

Hydrogen Interaction with Transition Metals in Silicon, Studied by Electron Paramagnetic Resonance

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Keywords: Magnetic Resonance, Silicon, TM-H Complexes, Transition Metals

Abstract

The interaction of hydrogen with the transition metals Pd, Au, and Pt in silicon has been investigated using electron paramagnetic resonance. Three transition-metal – hydrogen related EPR spectra are observed and identified as originating from complexes of one transition-metal atom with up to three hydrogen atoms. From the angular variation measurements, symmetries of the centers are established. The hyperfine interactions with transition metals and hydrogen atoms are determined. Microscopic atomic and electronic models are proposed.

Introduction

After the first observation of hydrogen passivation of defect levels in silicon reported in the nineteen-eighty decade, hydrogen as a multi-purpose impurity in silicon, either beneficial or detrimental, has attracted enormous research interest. It was soon discovered that the interaction with hydrogen not only can passivate the defect levels [1,2], but also, in several cases does create new hydrogen-related levels in the band gap of semiconductors, thus activating centers [3]. One of the important categories is the interaction of hydrogen with deep levels of technologically interesting transition-metal impurities in silicon. Results from experiments showed that hydrogen atoms sometimes introduced unintentionally through the chemical etching process, can easily interact with transition metal impurities, creating TM-H levels with almost all transition metals in silicon [4,5]. So far mostly results were reported using optical and electrical methods such as deep-level transient spectroscopy and Fourier-transform infrared absorption. These techniques, in spite of being very powerful for the detection of deep levels, do not provide any information about either defect structure or its chemical composition. In this paper, we report on the studies of transition-metal doped hydrogenated silicon by electron paramagnetic resonance (EPR). Three TM-H complexes have been detected and were 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. The angular dependencies of the spectra have been measured and symmetries of the corresponding centers were determined to be triclinic symmetry for Au-H₂, trigonal for Pt-H₃ and monoclinic-I for Pd-H₁. Further studies of thermal stability and formation probability of the centers also have been carried out. It was established that depending on transition metal, the TM-H complex can be stable up to 650 K and the formation probability is higher for the Au-H₂ and Pt-H₂ than for the Pd-H₁ center and is extremely low for Pt-H₃. On these bases, atomic models and electronic structures of the observed centers are established.

Experiment

The material for this study was prepared from n-type Czochralski-grown silicon phosphorus-doped, which has the room temperature resistivity of 0.75–1.25 Ωcm. The samples of 1.5×1.5×15 mm³ dimensions were covered with a thin layer of transition metal (Pt, Pd, or Au) by vacuum evaporation or by rubbing transition metal 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 °C for 30 minutes in the atmosphere of water vapor. After hydrogenation the samples were quenched to

water at room temperature. The EPR measurements were carried out using a K-band superheterodyne spectrometer operating at microwave frequency $f \approx 23$ GHz. The dispersion part of the magnetic susceptibility was recorded with the microwave power kept at the microwatt level. The sample was mounted with the $[0\bar{1}1]$ direction perpendicular to the plane in which the magnetic field could be rotated. The EPR spectra were measured at liquid-helium temperature 4.2 K.

Results

Si-NL68 spectrum of Pd-H₁ complex

In palladium-doped samples, experimental results showed that after hydrogenation the EPR spectrum of the substitutional palladium center $\text{Pd}_{\text{S}}^{\circ}$, which was observed strongly before in the samples, has disappeared. The EPR spectrum of the Fe° center, and in several samples the EPR spectrum of Pd-Fe pair, has emerged. No immediate Pd-H spectrum was detected. In Figs. 1 typical EPR spectra observed in the palladium-doped sample before and after hydrogenation are presented. The spectra clearly showed that even in case of formation of the Pd-Fe center after hydrogenation, the concentration of this center is much lower than the concentration of the $\text{Pd}_{\text{S}}^{\circ}$ center (see also Fig. (2a)), i.e., by the hydrogenation a loss of Pd-related EPR centers has occurred. This suggests that there must be a fraction of palladium atoms involved in the formation of Pd-H complexes. The fact that we do not observe these complexes by EPR might be due to either full passivation of the centers by hydrogen or the passivation products are non-paramagnetic.

