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Electrical properties of platinum-hydrogen complexes in silicon

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The interaction between hydrogen and platinum is studied in n- and p-type silicon using deep-level transient spectroscopy. Hydrogen is introduced by wet-chemical etching or during crystal growth. In both cases we find that hydrogen forms only electrically active complexes with platinum. Four platinum-hydrogen related deep levels are identified: E(90) at $E_C-0.18$ eV, E(250) at $E_C-0.50$ eV, H(150) at $E_V+0.30$ eV, and H(210) at $E_V+0.40$ eV. These levels belong to at least three different platinum-hydrogen complexes. Level E(250) is identical to the so-called midgap level in Pt-doped Si, which is believed to control the minority-carrier lifetime in Pt-doped silicon. Level H(150) is an acceptor and is present both in n- and p-type samples after hydrogenation. It belongs to a platinum-hydrogen complex which contains more hydrogen atoms than the complexes responsible for the other hydrogen-related levels. Annealing at temperatures above 600 K results in a complete dissociation of all the platinum-hydrogen related defects and the substitutional platinum concentration is fully restored. [S0163-1829(97)07724-2]

I. INTRODUCTION

The identification of platinum-induced defects in silicon has been a controversial issue for many years. Today, the coherent understanding of the Pt properties in Si makes this transition metal an ideal system for further studies on defects in semiconductors. Substitutional Pt forms a trivalent defect with a single acceptor level $\mathrm{Pt}^{-/0}$ approximately 0.2 eV below the conduction band, a single donor level $\mathrm{Pt}^{0/+}$ about 0.3 eV above the valence band, and a double donor level $\mathrm{Pt}^{+/++}$ about 0.1 eV above the valence band.[1–6] The Pt involvement in the single donor and acceptor levels was convincingly shown by the decay of radioactive isotopes.[7] Early structural studies by electron paramagnetic resonance (EPR) of the Pt^{-} level were questioned recently, but could be reconciled with a vacancylike model for substitutional Pt.[8] The determination of the optical cross section and the splitting under uniaxial stress in EPR as well as deep-level transient spectroscopy (DLTS) measurements relates the EPR and DLTS signals to the same center.[9,10]

Many additional deep levels with unknown origin have been observed in platinum-doped silicon.[4,5,10–12] A frequently encountered level at $E_V+0.50$ eV ($\sigma_n=2\times10^{-16}$ cm^2) is the so-called midgap level,[5,10,13,14] which was associated with the dominant recombination center used for controlling the minority-carrier lifetime in devices. Very speculative explanations for the nature of this defect center are given in the literature. Kwon, Ishikawa, and Kuwano[13] detected this level in concentrations much smaller than the substitutional Pt concentration and therefore associated the midgap level to a complex between Pt and a residual impurity like oxygen in Si. Bardeleben *et al.*[15] studied the EPR signal from Pt-Pt pairs and, based on the level position determined by photo-EPR, they correlated this signal with the midgap level. In a preliminary report on the hydrogen interaction with platinum, we recently assigned the midgap level to a platinum-hydrogen complex.[16]

The first report on hydrogen in Pt-doped Si was given by Pearton and Haller.[17] In samples which were treated in a hydrogen plasma at 300 °C a strong reduction of the concentration of the Pt acceptor level was reported. However, the single donor level was not affected by hydrogen. The changes in the Pt acceptor concentration due to hydrogen was called ''passivation'' in analogy to the effect of hydrogen on shallow donors or acceptors, where electrically inactive hydrogen donor or acceptor pairs are formed. However, the DLTS technique used in Ref. 17 monitors only deep levels in the upper half of the band gap in n-type samples and deep centers in the lower half of the band gap in p-type samples. Therefore, it is possible that ''passive'' Pt-H complexes have levels in the other half of the band gap or shallow levels which are not detectable by DLTS. To be consistent with other DLTS reports, we will use the word ''passivation'' in the sense of a concentration change of electrically active centers, without the creation of new centers in the same half of the band gap. One aim of this work is to give a careful comparison between the deep hydrogen-related Pt centers in p- and n-type silicon.

Wet-chemical etching was found to introduce hydrogen at room temperature without the creation of surface damage.[18] Hydrogen introduced by this technique not only passivates deep levels but also introduces new transition-metal-related deep levels in silicon.[19–26] Wet etching is typically the last processing step before Schottky contact deposition. This makes hydrogen incorporation close to the sample surface unavoidable in such structures. Since many of the previous studies were made using Schottky diodes it is not astonishing that several of the unidentified deep levels in Pt-doped silicon are hydrogen related.

Recently, a $\mathrm{PtH_2}$ complex was identified by EPR (Refs. 27–29) and vibrational spectroscopy.[27,29] Uftring *et al.*[29] showed that this $\mathrm{PtH_2}$ complex has two levels within the silicon band gap, one located between $E_C-0.045$ eV and $E_C-0.1$ eV and the other between $E_C-0.23$ eV (the platinum acceptor level) and $E_V+0.33$ eV (the platinum single-donor level).

In this paper, we report on a systematic study of platinum-hydrogen-related deep centers in silicon using deep-level transient spectroscopy (DLTS). The paper is organized as follows: We first demonstrate that hydrogen is introduced during etching. Thereafter, we will show that four deep levels are introduced after hydrogen injection. The correlation of the deep levels in *n*- and *p*-type samples is then detailed. Finally, we compare the data with spectroscopic studies on known Pt-H complexes.

II. EXPERIMENTAL

Phosphorus- or boron-doped float zone or Czochralski silicon with concentration in the range of 1×10^{14}–5×10^{16} cm^{-3} was used in this study. Platinum was introduced by two different methods, either by evaporation of platinum on one side of an as-received silicon wafer followed by heat treatment in a diffusion furnace between 800 °C and 1000 °C,[10] or by introducing platinum into the silicon melt during growth of float zone silicon in vacuum or argon ambient.[30] The total concentration of electrically active Pt atoms reached 1×10^{13}–5×10^{15} cm^{-3} in the diffused samples and $5-6\times10^{13}$ cm^{-3} in the melt doped samples. Hydrogenation of the samples was performed by wet-chemical etching in a 1:2:1 mixture of HF, HNO_3, and CH_3COOH before fabrication of the Schottky contacts. The Schottky diodes were formed at room temperature by vacuum evaporation of aluminum for *p*-type samples and gold for *n*-type samples through a metal mask. A eutectic InGa alloy was rubbed onto the back side of the samples to facilitate an Ohmic contact. In addition, cleaved *n*-type samples were made by breaking the samples from the crystal rod and forming the contacts directly onto the sample surfaces without any additional surface treatment. The cleaved samples are virtually free from hydrogen and are used as a reference.

