



# Hydrogen–rhodium complexes in silicon

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## Abstract

New hydrogen-induced deep levels in rhodium-doped n- and p-type silicon were observed after hydrogenation by wet-chemical etching. The levels were studied by DLTS measurements on Schottky diodes. We have found in n-type samples the levels E(150) at  $E_C - 0.33$  eV; E(90) at  $E_C - 0.16$  eV; and E(70) at  $E_C - 0.14$  eV. Levels E(150) and E(270) belong to the substitutional rhodium donor and acceptor. Evidence is presented that the level E(70), which was formerly ascribed to isolated rhodium, is due to a hydrogen–rhodium complex. In p-type samples two levels were detected: H(280) at  $E_V + 0.50$  eV and H(200) at  $E_V + 0.37$  eV. Two different hydrogen–rhodium complexes are assigned to these levels. The thermal stability of the levels was investigated up to temperatures of 600 K. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Rh–H complexes; Rh in Si; DLTS

## 1. Introduction

Rhodium is known to be one of the few transition metal impurities in Si which form haze on the Si surface [1]. Prerequisites for this behavior are a high diffusivity and solubility of the interstitial Rh. Quenching of Rh-doped samples from the diffusion temperatures to room temperature leads to the formation of electrically active substitutional Rh [2–4]. In this paper an identification of new hydrogen–rhodium complexes in Si is presented. We determine the level positions of the electrically active defects and clarify the assignments of the isolated substitutional rhodium levels.

## 2. Experimental

Rhodium was incorporated in n- and p-type silicon in concentrations of  $10^{13}$  cm<sup>-3</sup> during the floating zone (FZ) process under vacuum [2]. The n- and p-type samples have a phosphorous concentration of  $7 \times 10^{13}$  cm<sup>-3</sup> and a boron concentration of  $1 \times 10^{14}$  cm<sup>-3</sup>, respectively. Schottky diodes were fabricated by evaporating metal contacts of 2–3 mm diameter on either

cleaved or etched sample surfaces and by scratching an indium–gallium alloy on the backsides to form an Ohmic contact. Gold was used as contact metal in the case of n-type silicon and aluminium for p-type material. The wet-chemical etch for surface cleaning and hydrogen incorporation was performed in a mixture of HF, HNO<sub>3</sub>, and CH<sub>3</sub>COOH (1:2:1).

The samples were studied using a computerized lock-in deep-level transient spectroscopy (DLTS) system. Alternatively capacitance-transients at different temperatures were measured with a capacitance meter and directly recorded by a transient recorder card and a PC. For the determination of the carrier capture cross-sections the duration of the applied voltage pulses was varied between 300 μs and 30 ns.

## 3. Results and discussion

### 3.1. n-type Silicon

Schottky contacts were evaporated on a cleaved sample surface without prior cleaning, so that the isolated rhodium levels could be investigated without intentionally incorporated hydrogen. Three DLTS peaks—E(70), E(150), and E(270)—appear in the spectrum and are shown in Fig. 1(a). (See Table 1 for a list of energy

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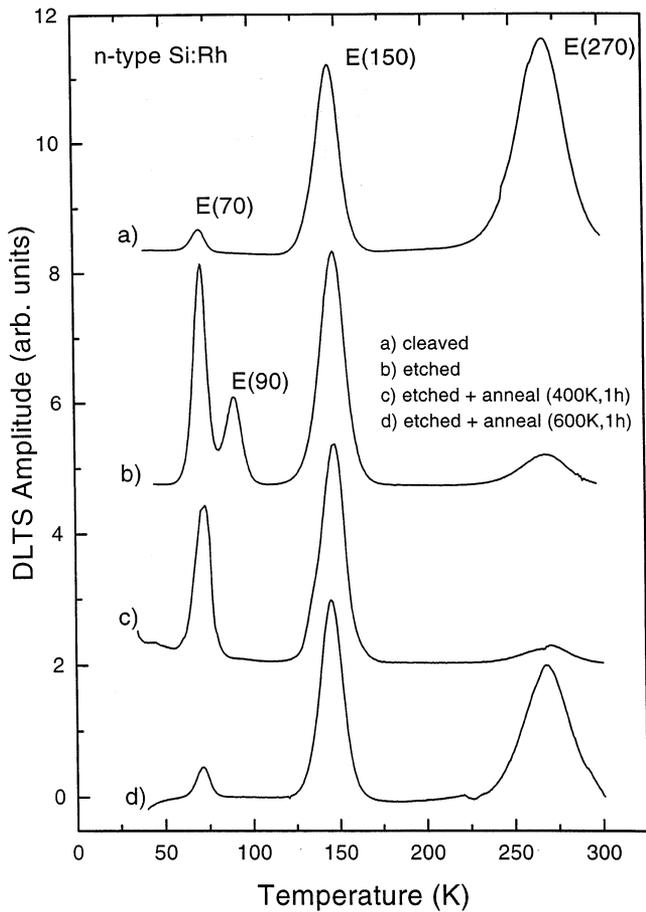