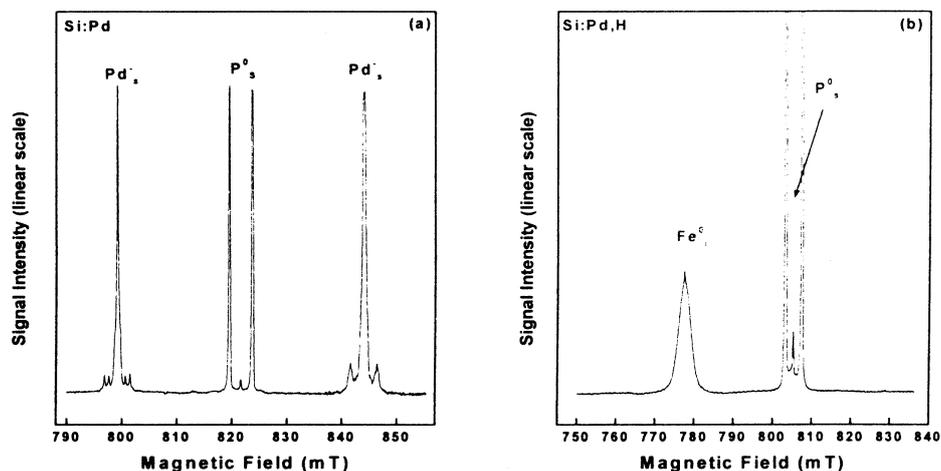


Fig. 1: Typical EPR spectra observed in platinum-doped sample (a) before hydrogenation, (b) after hydrogenation. A comparison clearly shows that after hydrogenation the EPR spectrum of the $\text{Pd}_{\text{S}}^{\circ}$ center has disappeared. No Pd-H related spectrum is observed immediately after hydrogenation.

It is known from DLTS experiments that by annealing the samples at temperatures of 400 to 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 [6]. There is a possibility that the new-formed complexes are paramagnetic and observable by magnetic resonance. Therefore, we have carried out isochronal thermal annealing of our samples. Results showed that after annealing at 450 K for 60 minutes, the EPR spectrum of the substitutional palladium center has weakly recovered (Fig. 2(a)). Further annealing revealed the gradual recovery of the $\text{Pd}_{\text{S}}^{\circ}$ center. At the same time a new EPR spectrum is emerged. This spectrum, labeled Si-NL68 for further references, achieves its highest

intensity after annealing at about 500 K for about 2 hours (Fig. 2(b)). The spectrum is characterised by small twofold splitting of order 7-10 MHz, see inset of Fig. 2(b), implying hyperfine interaction with a nucleus $I = 1/2$, and 100% abundance. The angular dependence of the Si-NL68 spectrum has been measured and shows monoclinic-I symmetry for the Si-NL68 center.