Hydrogen is injected into the sample surface region during etching. Figure 1 shows the evolution of the net active boron acceptor profiles after a 10-min anneal at 400 K with a reverse bias of 8 V applied to the Schottky diode. Initially after etching we observe a decrease of the net boron density near the sample surface. During the reverse bias annealing (RBA) reactivation of boron in the surface region takes place due to dissociation of electrically inactive boron-hydrogen pairs. The released positively charged hydrogen drifts through the space-charge region and piles up at the depletion layer edge where new boron-hydrogen pairs are formed. This causes the dip in the net active boron density at a depth of approximately 11 μm. The reactivation kinetics of boron close to the sample surface agree with dissociation rates of boron-hydrogen pairs reported in the literature.[31] We make use of the bias dependence of the hydrogen injection in the investigations presented below.

While hydrogen is incorporated only into the sample surface region by wet-chemical etching we found that crystal growth under argon ambient results in the occurrence of hydrogen in the whole silicon crystal. This enabled us to study platinum-hydrogen related complexes not only in a spatially limited region close to the sample surface but throughout the material. The reason for the hydrogenation during growth in argon ambient is not yet clear, but is probably related to traces of hydrogen in the Ar gas or water vapor on the chamber walls.

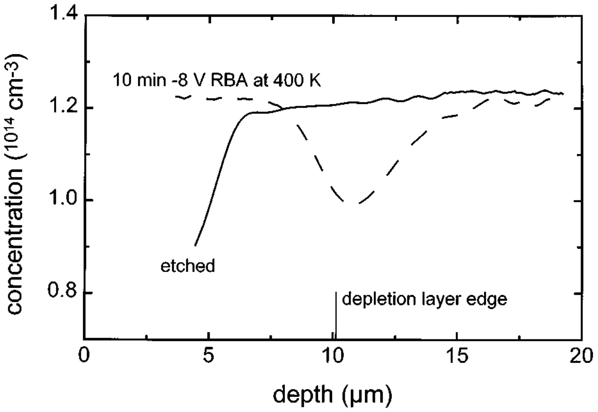

FIG. 1. Net boron acceptor profiles in platinum doped *p*-type silicon. Solid curve, after wet-chemical etching of the samples; dashed curve, after RBA at 400 K for 10 min using a reverse bias of −8 V. The depletion layer edge during the RBA is also indicated. The CV profiles were measured at room temperature.

The Schottky diodes deteriorate during annealing above about 150 °C resulting in a drastic increase of the leakage current under reverse bias. Annealing studies at higher temperatures are therefore made as follows: the samples are first etched, thereafter heat treated in a diffusion furnace in argon ambient, and finally the Schottky contacts are made without any additional etching prior to the metallization.

The experimental setup used in this study is a computerized lock-in DLTS system. The shallow dopant concentration profiles are determined by capacitance-voltage (CV) profiling (1 MHz). DLTS concentration profiling,[32] where the sample is held at a constant reverse bias while the filling pulse height is varied, was used to determine the distribution of the deep levels. The profiles are calculated taking into account the nonuniform shallow dopant profiles due to hydrogen passivation of the dopants. The error in the determination of the deep-level concentration is estimated to be in the order of ±10% of the absolute concentration. The capture cross sections of majority carriers are extracted from the electron or hole capture rates which are determined by the filling pulse method.[33]

III. RESULTS

A. Platinum-related deep levels in *p*-type silicon

1. Basic features of Pt-H complexes

We detect four DLTS signals in *p*-type Pt-doped Si samples. The concentration of the centers depends strongly upon the annealing procedure. Figure 2 gives an example of an anneal with no bias applied to the Schottky diode (zero bias anneal). The DLTS spectrum shown in Fig. 2(a) is recorded directly after the wet-chemical etching. Two dominant DLTS peaks are observed at 50 and 160 K. These peaks are detected in all the investigated platinum doped *p*-type

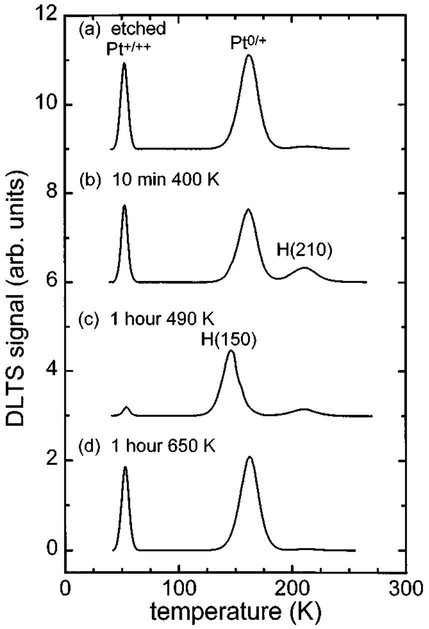

FIG. 2. DLTS spectra of Pt-doped p-type Si. Curve (a), after etching; curve (b), after etching and subsequent zero-bias annealing at 400 K for 10 min; curve (c), after etching and subsequent annealing at 490 K for 1 h; curve (d), after etching and subsequent annealing at 650 K for 1 h.

samples. The concentration depth profiles of the 50 and 160-K signals are identical in all samples within experimental error. Further, the activation energy and the hole capture cross section of the 160-K signal agree with the values reported for the single donor level of substitutional platinum Pt$^{0/+}$ (Refs. 1–4) and the 50-K signal is in agreement with the double donor level of the Pt center Pt$^{+/++}$.[5,6] The energy positions and capture cross sections are listed in Table I. We therefore assign the 160-K and the 50-K signals to the single and double donor levels of the platinum center, respectively. While the hole emission rate of the Pt single donor does not show dependence upon the electric field, we observe an increase of the emission rates of the Pt double donor with increasing electric field.

