

Physica B 308-310 (2001) 408-413



www.elsevier.com/locate/physb

Electronic and atomic structure of transition-metal-hydrogen complexes in silicon

P.T. Huy^{a,b,*}, C.A.J. Ammerlaan^a

^a Van der Waals–Zeeman Institute, University of Amsterdam, Valckenierstraat 65-67, NL-1018 XE Amsterdam, Netherlands ^b International Training Institute for Materials Science, ITIMS Building, Dai Hoc Bach Khoa Hanoi, 1 Dai Co Viet Road, Hanoi, Viet Nam

Abstract

Electron paramagnetic resonance investigations on transition-metal-doped silicon, hydrogenated at high temperature in an environment of water vapor, have revealed three transition-metal-hydrogen related paramagnetic centers Si-NL65, Si-NL64, and Si-NL68, respectively, in the samples doped with platinum, gold, and palladium. The spectra, from the sample preparation conditions, and the experimentally observed hyperfine structures of 1:3:3:1-4:12:12:4-1:3:3:1 for the Si-NL65, 1:2:1-1:2:1-1:2:1-1:2:1 for the Si-NL64, and 1:1 for the Si-NL68 spectrum, were identified as complexes of one-platinum-three-hydrogen (Pt-H₃), one-gold-two-hydrogen (Au-H₂), and onepalladium-one-hydrogen (Pd-H₁), respectively. A detailed analysis of the spin-Hamiltonian parameters of the centers, the transition-metal and hydrogen hyperfine interactions, has been carried out providing adequate materials for establishing electronic and microscopic models of the newly observed centers. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Si; Defects; Transition-metal-hydrogen complexes; EPR

1. Introduction

The properties of transition-metal-hydrogen complexes (TM-H) in crystalline silicon have been studied intensively in the last 15 years. As a result of this effort, the electronic levels, the local vibrational modes, and the structure of a number of TM-H defects have been identified mostly by deep level transient spectroscopy (DLTS) [1,2], Fourier transform infrared and local vibrational mode (FTIR-LVM) spectroscopy [3,4]. These techniques have given valuable information about the position of the TM-H levels in the band-gap, their electron and hole capture cross sections, local vibrational modes associated with hydrogen, and the numbers of hydrogen atoms as well as their positions within the structure of the defects have been determined. However, little direct information has been obtained

about the microscopic structure and the chemical composition of TM-H related defects as the electron paramagnetic resonance (EPR) has failed to detect TM-H related centers so far. Up to now, the Pt-H₂ center was the only case in which both the structure of the defect, and its electronic properties were convincingly established using the combined results from EPR, IR-LVM, and theoretical calculations [1,2,5-7]. To overcome the handicap, in this paper, we report on the studies of TM-doped hydrogenated silicon by EPR. Three TM-H complexes have been observed and identified as containing one transition-metal atom and one, two and three hydrogen atoms, respectively, for the Pd-H₁, Au-H₂ and Pt-H₃ centers. Symmetries of the centers have been measured and determined as monoclinic-I for the Pd-H₁, triclinic for Au-H₂ and trigonal for Pt-H3 centers. A detailed analysis of the experimental spectra has been carried out and enabled us to determine spin-Hamiltonian parameters of the centers. It was discovered that although the number of hydrogen atoms in each center is different, the hydrogen hyperfine

^{*}Corresponding author. Tel.: + 31-20-5255642; fax: + 31-20-5255788.

E-mail address: pthuy@science.uva.nl (P.T. Huy).

^{0921-4526/01/\$ -} see front matter C 2001 Elsevier Science B.V. All rights reserved. PII: \$0921-4526(01)00765-7

interactions are very similar with their isotropic and anisotropic parts of about 10 and 1 MHz, respectively. This common character of observed hydrogen hyperfine interaction is reflected in the electronic and atomic models proposed for the centers in which the hydrogen atoms are concluded to favor the interstitial antibonding sites to the silicon nearest-neighbor atoms.