Fig. 1. Deep-level transient spectroscopy spectra of floating zone n-type Si:Rh: (a) cleaved sample; (b) wet-chemically etched sample; (c) etched sample after 380 K anneal for 1 h; (d) after additional 400 K anneal.

levels and capture cross-sections, DLTS peaks are labeled according to the peak temperature measured for an emission rate of  $42 \text{ s}^{-1}$ . The two dominant peaks at 150 and 270 K can be associated with the rhodium donor and acceptor levels. Their concentration profiles

Table 1

List of energy levels and free carrier capture cross-sections (measured by the variation of filling-pulse width) of deep levels in rhodium doped n- and p-type silicon<sup>a</sup>

	$E_A$ (eV)	$\sigma_{n,p}$ ( $\text{cm}^2$ )	
E(70)	0.14	$2.4 \times 10^{-14}$	Rh-H <sub>1</sub>
E(90)	0.16	$4.9 \times 10^{-16}$	C-H-donor
EI(150)	0.33	$1.1 \times 10^{-14}$	Rh-acceptor
EII(150)	0.33	$2.2 \times 10^{-17}$	Rh-H <sub>2</sub> ?
E(270)	0.54	$3.8 \times 10^{-15}$	Rh-donor
H(55)	0.10	$6.5 \times 10^{-15}$	?
H(200)	0.37	$6.2 \times 10^{-16}$	Rh-H <sub>2</sub>
H(280)	0.50	$1.4 \times 10^{-17}$	Rh-H <sub>1</sub>

<sup>a</sup> Energies are given for electron traps (E) from the conduction band edge and for hole traps (H) from the top of the valence band.

are homogeneous and coincide over the whole measured range, showing that they belong to the same substitutional Rh defect. A small peak appears at 70 K which was reported previously in the literature [2]. In Fig. 2 the corresponding concentration profile is lower close to the surface and decreases with depth.

After hydrogen incorporation by wet-chemical etching an additional peak E(90) appears in the DLTS spectrum (Fig. 1(b)). Its activation energy  $E_A = 0.16 \text{ eV}$  and carrier capture cross-section  $\sigma_n = 4.9 \times 10^{-16} \text{ cm}^2$  are in good agreement with previously determined values for the C-H donor [5].

The fact that the peak E(150) is almost unchanged, while the level E(270) decreases in peak height seems, at first sight, to contradict the above conclusion that both levels belong to the same defect. However, the depth profiles in Fig. 2(b) verify that the profiles of the two levels coincide deeper in the bulk and show that while E(270) decreases in direction to the surface, E(150) shows only a small dip around  $5 \mu\text{m}$ . We propose the following interpretation: hydrogen reacts with the rhodium atoms to form hydrogen-rhodium complexes near the surface which lowers the concentration of isolated rhodium. The newly formed complex has an electrically active level, which lies at about the same energy  $E_C - 0.33 \text{ eV}$  as the rhodium-acceptor level, now labeled EI(150). Also shown in Fig. 2(b) is the difference between the depth profiles of E(150) and E(270) which is due to the profile of the new hydrogen-rhodium complex labeled EII(150).

Variation of the filling-pulse duration is used to separate the two levels at 150 K confirming the above interpretation. Two capture cross-sections  $\sigma_{n1} = 1.7 \times 10^{-14} \text{ cm}^2$  and  $\sigma_{n2} = 2.2 \times 10^{-17} \text{ cm}^2$  were extracted which differ by three orders of magnitude. The larger cross-section is in reasonable agreement with the value determined for the rhodium acceptor EI(150), from measurements on the cleaved sample (see Table 1). The smaller one is attributed to the hydrogen-rhodium complex EII(150).