A small peak at T=210 K labeled H(210) is also detected in the spectrum of Fig. 2(a). This signal is enhanced after annealing for 10 min at 400 K [Fig. 2(b)] while the substitutional platinum signals decrease by about the same amount.

Further heat treatments at temperatures between 400 and 510 K lead to a dramatic reduction of the substitutional Pt single and double donor signals. This is correlated with the appearance of a new peak, H(150), which overlaps with the Pt single donor signal. Figure 2(c) gives a DLTS spectrum of a sample where the H(150) signal was maximized by 1-h annealing at 490 K. The Pt donor level is only detected as a shoulder in the H(150) peak and the Pt double donor peak is significantly reduced.

Both H(150) and H(210) disappear after annealing at higher temperatures. The H(150) peak anneals out during a 1-h treatment at 550 K while H(210) is slightly more stable but disappears after a few hours at 650 K. An example of this behavior is the spectrum shown in Fig. 2(d) which is recorded after a 1-h heat treatment at 650 K. The reduction of H(150) and H(210) is accompanied by a corresponding increase of the Pt donor signals. The Pt donor signals are fully recovered and the spectrum is comparable with the initial one after etching [Fig. 2(a)].

2. Depth profiles of Pt-H centers and the effect of reverse bias annealing

The Pt-H-related signals shown in Fig. 2 can also be formed during reverse bias annealing. The main effect of the reverse bias is to drive the positively charged atomic hydrogen deeper into the bulk. It is possible to modulate the concentration depth profiles of the Pt-H complexes by adjusting the reverse bias. An example of this is given in Fig. 3.

The concentration depth profiles of the centers directly after etching the samples are shown in Fig. 3(a). Level H(210) is only detected close to the sample surface while the Pt single and double donor profiles are uniform. Figure 3(b) shows the dramatic effect of a 10-min RBA at 400 K. The H(210) signal increases at greater depths with a peak concentration at approximately 10 μm. We find that the H(210) profile depends strongly upon the amplitude of the reverse bias applied during annealing. The peak concentration always follows the depletion layer edge during annealing, i.e., it is located at the same depth as the minimum of the net boron density (see Fig. 1). No significant changes in the trap profiles are observed if the samples are reverse bias annealed at lower temperatures where the B-H pairs are stable. This demonstrates that the formation of H(210) is controlled by the movement of H$^+$ drifting through the space-charge layer. The increase of the concentration of H(210) centers is mirrored by an almost equal reduction in the substitutional platinum concentration. This strongly suggests that the H(210) center is platinum-hydrogen-related and contains only one Pt atom.

TABLE I. List of energy levels, capture cross sections, and the assignment of the deep levels observed in platinum doped silicon. The activation energies of E(90) and Pt(50) are field dependent and the values are given from extrapolation to zero field.

Level	Diode type	Activation energy (eV)	σ_n or σ_p(cm^2)	Assignment
E(90)	n-type	$E_C - 0.18 \pm 0.01$	1×10^{-17}	Pt-H related
Pt(120)	n-type	$E_C - 0.23 \pm 0.01$	5×10^{-15}	Pt$^{-/0}$
E(250)	n-type	$E_C - 0.50 \pm 0.01$	2×10^{-16}	Pt-H related
Pt(50)	p-type	$E_V + 0.09 \pm 0.01$	2×10^{-17}	Pt$^{+/++}$
H(150)	p-type	$E_V + 0.30 \pm 0.02$	9×10^{-16}	Pt-H related
Pt(160)	p-type	$E_V + 0.33 \pm 0.01$	8×10^{-16}	Pt$^{0/+}$
H(210)	p-type	$E_V + 0.40 \pm 0.03$	3×10^{-17}	Pt-H related

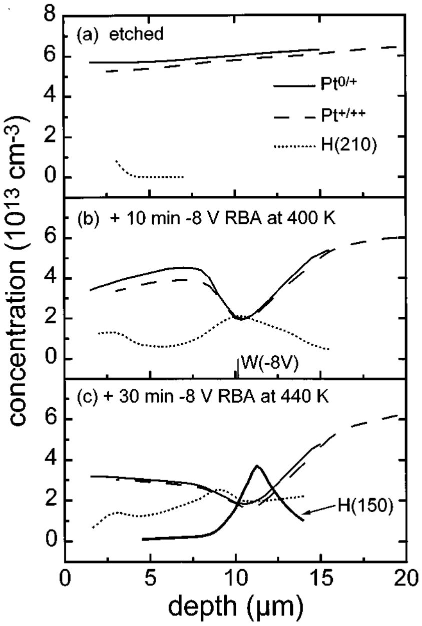

FIG. 3. (a) Depth profiles of the platinum-related defects $\mathrm{Pt}^{0/+}$, $\mathrm{Pt}^{+/++}$, H(210), and H(150) after wet-chemical etching, (b) after subsequent RBA at 400 K for 10 min using a reverse bias of -8 V, (c) after additional RBA at 440 K for 30 min.

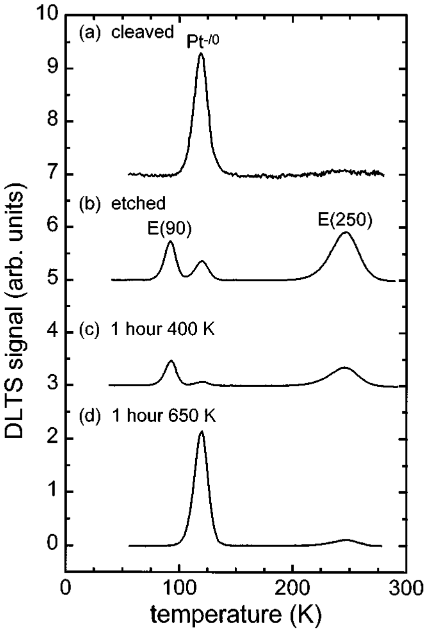

FIG. 4. DLTS spectra of Pt-doped n-type Si. (a) Cleaved sample, (b) after etching, (c) after etching and subsequent zero-bias annealing at 400 K for 1 h, (d) after etching and subsequent annealing at 640 K for 1 h.