2. Experimental

Phosphorus-doped Czochralski-grown silicon with room-temperature resistivity in the range of 0.75- 125Ω cm was used in this study. The crystal was oriented and cut into bar-shaped samples with typical dimensions of $1.5 \times 1.5 \times 15$ mm³, and with the longest side parallel to the $[0\overline{1}1]$ crystal direction. Transition metals gold, platinum, and palladium were introduced by two different methods, either by evaporation or by rubbing TMs to one or all surfaces of the samples, and then heated at 1200-1300°C for several hours. The hydrogenation process was typically performed at 1250-1300°C for 30 min in the atmosphere of water vapor. After hydrogenation the samples were quenched in water at room temperature, then stored in liquid nitrogen till the first measurement. Magnetic resonance experiments were carried out using a superheterodyne spectrometer operating in the microwave K-band with the frequency near 23 GHz. The EPR spectra were measured at temperatures of 4.2-20 K.

3. Results

In the platinum-doped hydrogenated samples, after hydrogenation, depending on the cooling rate of the samples, two different Pt-H related spectra are observed. The first spectrum, which has quite high formation probability and is observable in all samples investigated, is characterized by a typical hyperfine structure of 1:2:1-4:8:4-1:2:1, identifying the wellknown Pt-H₂ center [3-5]. The second spectrum, labeled Si-NL65, detectable only under visible-light illumination, has very low formation probability and is observable only in 2 of the 40 samples made with very fast cooling rate. The Si-NL65 spectrum, as depicted in Fig. 1, is characterized by a hyperfine structure with the relative intensity of the spectral lines typically of 1:3:3: 1-4:12:12:4-1:3:3:1 as being due to the hyperfine interaction with a platinum atom (I = 1/2, 33.8%)abundance), and three equivalent atoms with I = 1/2, 100% abundance. In Fig. 1 for comparison, the EPR spectrum of the Pt-H₂ center is also given and indicated by dashed arrows. The angular dependence of the Si-NL65 spectrum has been measured for the rotation of the magnetic field in the $(0\overline{1}1)$ plane from a [100] to a



Fig. 1. EPR spectrum of the Si-NL65 center associated with the trigonal Pt-H₃ center observed in the platinum-doped hydrogenated sample under visible-light illumination for the magnetic field B// [0 1 1] direction, T = 4.2 K, and microwave frequency f = 22.71369 GHz. The spectrum is characterized by a 1:3:3:1-4:12:12:4-1:3:3:1 hyperfine structure. The Pt-H₂ spectrum with hyperfine structure of 1:2:1-4:8:4-1:2:1 is also observed and is indicated by dashed arrows.

[011] direction, as shown in Fig. 2, revealing the trigonal symmetry of the underlying defect.

In palladium-doped samples, the experimental results showed that after hydrogenation the EPR spectrum of the Pd_s⁻ center, which was observed strongly in the samples, has disappeared [8]. The EPR spectrum of Fe_i^0 , and in several samples the spectrum of the Pd-Fe pair, has emerged [9]. No immediate Pd-H spectrum was detected. Practically, the observed disappearance of the Pd_s⁻ center after hydrogen treatment suggests a possibility that all Pd, centers have been converted to other Pdrelated centers including the Pd-Fe pair. But as in the experiments only the Pd-Fe pair is observed with much lower intensity after hydrogenation (or not observed at all), the possibility of formation of Pd-H complexes, which are neutral or non-paramagnetic, has to be taken into account. It is known from DLTS experiments that by annealing the samples at temperatures of 400-550 K, one can promote the conversion processes in which the hydrogen-related centers capture or release one or more hydrogen atoms to form new complexes [10,11]. There is a possibility that the new-formed complexes are paramagnetic and observable by EPR. We therefore have carried out the isochronal thermal annealing of our samples. Results showed that after annealing at 450 K