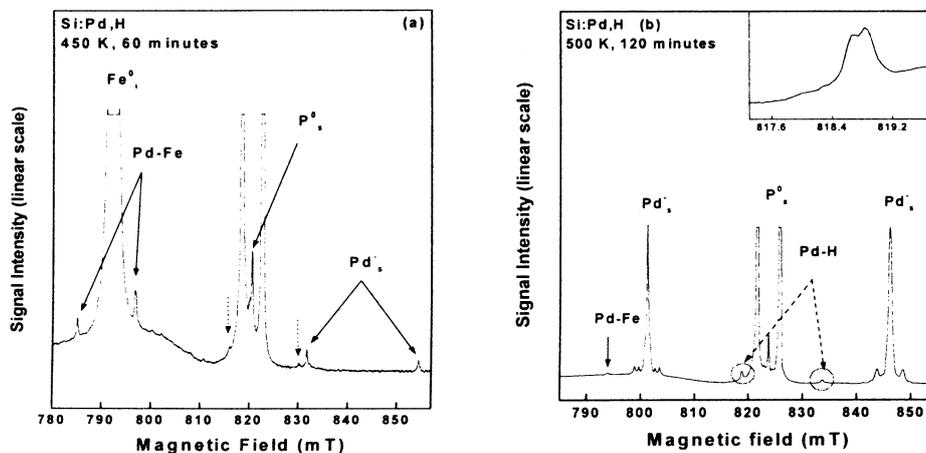


Fig. 2: EPR spectra observed in the palladium-doped hydrogenated sample after isochronal annealing at 450 K for 60 minutes (a), and at 500 K for 120 minutes (b). The Pd-H₁ spectrum is indicated by dashed arrows. The inset 2(b) shows twofold splitting due to hyperfine interaction with one hydrogen atom ($I = 1/2$, 100%).

Si-NL64 spectrum of Au-H₂ complex

In gold-doped samples, the EPR Si-NL64 spectrum of the Au-H₂ center is recorded directly after hydrogenation. No heat treatment is required. In Figs. 3, a comparison of EPR spectra observed before and after hydrogenation is made. It is clearly shown that after hydrogenation a very complicated EPR spectrum is observed while the two gold-related centers, the Au-Fe pair and the Si-NL62 center, which are detected before in the sample, are still observed. The spectrum depicted in Fig. 3(b) is observed under visible-light illumination showing typical hyperfine structure of 1:2:1:1:2:1:1:2:1:1:2:1 as being due to hyperfine interaction with one gold atom ($I = 3/2$, 100%) and two hydrogen atoms ($I = 1/2$, 100%). The spectrum has quite high formation probability and is observable in all samples with high concentration of gold. Annealing the sample at 500 K results in observableness the Si-NL64 spectrum under dark condition, i.e., without illumination. The spectrum is stable after annealing at 650 K for 2 hours. The spectrum has a rare low symmetry of triclinic.

Si-NL65 spectrum of Pt-H₃ complex

Formation of platinum-related defects is sensitive to the cooling rate after high-temperature diffusion. Different quenching speeds result in different observed complexes. This is also the case for the platinum-doped hydrogenated samples. It was established from previous experiments on hydrogen passivation of the substitutional platinum center in silicon that in fast-quenched samples the dominant EPR spectrum is Pt-H₂ [7,8]. Slower quenching rate (retarded) favors formation of a bigger center of [Pt-H₂]₃ complex [8].

In this experiment, repeating results of ref. [8], we observed the EPR spectrum of the Pt-H₂ center in all samples investigated after hydrogenation. Particularly, in fast-cooling sample, this center together with Pt-Fe and the Fe_i° centers dominate the observed spectrum. The observation of the Si-NL65 spectrum of Pt-H₃ center is an exceptional case as the underlying center has extremely low formation probability. The spectrum was observable only in 2 of 40 samples made with very fast

quenching rate and in the conditions of very low concentration of Fe^0 and Pt-Fe centers formed or without these centers. The typical Si-NL65 spectrum is depicted in Fig. 4 disclosing hyperfine structure of 1:3:3:1 – 4:12:12:4 – 1:3:3:1 due to hyperfine interaction with one platinum atom and three equivalent hydrogen atoms. The spectrum of the Pt-H₂ center with hyperfine structure of 1:2:1 – 4:8:4 – 1:2:1 is also observed and indicated. Angular dependencies of the spectra have been measured showing the orthorhombic-I symmetry of Pt-H₂ center and trigonal symmetry for the Pt-H₃ complex. The spectrum is stable when annealing at 500 K for 1 hour, but was removed after annealing at 600 K for 2 hours.

