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Hydrogen interaction with transition-metals impurities in silicon

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An electron paramagnetic resonance study of hydrogen interaction with transition metals (Pt, Au and Pd) in silicon is presented. Three transition-metal–hydrogen related spectra are observed and identified as originating from complexing of one transition-metal atom and up to three hydrogen atoms. The hyperfine interaction with transition metal and hydrogen atoms for each center is determined. A detailed analysis of the spin-Hamiltonian parameters of the centers has been carried out providing adequate materials for establishing electronic and microscopic models of the newly observed centers.

1. Introduction

One of the most exciting aspects of semiconductor materials science has been the discovery of hydrogen-induced passivation (deactivation of electrical activity) of shallow acceptors, donors, and transition metals (TMs) in silicon. Due to its small size and the open lattice of the diamond structure, the hydrogen atom or ion can easily penetrate the bulk of the material. The activation energy for migration is only 0.48 eV, which is among the lowest for impurities in silicon. Hydrogen can easily intentionally be introduced by diffusion, implantation, hydrogen plasma treatment, wet chemical etching or by boiling in water. Since hydrogen exists in one chemical form or another at almost every stage of device processing in modern semiconductor technology, investigation of its undesirable role, as well as its useful influence, continues to be one of the hot topics of applied and fundamental semiconductor physics [1, 2].

In this paper, we report on the studies of TM-doped hydrogenated silicon by electron paramagnetic resonance (EPR). Three TM–H complexes have been observed and identified containing one TM atom and one, two and three hydrogen atoms, respectively, for the Pd–H_1, Au–H_2 and Pt–H_3 centers.

2. Experimental

Phosphorus-doped Czochralski-grown silicon with room-temperature resistivity in the range of 0.75–125 Ωcm was used in this study. The crystal was oriented and cut into bar-shape samples with typical dimensions of $1.5 \times 1.5 \times 15$ mm^3, and with the longest side parallel to the $[0\bar{1}1]$ 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 minutes in the atmosphere of water vapor. 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 well-known Pt–H_2 center [3, 4]. The second spectrum, labeled Si-NL65 detectable only under visible-light illumination, has very low formation probability and is observable only in 2 of 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. The angular dependence of the Si-NL65 spectrum has been measured for the rotation of the magnetic field in the $(0\bar{1}1)$ plane revealing the trigonal symmetry of the underlying defect.

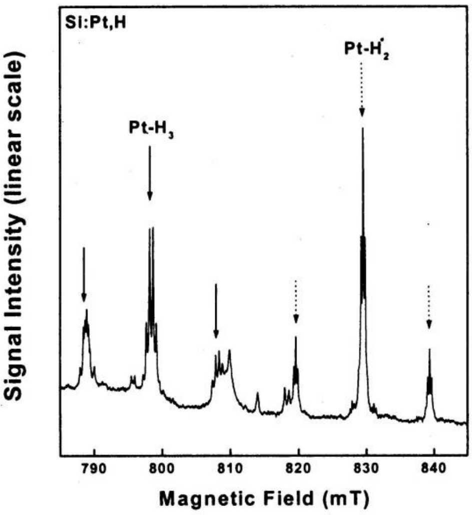

Fig.1: EPR spectra of the Si-NL65 center associated with the trigonal Pt–H_3 center observed in the platinum-doped hydrogenated sample under visible-light illumination for the magnetic field B // [011] direction, T = 4.2 K, and microwave frequency f = 22.71369 GHz.

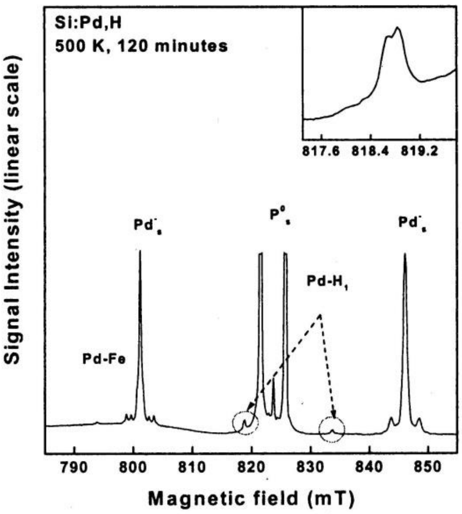

Fig. 2: EPR spectrum of the Si-NL68 center observed in the palladium-doped hydrogenated sample after an isochronal annealing at 500 K for 120 minutes. The Si-NL68 spectrum is characterized by a twofold splitting in each of the spectra lines, as shown in the inset.

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. 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_s^- centers have been converted to other Pd-related centers including the Pd–Fe pair. But as in the experiments, only the Pd–Fe pair is observed in the samples 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 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 [5]. 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 for 60 minutes, 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 minutes, see Fig.2. Especially, at the main directions [100] and [011], where the intensity of the spectrum is higher, we observed twofold splitting in each of the spectral lines. The Si-NL68 center has a low symmetry of monoclinic-I.