Further RBA at 440 K results in a formation of the H(150) center. This is shown in Fig. 3(c). The sharp profile of H(150) resembles the hydrogen profile during the annealing. The atomic hydrogen piles up at the depletion layer edge where H(150) is formed. Within the same region a suppression of the platinum donor signals is evident. It should be noted that H(210) is also reduced during formation of H(150). This indicates that some of the H(210) traps transform into H(150) while the density of H(210) traps remains constant after the H(150) signal has been maximized. From these studies we conclude that also the H(150) level must be platinum-hydrogen-related.

Capacitance-voltage (CV) profiling reveals the single acceptor character of the H(150) level. CV profiles, measured between 200 and 300 K, show a corresponding increase in the net acceptor density at a depth where the H(150) signal is maximized. At these temperatures the hole emission rate of H(150) is faster than the frequency used to step the voltage during the CV profiling. The H(150) trap is therefore occupied during the measurements, which is detected as an addition to the net acceptor density.[34]

B. Platinum-related centers in *n*-type silicon

1. *Basic features of Pt-H complexes*

In n-type Si we observe in cleaved samples, i.e., before etching, only one peak at 120 K [Fig. 4(a)]. The activation energy and the electron-capture cross section of this DLTS level agree with the values reported on the acceptor level of substitutional platinum $\mathrm{Pt}^{-/0}$.[1–4] The concentration profile of the platinum acceptor is always uniform in the cleaved samples and is used as a reference. In contrast to p-type Si we observe that directly after wet-chemical etching the Pt acceptor signal decreases significantly while two new peaks appear in the spectrum at 90 and 250 K [Fig. 4(b)]. The level E(250) coincides with the so-called midgap level[5,10,13,14] and the level E(90) has previously been observed in Pt-doped samples by Lemke[5] and Stöffler and Weber.[10] A first identification of these two levels as platinum-hydrogen centers was given in Ref. 16.

We studied the field dependence of the emission rates for all three levels. The electron emission rates of the platinum acceptor and E(250) do not exhibit any field dependence. However, the emission rate of E(90) increases with higher electric field, suggesting that E(90) is a donor trap.[35]

A 1-h zero-bias annealing step at 400 K results in a decrease of all signals [Fig. 4(c)]. No new peak appears, but annealing at higher temperatures leads to a reactivation of the platinum acceptor which is accompanied by a decrease of the E(90) and E(250) signals. Spectrum (d) in Fig. 4 shows the corresponding DLTS spectrum after a 1-h anneal at 650 K. The concentration of E(90) and E(250) is strongly reduced while the platinum acceptor concentration is significantly increased.

2. *Net donor profiles*

We first demonstrate significant differences in the annealing behavior of the net phosphorus donor concentration profiles in platinum-doped samples and reference samples not containing platinum. This is depicted in Fig. 5. The samples were wet-chemically etched, contacted, and then subsequently annealed at 350 K under a reverse bias of 10 V. The net donor concentration after etching is reduced close to the sample surface (at depths $\leqslant 4$ μm). Reverse bias annealing of the reference sample causes a reactivation of phosphorus donors in the surface region due to the dissociation of electrically inactive phosphorus-hydrogen pairs [see Fig. 5(a)]. A 1-h heat treatment results in a flat phosphorus profile. The reactivation rates of phosphorus dopants agree with dissocia-

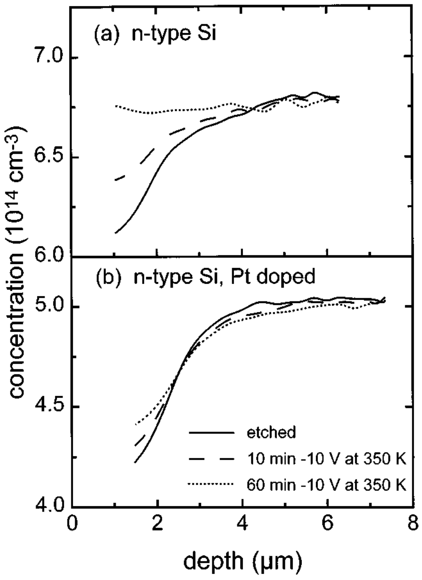

FIG. 5. (a) Net phosphorous donor profiles in n-type silicon (reference sample) at room temperature. (b) Net phosphorus donor profiles in platinum-doped n-type silicon at room temperature. Solid curve, after wet-chemical etching; dashed curve, after RBA at 350 K for 10 min using a reverse bias of -10 V; dotted curve, after RBA at 350 K for 60 min.

tion rates of P-H pairs.[36,37] In contrast to p-type material (compare Fig. 1) we do not observe a drift of the released hydrogen to the end of the space-charge region during annealing. This agrees with previous studies of lightly phosphorus doped silicon.[37]

The behavior in Pt-doped samples is different. Directly after etching a reduction in the net donor density is observed as in the reference sample [Fig. 5(b)]. However, the RBA treatment results in only a minor recovery of the net donor concentration in the surface region in contrast to the reference sample. Annealing for longer periods than 1 h at this temperature does not significantly change the net donor profile. Since the P-H pairs caused by the wet-chemical etching are dissociated after such a treatment the decrease of the net donor density in the near-surface region is due to some other phenomenon than P-H pairs. This suggests that complexing of hydrogen with phosphorus is inefficient in Pt-doped silicon presumably because the platinum and phosphorus are competing for the hydrogen. One possible explanation for the decrease of the net donor profile close to the sample surface is compensation by an acceptor state below midgap which is filled during the CV profiling. Such an acceptor would be platinum-hydrogen-related and would exist only in the hydrogenated region. In this work, we demonstrate that this most likely is the case in Pt-doped silicon. Based on annealing studies, detailed below, we suggest that the acceptor level H(150) (detected in p-type samples) is responsible for the decrease in the net donor density shown in Fig. 5(b).