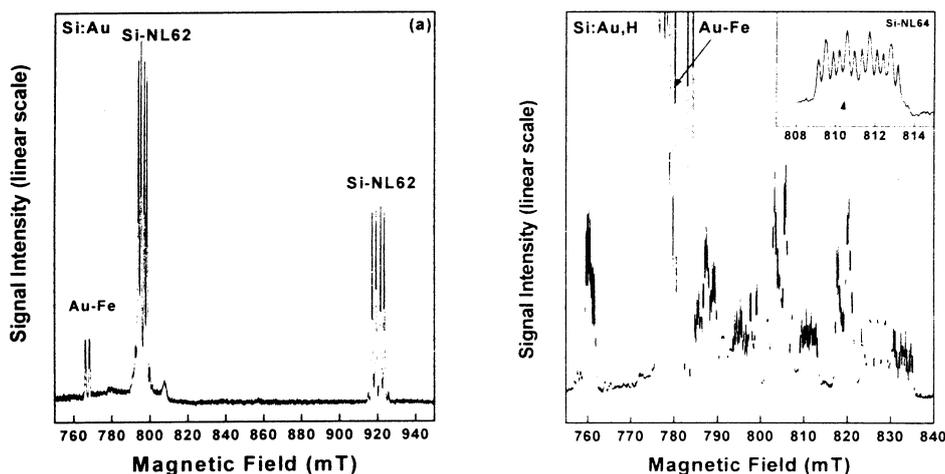


Fig. 3: EPR spectra observed in the gold-doped hydrogenated sample (a) before hydrogenation, (b) after hydrogenation and under visible-light illumination. The inset 3(b) shows the hyperfine structure of 1:2:1:1:2:1:1:2:1:1:2:1 as due to interaction with one gold atom ($I = 3/2$) and two nearly equivalent hydrogen atoms ($I = 1/2$).

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 ^{105}Pd 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 1:2:1 – 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 ^{195}Pt 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 structure becomes 1:3:3:1. Consequently, 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 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 ^{105}Pd isotope ($I = 5/2$, 22.2%) are not resolved. 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. The correlation with results from DLTS is also taken into account [6].

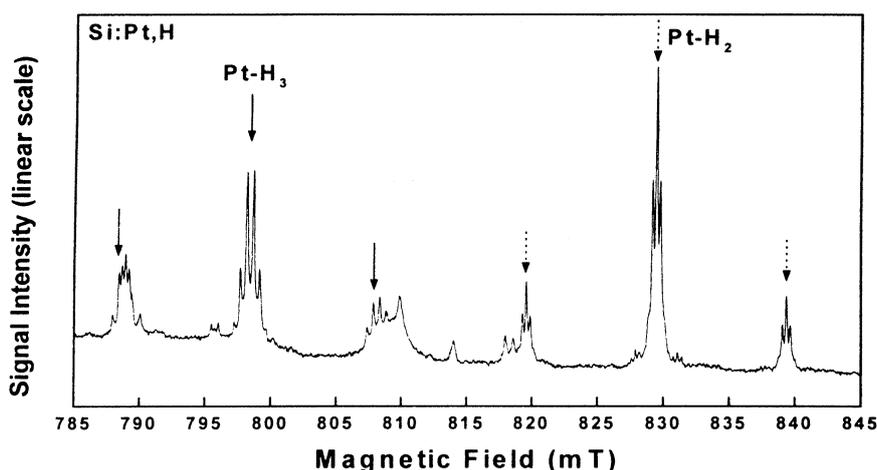


Fig. 4: EPR spectrum of the Si-NL65 center observed under visible-light illumination for magnetic field $B \parallel \langle 011 \rangle$ direction, temperature $T = 4.2$ K, and microwave frequency $f = 22.71369$ GHz. The spectrum is characterized by a 1:3:3:1 – 4:12:12:4 – 1:3:3:1 hyperfine structure. The spectrum of Pt-H₂ center with hyperfine structure of 1:2:1 – 4:8:4 – 1:2:1 is also observed and indicated.