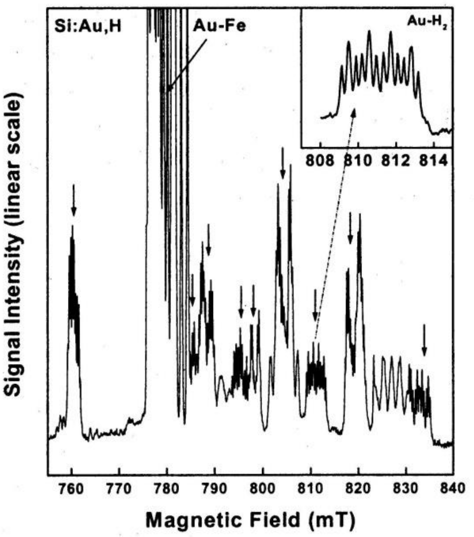

Fig. 3: Typical EPR spectrum of the Si-NL64 center observed in the gold-doped hydrogenated sample under visible-light illumination for the magnetic field about 10° away from the [011], with microwave frequency f = 23.0217 GHz, temperature T = 4.2 K.

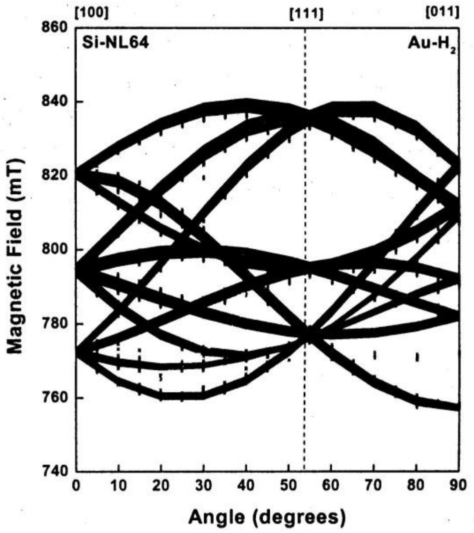

Fig. 4: Triclinic angular dependence pattern of the Si-NL64 spectrum observed for the rotation of the magnetic field in the (0-11) plane. Experimental data recorded at T = 4.2 K, microwave frequency f = 23.0217 GHz.

In gold-doped samples, the EPR Si-NL64 spectrum of the Au–H_2 center is recorded directly after hydrogenation. The spectrum, as depicted in Fig.3, is observed under visible-light illumination for the magnetic field about 10° away from the [011] direction, showing a very complicated hyperfine structure with a large number of 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. 3, 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. 4.

4. Discussion

In all cases, from the experimental results as described above, the identification of the spectra as originating from TM-H complexes are directly established. 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 Si-NL68, Si-NL64 and Si-NL65 centers.

The number of transition-metal atom involved can also be determined from observed hyperfine structures as well. The Si-NL65 spectrum is observed in the platinum-doped sample simultaneously with the Pt–H_2 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 Pt–H_2 center in which a third equivalent proton is added. As already concluded for the Pt–H_2 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 create 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, create 1:3:3:1–4:12:12:4–1:3:3:1 hyperfine structure when combine with a single platinum atom. This is the case for the Si-NL65 spectrum of Pt–H_3 center.

Similar interpretation is applied for the Si-NL64 spectrum of Au–H_2 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 (generate fourfold splitting) and two equivalent or nearly equivalent hydrogen atoms (generate 1:2:1 structure). For the Si-NL68 spectrum, due to low intensity of the spectrum, the hyperfine lines whose responsible for hyperfine interaction with ^{105}Pd isotope ($I = 5/2$, 22.2%) are not resolved, the assignment to a Pd–H_1 complex, therefore, is tentatively and is based on the experimental observation of twofold splitting as due to interaction with one hydrogen atom and in correlation with reported results from DLTS [5]. Summary of the spin-Hamiltonian parameters of the spectra Si-NL64, Si-NL65 and Si-NL68 as well as of the Pt–H_2 center obtained from experimental spectra are given in Table 1.

Table 1: Spin-Hamiltonian parameters for the Pd–H_1, Au–H_2 and Pt–H_3 centers obtained by computer fits and simulations of the EPR angular dependencies. The standard LCAO analysis is applied for all cases.

Center	Symmetry	Tensors	Principal directions		
$(Au\text{-}H_2)^0$ Si-NL64	Triclinic	g	2.1282	2.0689	2.0039
		A^{Au}	13.8	23.5	18
		A^{H}	8.67	11.39	8.54
		$\eta^2(H)$	~0.6%		
		b^{H}	~0.9 MHz		
		r	~0.4-0.5 nm		
$(Pt\text{-}H_3)^-$ Si-NL65	Trigonal	g	2.1569		
		A^{Pt}	52.2		
		A^{H}	12.7		
		$\eta^2(H)$	~0.9%		
		b^{H}	~0.6 MHz		
		r	~0.4-0.5 nm		
$Pd\text{-}H_1$ Si-NL68	Monoclinic-I	g	1.998	2.0361	1.9651
		A^{H}	~0.7MHz		
		b^{H}	~1 MHz		
		r	~0.4-0.5 nm		

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