Fig. 2. Angular dependence pattern of the Si-NL65 spectrum as measured for rotation of the magnetic field in the $(0\bar{1}1)$ plane from the [100] to [011] directions. The experimental data recorded for temperature T = 4.2 K and microwave frequency f = 22.731688 GHz are presented as solid circles. The trigonal symmetry of the Pt-H₃ is clearly determined.

for 60 min, the EPR spectrum of the Pd_s⁻ center has weakly recovered. Further annealing revealed the gradual recovery of the Pd_s⁻ center. At the same time a new EPR spectrum is emerging. This spectrum, labeled Si-NL68 for further reference, achieves its highest intensity after annealing at 500 K for about 120 min, see Fig. 3. One of the difficult points in this experiment is, as can be seen in Fig. 3, the very low intensity of the Si-NL68 spectrum, even at its highest concentration. Also, the spectral lines are superimposed, in many parts, on the much stronger Pd_s^- and P_s^0 spectra. Fortunately, by careful measurements with slower scanning speed and highest resolution, we were still able to collect the positions of all the spectral lines versus the magnetic field when rotated in the $(0\overline{1}1)$ plane from the [100] to [011] directions. The corresponding pattern is shown in Fig. 4 presenting monoclinic-I symmetry for the Si-NL68 center. Especially, at the main directions [100] and [011], where the intensity of the spectrum is higher, we observed extra twofold splitting in each of the spectral lines. This splitting is in the order of 7-10 MHz and is anisotropic, providing evidence for the hyperfine interaction with a nucleus with spin I = 1/2 and 100% abundance.

In gold-doped samples, the EPR Si-NL64 spectrum of the $Au-H_2$ center is recorded directly after hydrogena-



Fig. 3. EPR spectrum of the Si-NL68 center observed in the palladium-doped hydrogenated sample after an isochronal annealing at 500 K for 120 min. The Si-NL68 spectrum is characterized by a twofold splitting in each of the spectral lines as due to hyperfine interaction with one hydrogen atom (I = 1/2, 100%), as shown in the inset. Magnetic field B// [100].



Fig. 4. Angular dependence pattern of the Si-NL68 spectrum observed for the rotation of the magnetic field in the $(0\bar{1}1)$ plane from the [100] to [011] directions, disclosing the monoclinic-I symmetry for the corresponding defect.

tion. The spectrum, as depicted in Fig. 5, as observed under visible-light illumination for the magnetic field about 10° away from the [0 1 1] direction, shows a very complicated hyperfine structure with a large number of



Fig. 5. Typical EPR spectrum of the Si-NL64 center observed in the gold-doped hydrogenated sample under visible-light illumination for the magnetic field about 10° away from the [011] direction, with microwave frequency f = 23.0217 GHz, at temperature T = 4.2 K.

groups of spectral lines. This complexity of the spectrum makes the task of identification of the Si-NL64 center difficult. Fortunately, as shown in an extended view in the inset of Fig. 5, each group of spectral lines of the Si-NL64 spectrum is characterized by a very informative hyperfine structure with the relative intensity of 1:2: 1-1:2:1-1:2:1-1:2:1 which can be attributed to the hyperfine interaction with one gold atom (I = 3/2, 100%) and two hydrogen atoms (I = 1/2, 100%). The spectrum has the rare low symmetry of triclinic, as given in Fig. 6.

4. TM-H identification

In all cases, from the experimental results as described above, the identification of the spectra as originating from TM-H complexes is directly established (except for ¹⁰⁵Pd in the Pd-H₁ center). Firstly, all spectra Si-NL64, Si-NL65, and Si-NL68 are observed after hydrogenation. They all exhibit extra splitting of twofold (1:1), threefold (1:2:1), and fourfold (1:3:3:1) revealing hyperfine interaction with one, two, and three hydrogen atoms, respectively, for the Si-NL68, Si-NL64 and Si-NL65 centers. The Si-NL65 spectrum is observed in the platinum-doped sample simultaneously with the Pt-H₂ spectrum. One can practically view the hyperfine structure of 1:3:3:1-4:12:12:4-1:3:3:1 as an extended picture of the hyperfine structure of 1:2:



Fig. 6. Triclinic angular dependence pattern of the Si-NL64 spectrum observed for rotation of the magnetic field in the $(0^{1}1)$ plane from the [100] to [011] crystallographic directions. Experimental data recorded at T = 4.2 K, microwave frequency f = 23.0217 GHz.