Electronic and microscopic structure

The electronic and microscopic structure of a center is established based on spin-Hamiltonian parameters obtained from analysis of experimental spectra. As summarized in table 1, the g tensors of all centers largely deviate from $g_e = 2.0023$ of the free electron, implying the involvement of a transition-metal impurity in the microscopic structures. The hydrogen hyperfine interaction tensors also show a striking similarity for all centers with isotropic part a of about 9 MHz. This value, in an analysis using a linear-combination-of-atomic-orbitals (LCAO) approximation, results in a small electron localization of about 0.6% on the proton. The small anisotropic b^H of the hydrogen hyperfine interaction, may be ascribed to the dipole-dipole interaction between the spins of proton and the electron, considered as classical dipoles with separation R . From the observed values of b around 0.6-0.9 MHz, a distance of $R = 0.4$ -0.5 nm is determined. This value means a distance of 0.4-0.5 nm between the transition-metal atom and the proton, i.e., 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 suggesting the substitutional position for the transition-metal atom. On this basis, a general atomic model for all centers can be proposed, in which the transition-metal atom occupies the substitutional position, the hydrogen atom is interstitial and anti-bonding to silicon nearest neighbor atom. As neutral gold is iso-electronic to negative platinum, quite likely spectrum Si-NL64 corresponds to the $[\text{Au}_5\text{-(H)}_2]^0$ center observed in the neutral charged state (the $(\text{Pt-H}_2)^-$

center is observed in negative charge state, see [7,8]). For the same reason, the Si-NL65 spectrum of $(\text{Pt-H}_3)^0$ center is observed in the neutral charge state as well.

Table 1: Spin-Hamiltonian parameters for the Pd-H₁, Au-H₂ and Pt-H₃ centers obtained by computer fits and simulations of the EPR angular dependencies. The standard LCAO analysis is applied for all cases. The values of the Pt-H₂ center are also given for comparison.

CENTER	SYMMETRY	TENSORS	PRINCIPAL DIRECTIONS		
$(\text{Pt-H}_2)^-$	Orthorhombic-I (C _{2v})	g A^{Pt} A^{H} $\eta^2(H)$ b^{H} R	2.1299 ([100]) 175.7 9.8 ~0.6% ~0.6 MHz ~0.4-0.5 nm	1.9558 ([0 $\bar{1}$ 1]) 541.2 7.9	2.1683 ([011]) 237.3 8.2
$(\text{Au-H}_2)^0$ Si-NL64	Triclinic	g A^{Au} A^{H} $\eta^2(H)$ b^{H} R	2.1282 (g ₁) 13.8 8.67 ~0.67% ~0.9 MHz ~0.4-0.5 nm	2.0689 (g ₂) 23.5 11.39	2.0039 (g ₃) 18 8.54
$(\text{Pt-H}_3)^0$ Si-NL65	Trigonal (C _{3v})	g A^{Pt} A^{H} $\eta^2(H)$ b^{H} R	1.9673 (g) 708.8 14.5 ~0.9% ~0.6 MHz ~0.4-0.5 nm	2.1569 (g _⊥) 52.2 12.7	
Pd-H ₁ Si-NL68	Monoclinic-I	g A^{H}	1.998 ~7-10 MHz	2.0361	1.9651

Conclusions

Hydrogen interaction with the transition metals palladium, gold, and platinum in silicon results in three paramagnetic centers observable by electron paramagnetic resonance. The identification of these centers as TM-H complexes has been carried out on the basis of analyzing experimentally observed spectra. It is concluded that the Si-NL68, Si-NL64, and Si-NL65 spectra, respectively, correspond to three TM-H complexes namely Pd-H₁, Au-H₂, and Pt-H₃. Electronic and microscopic structures are established.

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