Hydrogen-atom number in platinum-hydrogen complexes in silicon

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Four different platinum-hydrogen complexes are identified in silicon by transient capacitance spectroscopy. From deep-level depth profiling, we are able to identify the number of hydrogen atoms in the defect complexes. Three of the platinum-hydrogen complexes are electrically active, and contain one, two, and three hydrogen atoms, respectively. A complete electrical passivation of substitutional Pt is achieved by at least four hydrogen atoms. Our results are in agreement with experimental data on a Pt-H_2 complex and a theoretical study on the structure and level positions of these defect complexes. [S0163-1829(99)04328-3]

The formation of defect complexes between transition-metal impurities and hydrogen in silicon leads to a complete passivation of the metal defect or new electrically active metal-hydrogen complexes.[1–12] In most cases the assignment to hydrogen-related complexes was based on the appearance of electrical levels, which appear after sample hydrogenation, and on the fact that the corresponding defects were only detected at depths where hydrogen had been incorporated. However, little is known about the basic reactions leading to the complex formation and the structure of the complexes themselves. In most of the studies the defect properties were investigated by deep-level transient spectroscopy (DLTS), which usually does not give microscopic information. Substitutional platinum is the only metal for which information on the structure of a hydrogen-related complex containing two hydrogen atoms is available.[13] This Pt-H_2 complex, which has been identified by electron paramagnetic resonance (EPR) and infrared absorption (IR) spectroscopy, is electrically active and has two acceptor levels within the band gap. Our DLTS studies on Pt-doped silicon revealed that the interaction of hydrogen with platinum in silicon results in the appearance of four levels which can be related to at least three different Pt-H complexes.[10] In this paper we will extract from these DLTS measurements the number of hydrogen atoms in the complexes. With this information a direct comparison with the IR and EPR studies is now possible.

Before we give an interpretation of the reported depth profiles, we will summarize the results obtained in Ref. 10. After hydrogenation, four Pt-H-related levels are detected in platinum-doped silicon: $H(210)$ and $H(150)$ in p-type Si and $E(90)$ and $E(250)$ in n-type Si, respectively. The corresponding activation energies and capture cross section are shown in Table I. Heat treatments between 400 and 600 K result in several transformations between the different hydrogen-related complexes. Based on qualitative considerations of the transformation and hydrogenation process, $H(150)$ was associated with a complex containing more H atoms than the other centers. However, a better assignment of all levels is possible by a detailed comparison of the concentration depth profiles of all the levels in both n- and

p-type samples, and by using a simple model describing the process of complexing as will be presented below. First we have to take into consideration that the formation of platinum-hydrogen complexes and their depth distributions at room temperature are strongly affected by the interaction between hydrogen and the shallow dopants. In p-type Si, most hydrogen binds to the boron acceptors, and an additional heat treatment is necessary to form Pt-H-related complexes. In contrast, in n-type material phosphorus donors are less efficient in capturing hydrogen, which enables the formation of a significant number of Pt-H complexes after etching at room temperature. At temperatures above 450 K, however, both boron- and phosphorus-hydrogen pairs dissociate completely, so that the different influence of the shallow dopant species can be neglected. This means that under such conditions Pt-H complexes should behave similar in both n- and p-type Si.

Figure 1 shows the depth profiles of all platinum-related levels after etching and a subsequent 1-h heat treatment at 470 K. Because of different nominal Pt concentrations in p- and n-type material, we compare relative entities which are related to the original platinum concentration. Furthermore, the different shallow donor and acceptor concentrations in n- and p-type samples are accounted for by using the depth profile of the isolated defects as a reference, i.e., the profiles of the respective donor level in p-type Si and the respective acceptor level in n-type Si are scaled to coincide. After annealing at 470 K all the defects are distributed inhomogenu-

TABLE I. List of energy levels, activation energies E_A, capture, cross sections for majority carriers $\sigma_{n,p}$, barrier heights E_σ for thermally activated capture, and activation enthalpies H_A. The values of E_A and H_A for $E(90)$ are given from extrapolation to zero electric field.