1-4:8:4-1:2:1 of the Pt-H₂ center in which a third equivalent proton is added. As already concluded for the Pt-H₂ spectrum, the presence of one platinum atom is indicated by the resolved hyperfine splitting related to the ¹⁹⁵Pt isotope, nuclear spin I = 1/2 and natural abundance of 33.8%, resulting in the characteristic splitting of the resonance in three components with the intensity ratio of about 1:4:1. Presence of two equivalent hydrogen atoms is revealed by triplet structure with amplitudes scaling as 1:2:1 of all resonances due to the hyperfine fields created by two hydrogen atoms (I = 1/2, 100%). Combination of these interactions produces the hyperfine structure of 1:2: 1-4:8:4-1:2:1 as observed in the experiments. Adding the third hydrogen atom, the hydrogen hyperfine becomes 1:3:3:1. Consequently, structure the 1:3:3:1-4:12:12:4-1:3:3:1 hyperfine structure is created when combined with hyperfine interaction due to a single platinum atom. This is the case for the Si-NL65 spectrum of the Pt-H₃ center. A similar interpretation is applied for the Si-NL64 spectrum of the Au-H₂ center. In this case, the observed structure of 1:2:1-1:2:1-1:2:1-1:2:1 can be explained as due to hyperfine interaction with one gold atom, nuclear spin I = 3/2 and 100% natural abundance (generating fourfold splitting) and two equivalent or nearly equivalent hydrogen atoms (generating 1:2:1 structure). For the Si-NL68 spectrum, due to low intensity of the spectrum, the hyperfine lines which represent the hyperfine

interaction with ¹⁰⁵Pd isotope (I = 5/2, 22.2%) are not strong enough for observation. The assignment to a Pd-H₁ complex, therefore, is tentative and based on the experimental observation of twofold splitting as due to interaction with one hydrogen atom and the appearance of only palladium-related centers in the investigated samples.

5. Electronic and atomic structure of TM-H complexes

From a summary of the spin-Hamiltonian parameters of the centers, as obtained from fittings of the angular dependencies (Figs. 2, 4 and 6) and results of the standard analysis based on linear-combination-of-atomic-orbitals (LCAO), given in Table 1, one can recognize that the g tensors of all centers largely deviate from $g_e =$ 2.0023 of the free electron, implying the incorporation of a transition-metal impurity in the microscopic structures of the centers. The hydrogen hyperfine interaction tensors also show a striking similarity for all centers with isotropic part a of about 10 MHz, corresponding to a very low s-type spin density around 0.7% on the hydrogen positions. The small anisotropic component $b^{\rm H}$ of the hydrogen hyperfine interaction, may be

ascribed to the dipole-dipole interaction between the spins of proton and electron, considered as classical dipoles with separation R. From the observed values of b of around 1 MHz, a distance of R = 0.4 - 0.5 nm is calculated. This value means a distance of 0.4-0.5 nm between the transition-metal atom and the proton, i.e., the hydrogen atom is anti-bonding to the silicon nearest neighbor. In all cases, the observed centers are stable at room temperature and have low symmetry, trigonal for the Pt-H₃, monoclinic-I for the Pd-H₁, and triclinic for the Au-H₂ centers, suggesting the substitutional position for the transition-metal atom. On this basis, the atomic model for each center is proposed, as sketched in Fig. 7, in which the transition-metal atom occupies the substitutional site, the hydrogen atom is interstitial and anti-bonding to a silicon nearest-neighbor atom. The position of the TM atom is depicted with respect to the symmetry of each center. As neutral gold is isoelectronic to negative platinum, quite likely spectrum Si-NL64 corresponds to the $[Au_s - (H_i)_2]^0$ center observed in the neutral charged state (the $(Pt-H_2)^-$ center is observed in negative charge state, see Refs. [3,5]). For the same reason, the Si-NL65 spectrum of the $(Pt-H_3)^0$ center is observed in the neutral charge state as well.

