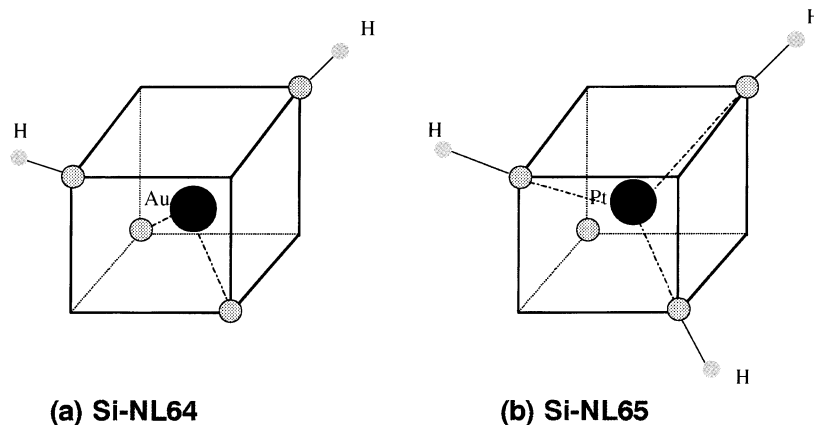


Fig. 4. Microscopic models for (a) the Si-NL64 center of AuH₂ and (b) the Si-NL65 center of PtH₃. In the models, the transition metal atoms occupy the substitutional sites. Hydrogen atoms are all at the interstitial site anti-bonding to the silicon nearest-neighbor atoms.

In summary, the interaction of hydrogen with the transition metals gold and platinum in silicon has been investigated by electron paramagnetic resonance. Three centers have been detected and identified as defects of two non-equivalent gold atoms and an undetermined number of hydrogen atoms, one-gold–two-hydrogen and one-platinum–three-hydrogen complexes, respectively, for the Si-NL63, Si-NL64 and Si-NL65 spectra. The symmetries and the spin-Hamiltonian parameters of the centers have been determined and analyzed and compared to that of the well-known PtH_2 center. It was found that although symmetries are different, the properties of hydrogen hyperfine interactions of the centers are very similar with the isotropic part a of about 10 MHz and the anisotropic part b of about 1 MHz. This, in addition to the fact that the transition metal atoms are usually more stable at the substitutional site, leads to a similar atomic model for the centers in which the gold or platinum atoms are at a substitutional position, and hydrogen atoms are at interstitial sites anti-bonded to silicon nearest-neighbor atoms.

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