3. Depth profiles of the different Pt-H defects

We first consider the evolution of the CV profiles and the deep trap profiles upon annealing at 400 K. Figure 6(a) compares the net donor profiles of a sample directly after etching and after a subsequent zero-bias annealing at 400 K for 30 min. The heat treatment results in an inward shift of the net donor profile. The corresponding trap profiles from DLTS depth profiling are shown in Figs. 6(b) and 6(c). After etching [Fig. 6(b)] the Pt acceptor concentration decreases towards the surface while E(250) and E(90) have a maximum concentration at depths between 1.5 and 2 μm and then decrease rapidly towards the bulk. The sum of the concentrations of $\mathrm{Pt}^{-/0}$, E(250), and E(90) is also shown. Assuming that each center contains one platinum atom we note that the total concentration of electrically active platinum (isolated or involved in complexes) is uniform except very close to the surface where the sum decreases. At depths greater than 2 μm, the sum equals the platinum concentration in the cleaved sample (before etching).

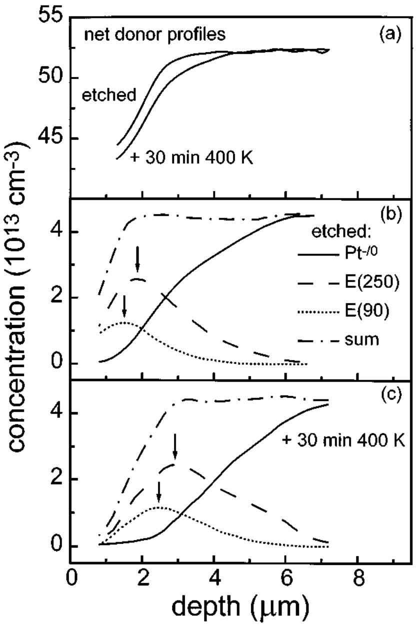

FIG. 6. (a) Depth profiles of the net shallow phosphorus concentrations after etching and after subsequent annealing at 400 K for 30 min. (b) Depth profiles of the platinum-related defects $\mathrm{Pt}^{-/0}$, E(90) and E(250) after etching. The sum of the concentrations of these defects is also shown. (c) Depth profiles after additional annealing at 400 K for 30 min. The arrows mark the peak positions of the E(90) and E(250) signals.

Upon heat treatment at 400 K [Fig. 6(c)], all trap profiles shift inwards resulting in a rapid decrease of the sum profile towards the sample surface at depths less than 3 μm. This behavior above is consistently observed and we made sure that this is no artifact of the experiment. The shift of the net donor profile [Fig. 6(a)] is always accompanied with a corresponding shift of the profiles of the deep traps [compare Figs. 6(b) and 6(c)]. This is explained as hydrogen diffusion from the sample surface region towards the bulk during the annealing at 400 K. The incoming hydrogen interacts with the substitutional platinum and the already formed Pt-H centers E(90) and E(250). Closest to the sample surface, an electrically active Pt-H complex is formed having an acceptor level below midgap. This center is formed at the cost of $\mathrm{Pt}^{-/0}$, E(90), and E(250). Although not observable with DLTS, this complex is detected indirectly as a compensation of phosphorus donors [Fig. 6(a)] and a decrease of the sum

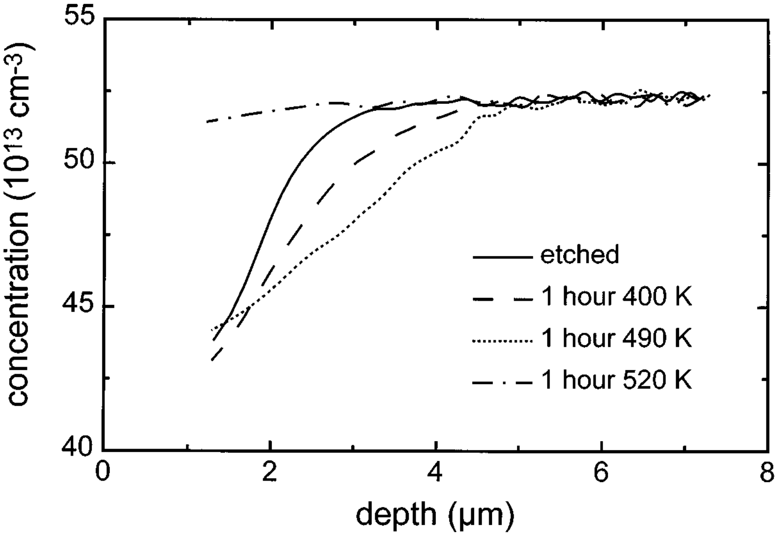

FIG. 7. Net phosphorus donor profiles in platinum doped n-type silicon at room temperature after etching, and after subsequent annealing steps for 1 h at the temperatures indicated.

profile [Fig. 6(c)]. According to our hypothesis, the net donor profile and the sum profile should both provide information on the concentration of this Pt-H acceptor center. However, a quantitative comparison between the CV profiles in Fig. 6(a) and the trap depth profiles is not possible due to uncertainties in the absolute concentrations values of the deep traps extracted from CV profiling.

The shift of the profiles of E(90) and E(250) after the heat treatment [Figs. 6(b) and 6(c)] is explained in a similar way. Closest to the surface where the hydrogen concentration is highest the Pt-H acceptor center is favored, while deeper in the bulk, where the hydrogen density is lower, E(90) and E(250) are the only Pt-H centers. During the annealing at 400 K hydrogen diffuses deeper into the sample resulting in a transformation of the E(90) and E(250) centers into the Pt-H acceptor center (at depths $\leqslant 3$ μm). At the same time new E(90) and E(250) centers are formed at greater depths [Fig. 6(c)].

No significant change is observed in either the net donor profiles or the profiles of the deep traps upon further annealing at 400 K. This means that no free hydrogen is available for complexing with platinum after 30 min at 400 K. It should be noted that from the CV profiles presented in Fig. 5(b) it appears as if the source of hydrogen is not only P-H pairs. Possibly some hydrogen is also trapped in the sample surface layer and this additional hydrogen is already consumed after 30 min at 400 K.

The shift of the net donor and deep trap profiles depicted in Fig. 6 can be reduced by applying a reverse bias to the sample during the annealing at 400 K. Likewise, a preannealing at 350 K (as in Fig. 5) using reverse bias followed by a zero-bias annealing at 400 K results in a significantly smaller shift of the net donor and the deep trap profiles than in Fig. 6. This means that a considerable fraction of the atomic hydrogen is lost during annealing under reverse bias. One possible way of explaining this is that the atomic hydrogen becomes positively charged within the space-charge region[38] and is driven to the sample surface during the heat treatment instead of diffusing into the bulk. We have not studied this effect of the reverse bias any further since it is of minor importance in this particular study of Pt-H complexes.