Table 1

Summary of spin-Hamiltonian parameters and some results of the analysis by the method of linear combination of atomic orbitals (LCAO) for transition-metal—hydrogen complexes

Center (Pt-H ₂) ⁻	Symmetry Orthorhombic-I (C _{2v})	$Tensors$ g A^{Pt} A^{H} $\eta^{2}(H)$ b^{H} R	Parameters of spectra and centers		
			2.1299 ([1 0 0]) 175.7 MHz 9.8 MHz ~0.6% ~0.6 MHz ~0.4-0.5 nm	1.9558 ([0 Ī 1]) 541.2 MHz 7.9 MHz	2.1683 ([0 1 1]) 237.3 MHz 8.2 MHz
(Pt-H ₃) ⁰ (Si-NL65)	Trigonal (C _{3v})	g Α ^{Ρτ} Α ^Η η ² (Η) b ^Η <i>R</i>	1.9673 (g) 708.8 MHz 14.5 MHz ~0.9% ~0.6 MHz ~0.4-0.5 nm	2.1569 (g⊥) 52.2 MHz 12.7 MHz	
Pd-H1 (Si-NL68)	Monoclinic-I	g A ^H b	1.998 ([100]) ∼7–10 MHz ∼1 MHz	2.0361 22° away from [0 1 1]	1.9651 22° away from [100]
(Au-H ₂) ⁰ (Si-NL64)	Triclinic	g A ^A u A ^H η ² (H) b ^H R	2.1282 (g _{xx}) 13.8 MHz 8.67 MHz ~0.67 ~0.9 MHz ~0.4-0.5 nm	2.0689 (g _{yy}) 23.5 MHz 11.39 MHz	2.0039 (g ₂₂) 18 MHz 8.54 MHz



Fig. 7. Atomic models proposed for the monoclinic-I Pd- H_1 (a), the triclinic Au- H_2 (b), and the trigonal Pt- H_3 centers (c).

References

- J. Weber, in: N.H.Nickel, W.B. Jackson, R.C. Bowman, R.G. Leisure (Eds.), Hydrogen in Semiconductors and Metals, Materials Research Society, Warrendale, 1998, p. 345.
- [2] J. Weber, W. Jost, H. Lemke, A. Mesli, J.-U. Sachse, E.Ö. Sveinbjörnsson, N. Yarykin, Mat. Res. Soc. Symp. Proc. 512 (1988) 345.
- [3] P.M. Williams, G.D. Watkins, S. Uftring, M. Stavola, Phys. Rev. Lett. 70 (1993) 3816.
- [4] M.J. Evans, M. Stavola, M.G. Weinstein, S.J. Uftring, Mater. Sci. Eng. B 58 (1999) 118.
- [5] M. Höhne, U. Juda, Yu.V. Martynov, T. Gregorkiewicz, C.A.J. Ammerlaan, L.S. Vlasenko, Phys. Rev. B 49 (1994) 13423.

- [6] S.J. Uftring, M. Stavola, P.M. Williams, G.D. Watkins, Phys. Rev. B 51 (1995) 9612.
- [7] A. Resende, R. Jones, S. Öberg, P.R. Briddon, Phys. Rev. Lett. 82 (1999) 2111.
- [8] H.H. Woodbury, G.W. Ludwig, Phys. Rev. 126 (1962) 466.
- [9] A.B. van Oosten, N.T. Son, L.S. Vlasenko, C.A.J. Ammerlaan, Mater. Sci. Forum 38-41 (1989) 355.
- [10] J.-U. Sachse, J. Weber, H. Lemke, Mater. Sci. Forum 258-263 (1997) 307.
- [11] E.Ö. Sveinbjörnsson, O. Engström, Phys. Rev. B 52 (1995) 4884.