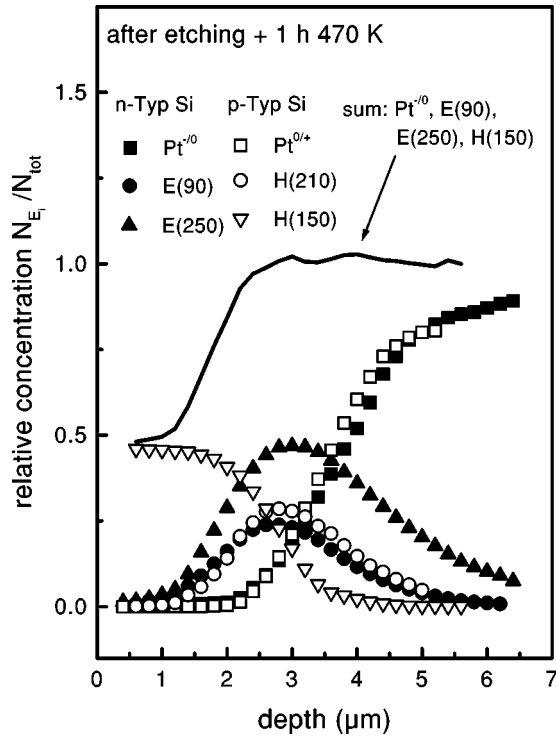| Level	E_A (eV)	$\sigma_{n,p}$ (cm^2)	E_σ (eV)	H_A (eV)
$E(90)$	E_C - 0.18	1×10^{-17}	0.02	E_C - 0.16
$E(250)$	E_C - 0.50	2×10^{-16}	0	E_C - 0.50
$H(150)$	E_V + 0.30	9×10^{-16}	0	E_V + 0.30
$H(210)$	E_V + 0.40	3×10^{-17}	0	E_V + 0.40

FIG. 1. Concentration of all Pt-related levels N_{E_i} after etching and subsequent annealing at 470 K for 1 h, relative to the total concentration of substitutional Pt before wet chemical etching.

ously in the region studied. The most remarkable fact is the good agreement in the depth distributions of the levels $E(90)$ and $H(210)$. This is also observed after annealing at higher temperatures, and indicates that both levels belong to the same defect. The levels $E(250)$ and $H(150)$, however, are related to different Pt-H complexes because of significant differences in their profiles. The sum of the concentrations of the Pt-H related levels $E(90)$, $E(250)$, and $H(150)$ and isolated platinum is also shown in Fig. 1. Assuming that each center contains only one platinum atom and that $H(210)$ is taken into account by $E(90)$, we note that the total concentration of electrically active platinum (isolated or involved in complexes) is uniform, and agrees with the initial Pt concentration except for a region very close to the surface (≤ 2 μm), where the total concentration is reduced by almost 50%. We suggest that this decrease is caused by the formation of another complex which is electrically passive, since all electrically active centers have been considered in the summation. The incorporation of only one hydrogen atom in the defect forming the $H(210)$ level was verified in Ref. 10. In our low-doped Pt samples no levels due to larger Pt complexes are detectable. The reported formation and dissociation kinetics of our Pt-H complexes give no evidence for several Pt atoms in the complexes.

A semilogarithmic plot as shown in Fig. 2 reveals that the profiles of all hydrogen-related defects decrease exponentially with the depth toward the bulk. This behavior was explained by a model proposed by Feklisova and Yarykin which describes the complex formation as a subsequent addition of hydrogen atoms to the isolated metal impurity.[14] Under these conditions the concentration of a complex
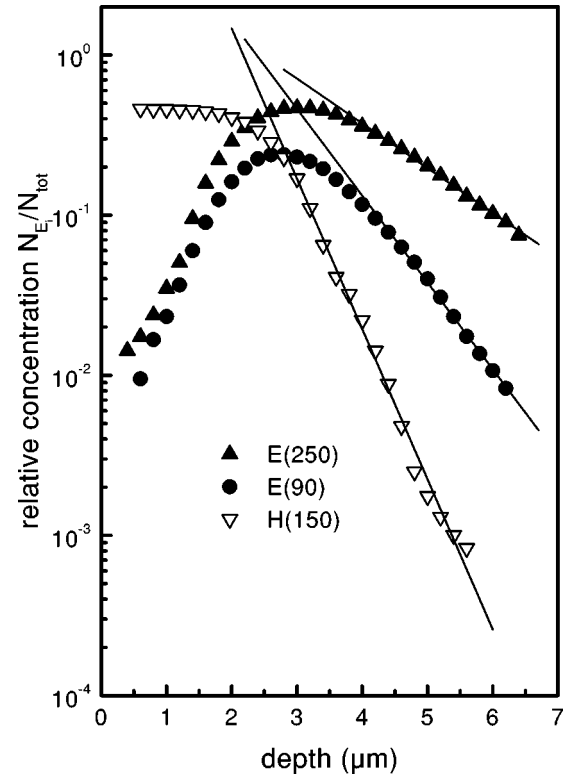

FIG. 2. Depth profiles of the Pt-H-related levels $E(250)$, $E(90)$, and $H(210)$ after etching and subsequent annealing at 470 K for 1 h. The solid lines represent fits using Eq. (1), and provide the corresponding penetration depth L_i.