4. Annealing behavior of platinum-hydrogen-related complexes

We now turn to the annealing behavior of the Pt-H complexes at higher temperatures. Several samples with identical platinum concentrations were wet-chemically etched and annealed subsequently at temperatures between 400 and 650 K for 1 h followed by the Schottky contact preparation.

Figure 7 shows the evolution of CV profiles upon annealing. The heat treatment at 400 K results in an inward shift of the net donor profile as already discussed above. No free hydrogen is left in the samples after 30 min at 400 K. The phosphorus-hydrogen pairs are fully dissociated[36,37] and most of the hydrogen is probably either complexed with platinum or lost as inert H_2.[39] Additional annealing at temperatures below approximately 470 K results in no further change of the CV profiles (not shown). However if the annealing temperature is raised to approximately 490 K a significant inward shift of the donor profile is observed. This is accompanied by a slight recovery of the donor density closest to the surface. Annealing at 520 K results in a flat donor profile with the density equal to that obtained in a cleaved (hydrogen free) sample.

The corresponding deep trap depth profiles are shown in Fig. 8. We have also calculated the depth profile of the Pt-H acceptor center by subtracting the sum of the concentrations of E(90), E(250), and the $Pt^{-/0}$ acceptor from the uniform platinum concentration determined in the cleaved sample [see Fig. 8(d)].

As already discussed, a heat treatment at 400 K results in an inward shift of the profiles of all Pt-H complexes and a reduction of the $Pt^{-/0}$ acceptor at greater depths (dashed lines in Fig. 8). The shift is caused by the diffusion of atomic hydrogen deeper into the bulk and the formation of new Pt-H complexes. As in the CV profiles, we find virtually no difference between the depth profiles in samples annealed between 400 and 470 K for 1 h. We also did not observe any changes of the profiles in samples which were annealed at 400 K, then measured and subsequently annealed again at higher temperatures (up to 470 K).

Annealing at 490 K causes, however, a further shift of the maximum concentration of E(90) and E(250) (dotted lines in

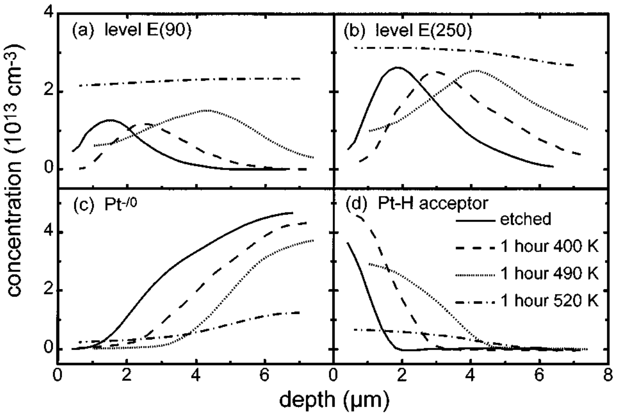

FIG. 8. Depth profiles of the platinum-related defects in *n*-type Si after etching, and after subsequent annealing steps for 1 h at the temperatures indicated. (a) The E(90) center, (b) the E(250) center, (c) the Pt acceptor, and (d) the Pt-H acceptor.

Fig. 8). The Pt-H acceptor complex extends deeper into the bulk while its concentration decreases at depths $\leqslant 1.5\ \mu$m. This reduction in the concentration close to the surface is accompanied by an increase of E(90) and E(250) while the concentration of the $\mathrm{Pt}^{-/0}$ acceptor level remains negligible. This indicates the transformation of the Pt-H acceptor centers into E(90) and E(250) without an involvement of the substitutional Pt. At greater depths ($\geqslant 3\ \mu$m) we detect an additional reduction of the $\mathrm{Pt}^{-/0}$ acceptor which is accompanied by an increase of the concentration of all the platinum-hydrogen-related defects [E(90), E(250), and Pt-H acceptor].

Further increase of the annealing temperature (520 K) results in a flattening of all profiles (dashed-dotted lines in Fig. 8) whereby several processes can be distinguished. First, the concentration of the Pt-H acceptor decreases and it is almost completely dissociated after 1 h at 520 K [see Fig. 8(d)]. Second, the concentrations of E(90) and E(250) increase in the same region, i.e., at depths $\leqslant 5\ \mu$m, supporting the suggestion that the Pt-H acceptor transforms into E(90) and E(250). The annealing behavior of the Pt-H acceptors as extracted from DLTS depth profiling of E(90), E(250), and the $\mathrm{Pt}^{-/0}$ centers is remarkably similar to the changes in the depth profile of the net phosphorus concentration (see Fig. 7). This strongly supports our idea of a Pt-H acceptor center below midgap.

At 520 K we also observe a substantial increase of E(90) and E(250) at greater depths ($\geqslant 5\ \mu$m) where the Pt-H acceptor is not present. At the same time, the reduction of the $\mathrm{Pt}^{-/0}$ acceptor extends deeper into the bulk. The reduction of the substitutional Pt concentration equals the increase in the E(90) and E(250) concentration. This means that additional hydrogen is needed at depths $\geqslant 5\ \mu$m for the creation of the platinum-hydrogen-related defects E(90) and E(250). As mentioned above all phosphorus-hydrogen pairs are dissociated at lower temperatures and can be neglected as a source of hydrogen. The most probable explanation is that excess hydrogen is released during the transformation of the Pt-H acceptor complex into E(90) and E(250) in the region closer to the surface ($\leqslant 5\ \mu$m). The hydrogen diffuses into the bulk leading to the decrease in the substitutional Pt concentration and the increase of E(90) and E(250). If this assumption is correct the Pt-H acceptor complex should contain more hydrogen than the electrically active defects E(90) and E(250). A rough estimate from the concentration depth profiles gives that the Pt-H acceptor center contains 2–3 times more hydrogen than the E(90) and E(250) centers.

After the Pt-H acceptor has annealed out we observe a gradual reactivation of the platinum acceptor and a corresponding reduction of E(90) and E(250) with increasing annealing temperatures. The resulting platinum depth profiles after 1 h at 650 K are flat and the concentration approaches the value in the cleaved sample. We find that E(90) anneals out at slightly lower temperatures than E(250). The concentration of E(90) is always significantly lower than the corresponding concentration of E(250) (see Fig. 8). These properties suggest that E(90) and E(250) belong to two separate platinum-hydrogen complexes.

IV. DISCUSSION

A. Correlation between different Pt-H levels in *p*- and *n*-type Si

In this section we intend to give possible relations between the Pt-related deep levels in *p*- and *n*-type samples. The electrical data of all the levels is presented in Table I. In *p*-type silicon two platinum-hydrogen-related deep levels H(210) and H(150) are observed. H(150) is an acceptor level. The levels belong to two separate Pt-H complexes. H(150) probably contains more hydrogen than H(210). A portion of the H(210) centers transforms into H(150) during annealing between 400 and 500 K (see Fig. 3). In *n*-type samples Pt-H complexes with levels E(90) and E(250) are detected and an additional Pt-H defect is present with an acceptor level below midgap. This acceptor center contains most likely more hydrogen than E(90) and E(250). The Pt-H acceptor dissociates above 500 K and the released hydrogen generates an increase in the E(90) and E(250) signals (see Fig. 8).

The main drawback of the DLTS technique used in this work is that only traps in the lower half of the band gap are monitored in *p*-type samples and in analogy, only traps in the upper half of the band gap are accessible in *n*-type samples. In principle it is possible to obtain information on deep levels within the whole band gap with the help of minority-carrier injection using light. Preliminary studies with minority-carrier injection in *p*-type samples reveal that the midgap trap E(250) is present with higher concentration than the H(210) signal. This suggests that E(250) and H(210) do not belong to the same defect center. Measurements under minority-carrier injection in *n*-type samples were not successful.

The formation of Pt-H complexes depends strongly upon the interaction between hydrogen and the shallow dopants in the samples. In *p*-type Si, most of the hydrogen is complexed with boron after etching. In contrast, pairing of phosphorus and hydrogen in *n*-type Si is much less efficient, which allows a considerable formation of Pt-H complexes already at room temperature. A similar difference between the formation rate of Au-H and Co-H complexes in *n*- and *p*-type silicon was recently reported.[20,23,24] However, the dopant-hydrogen pairs are less thermally stable than the Pt-H complexes. This makes the effect of different dopants insignificant at higher temperatures where the dissociation of Pt-H complexes is investigated.

We can separate the different Pt-H related features in two groups according to the thermal stabilities of the levels: E(90), E(250), and H(210) anneal out between 600–650 K while H(150) and the compensating Pt-H acceptor in *n*-type Si disappear already at about 520 K.

Concerning the first group, the concentration of E(250) is always significantly larger than the concentration of E(90) and extends deeper into the bulk. This strongly suggests that E(90) and E(250) belong to separate Pt-H complexes. Also, as mentioned above, H(210) and E(250) belong to different Pt-H complexes. The only possible connection within this group is then between H(210) and E(90). Further studies are needed to establish if these levels belong to the same Pt-H complex.

Below, we concentrate on the possible connection between the Pt-H acceptor in *n*-type Si and the H(150) acceptor level in *p*-type Si. Indeed, all the experimental observations support that these two states are identical. First of all, from the compensation of the shallow phosphorus donors upon hydrogenation, it is clear that there exists a Pt-H center with an acceptor level below midgap. The thermal stability of the Pt-H acceptor and H(150) is also strikingly similar, both anneal out just above 500 K. In addition, both centers need high concentrations of free atomic hydrogen to be formed. The hydrogen richest regions in *n*-type samples are always closest to the sample surface while we can use RBA to control the hydrogen density in *p*-type samples. During formation of the Pt-H acceptor and H(150) a simultaneous decrease of the density of the other Pt-H centers is observed. Similarly, the dissociation of the Pt-H acceptor and H(150) is accompanied with an increase of the other Pt-H related signals. In summary, the experimental data supports that the H(150) level in *p*-type samples is the acceptor level of a Pt-H complex observed as compensation of the phosphorus donors in *n*-type Si. This is schematically shown in Fig. 9 together with all the reactions which we observe between hydrogen and platinum in *p*- and *n*-type silicon.

B. Comparison with previous DLTS studies of Pt-doped silicon

Deep levels similar to the ones reported in the present work have previously been observed in Pt-doped Schottky diodes. A frequently encountered level is the midgap level in *n*-type Si, in our notation E(250). In a preliminary report[16] we compare E(250) with previous work[5,10,13,14] and found that this level was observed by a number of authors but not interpreted as belonging to a platinum-hydrogen complex. In addition E(90) and H(210) were reported by one of us.[5] A level with a similar activation energy as H(210) has often been observed in platinum-doped *p*-type Si.[2,11,12] However, this particular level is detected in n^+p junctions after heat treatments above 700 °C which disagrees with the thermal stability of H(210). One possible candidate for this level in the n^+p junctions is the interstitial iron donor level.

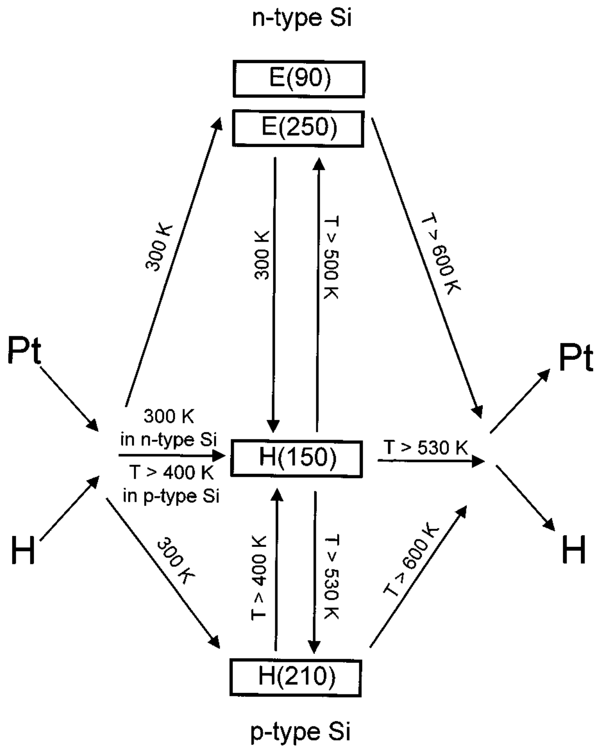

FIG. 9. Schematic diagram of the reactions observed involving platinum and hydrogen. The levels E(90), E(250), and H(210) appear after wet-chemical etching. Level H(150) is formed in *p*-type Si during annealing at T>400 K, but can already be detected as compensation of phosphorus donors in *n*-type Si directly after etching. H(150) dissociates at T>500 K, while E(90), E(250), and H(210) are thermally more stable.