[TM-H$_i$] with i hydrogen atoms can be described in a quasistationary solution by an exponential decrease at greater depths x:

$$[\text{TM-H}_i] \sim \exp\left(\frac{x}{L_i}\right). \tag{1}$$

Furthermore, the characteristic penetration depth L_i is inversely proportional to i. Thus the ratios of the penetration depths obtained by fitting the slopes of the concentration depth profiles with Eq. (1) can be formed for the various complexes, and give an estimate for the corresponding values for i. An analysis of the depth profiles shown in Fig. 2 provides the values of the penetration depth for the various hydrogen related levels (see Table II). We find that $E(250)$ has the largest penetration depth, and therefore assign it to a complex with only one H atom. The penetration depths of all the other H-related levels are put into ratio to L_1 $[E(250)]$ (see Table II). From these ratios we conclude that $E(90)$ and

TABLE II. Characteristic penetration depth L_i of Pt-H complexes. The ratio L_1/L_i gives the number i of hydrogen atoms in the defect complexes.

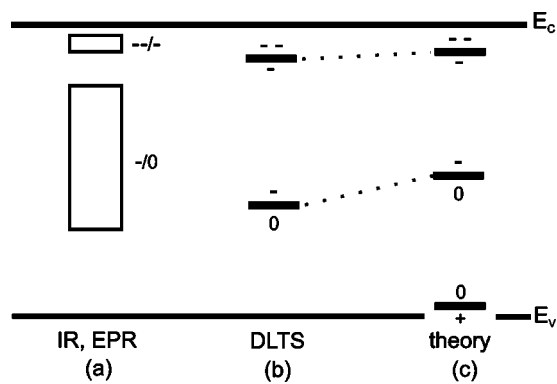| Level	L_i	L_1/L_i	i	Identification
$E(90)$	0.80 ± 0.02	1.95 ± 0.1	2	Pt-H$_2$
$E(250)$	1.55 ± 0.05	1	1	Pt-H$_1$
$H(150)$	0.48 ± 0.05	3.2 ± 0.4	3	Pt-H$_3$
$H(210)$	0.78 ± 0.02	2.0 ± 0.1	2	Pt-H$_2$

FIG. 3. Comparison of energy-level positions of the Pt-H$_2$ complex. (a) From Uftring *et al.* (Ref. 13), (b) from Sachse *et al.* (Ref. 10), and (c) from Jones *et al.* (Ref. 15).

$H(210)$ are different levels of a complex with two H atoms. We further assign $H(150)$ to a Pt-H$_3$ complex, although the fit of the profile gives a slope with larger error bar. The depth profile of the passive complex is quite uncertain due to its indirect determination via the profiles of all the other defects. The occurrence of the passive complex only in the hydrogen-richest region very close to the sample surface suggests that it contains more H atoms than all the other electrically active complexes. A rough estimate gives four or more H atoms for this passive configuration. The assignment of the H-related levels to three different electrically active Pt-H complexes is illustrated in Fig. 3. In this energy-level scheme the acceptor or donor character of the levels is also presented. The acceptor behavior of $H(150)$ could be shown by capacitance-voltage profiling in p-type samples after hydrogenation and subsequent heat treatments.[11] In contrast to our early assumption that $E(90)$ acts as a donor, detailed studies of the emission and capture behavior of this center give evidence that $E(90)$ has a double acceptor character. This assignment is based on both the weak dependence of the emission rates on the electric field and the experimental finding that $E(90)$ has a small, but thermally activated electron capture cross section (see Table I). The assignment of $E(90)$ and $H(210)$ to the same defect therefore leaves $H(210)$ as the first acceptor level of this Pt-H$_2$ complex.

The identification of the Pt-H$_2$ complex by means of DLTS depth profiling gives the possibility for a direct comparison with the results of the IR and EPR studies by Uftring *et al.*[13] After high-temperature annealing of Pt-doped samples in hydrogen ambient, these authors observe an electrically active Pt-H$_2$ complex with two acceptor levels within the band gap, and give ranges for the corresponding activation energies which are depicted in Fig. 3(b). The agreement in the activation energies supports our assignment of $H(210)$ to the single-acceptor level of Pt-H$_2$. Level $E(90)$ is about 80 meV deeper than the corresponding double-acceptor level observed by EPR. The difference is larger than the error in determining energies in the experiments and the discrepancy is not fully understood at the moment.

Based on the microscopic structure suggested in Ref. 13, Jones *et al.* calculated possible energy levels for a Pt-H$_2$ complex [see Fig. 3(c)].[15] The values for the two acceptor levels agree quite well with our experimental results. An additional donor level close to the valence-band edge could not be detected by experimental means and is either too shallow or located in the valence band.

In summary, we have identified four different Pt-H complexes by DLTS. Three of them are electrically active and contain one, two, and three hydrogen atoms, respectively. A complete electrical passivation of platinum is achieved by probably four H atoms. The agreement with other experimental and theoretical results gives evidence that DLTS depth profiling is an appropriate method to identify transition metal-hydrogen complexes and determine the number of H atoms involved in the complexes.

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