Pearton and Haller[17] reported on hydrogen passivation of the platinum acceptor in *n*-type Si using remote plasma hydrogenation. In contrast, the platinum single donor level in *p*-type Si remained unaffected. This observation disagrees with our data. It is also surprising that the authors did not observe any platinum-hydrogen-related deep levels. Also, the second donor level of platinum is not present at all in their spectrum while it is systematically observed in all our substrates. We suggest above that the Pt-H complex which is indirectly observed as passivation of platinum acceptors actually has an acceptor level below midgap, H(150). No such level is reported in the studies of Pearton and Haller[17] and the spectra indicate no shift or change of the platinum single donor peak. In summary, our data disagree with the results of Pearton and Haller.[17] We have no explanation for this discrepancy. Further studies on silicon hydrogenated by plasma are needed to clarify this issue.

C. Previous spectroscopic studies of Pt-H complexes

Uftring *et al.*[29] reported on a PtH_2 complex using electron paramagnetic resonance and vibrational spectroscopy techniques. The authors also observed several other vibrational bands that belong to separate Pt-H complexes. In these studies hydrogen was introduced by annealing the samples in hydrogen ambient at 1250 °C. Such a treatment results in a uniform atomic hydrogen density in the bulk of the order of 10^{15} cm^{-3}.This differs from our samples where hydrogen is introduced to the sample surface layer by wet-chemical etching.

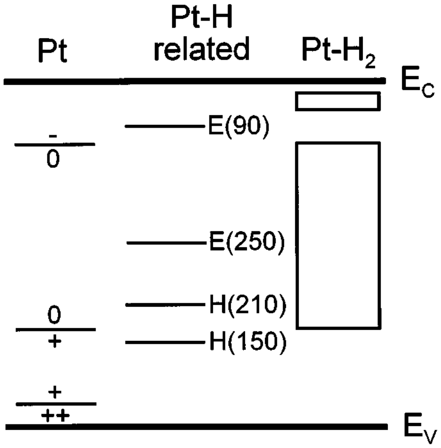

FIG. 10. Energy-level diagram showing the levels of Pt, Pt-H related centers (this work), and PtH_2 (Ref. 29). The open rectangles indicate that the second acceptor level of the PtH_2 complex is between $E_C-0.045$ eV and $E_C-0.1$ eV and that the first acceptor level is between $E_C-0.23$ eV and $E_V+0.33$ eV.

We have attempted to fabricate samples with uniform hydrogen density to enable more direct comparison with the data of Uftring *et al.*[29] For these purposes Pt-doped samples were annealed in hydrogen gas at 1200 °C for 30 min. However, DLTS studies of such samples reveal many new signals which dominate the DLTS spectrum. By comparison with reference samples not doped with platinum we find that the new levels are probably caused by intrinsic defects.

Recently, we have grown Pt-doped crystals in argon gas ambient containing trace amounts of hydrogen. Interestingly, the DLTS spectra of such samples are identical to the ones presented above. The only difference is that the hydrogen-platinum-related traps are now uniformly distributed throughout the bulk. This shows that hydrogenation during crystal growth gives rise to the same Pt-H centers as hydrogenation performed at room temperature by wet-chemical etching. This suggests that the samples in the study of Uftring *et al.*[29] should contain similar Pt-H complexes as our samples. One important difference though is that the platinum concentration in their samples is presumably 2–3 orders of magnitude higher than in our samples (which also excludes DLTS studies on their samples).

The PtH_2 complex is amphotheric with two levels within the silicon band gap,[29] a double acceptor level located between $E_C-0.045$ eV and $E_C-0.1$ eV, and a single acceptor level lying between the single acceptor level of platinum ($E_C-0.23$ eV) and the single donor level ($E_V+0.33$ eV). This is depicted in Fig. 10 together with the deep levels observed in the present study. The PtH_2 complex anneals out at 600 °C[29] but is unstable already at temperatures above 400 °C. If we compare the thermal stability with the deep centers in the present study, E(90), E(250), and H(210) could be levels of such a complex. However, as mentioned earlier, E(90) and E(250) most likely belong to different Pt-H complexes. E(90) is also too deep to be the second acceptor level of PtH_2 and the field dependence of the electron emission rate suggests that E(90) is a donor trap. It is also possible that the second acceptor level of PtH_2 is too shallow to be detected with DLTS. This leaves us with E(250) and H(210) as possible candidates for the first acceptor level of PtH_2. Further DLTS studies of samples containing PtH_2 are needed to establish such a correlation.

V. CONCLUSIONS

Four platinum-hydrogen related deep levels are identified in hydrogenated Pt-doped silicon. These four levels belong to at least three different Pt-H complexes. We observe the Pt-H centers in samples where hydrogen is introduced by wet-chemical etching and in samples where hydrogen is incorporated during crystal growth. In contrast to earlier reports[17] we find that hydrogen forms only electrically active platinum-hydrogen complexes. One of these complexes has an acceptor level, H(150), approximately 0.3 eV above the valence band. It contains more hydrogen than the other Pt-H related defects and is readily formed both in *n*- and *p*-type silicon. At temperatures between 400 and 500 K we observe partial transformations between the different hydrogen-related complexes resulting in an increase of the one containing more hydrogen. This hydrogen-rich complex is thermally unstable above 500 K and upon its dissociation the concentration of both isolated platinum and other hydrogen-related complexes increases accordingly. Annealing above 600 K results in a complete dissociation of all complexes and the substitutional Pt concentration reaches its initial value before hydrogenation.

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