The hydrogen incorporation also leads to an increase in intensity of the level E(70). The depth profiles in Fig. 2 show that the concentration is greatly enhanced near the surface and falls off towards greater depth as in the case of the cleaved sample. This indicates that the level is hydrogen related contrary to previous interpretation of E(70) as a level introduced by isolated rhodium [2]. A small amount of hydrogen seems to be present in our samples even before the wet-chemical etch. The origin of this contamination is unknown.

According to the model of Feklisova and Yarikin [6], which describes the hydrogen complex formation during wet-chemical etching, the penetration depth of a complex should be inversely proportional to the number of hydrogen atoms in the complex. The penetration

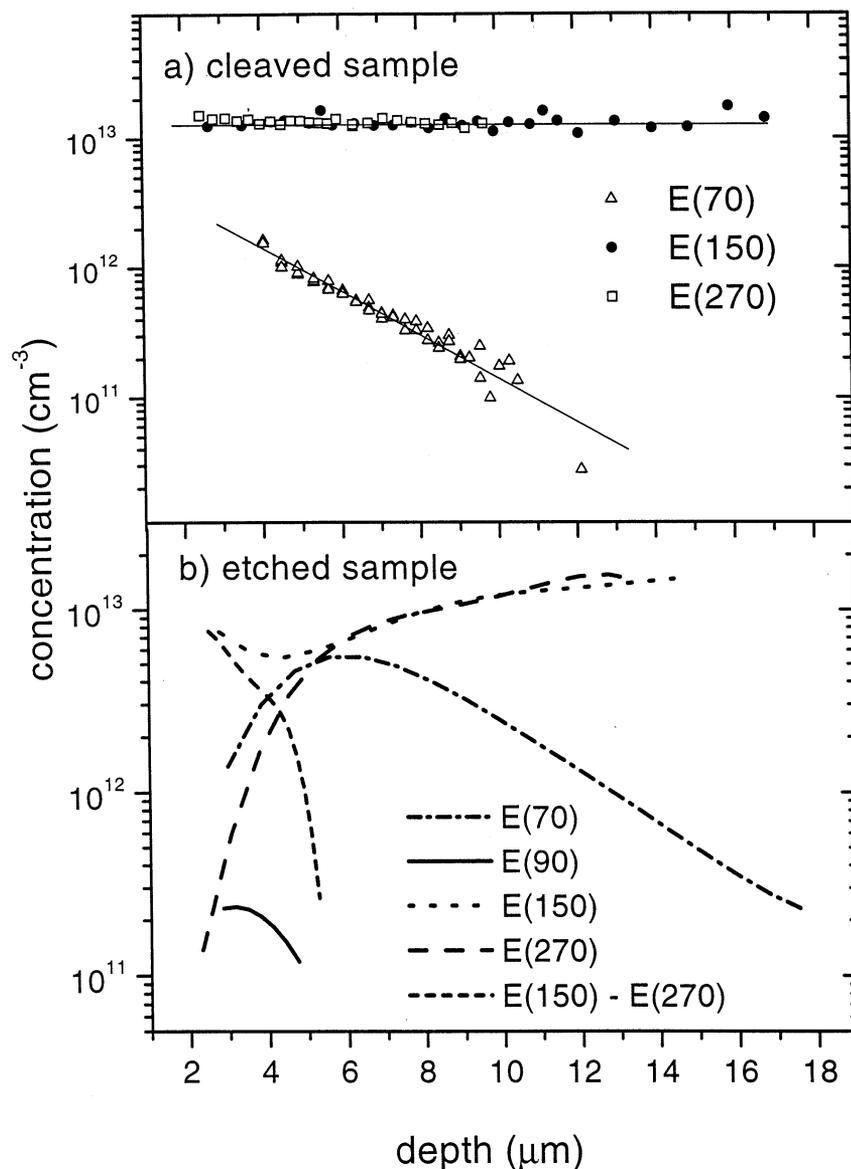


Fig. 2. Depth profiles of deep levels in n-type Si:Rh: (a) cleaved sample; (b) etched sample.

depth for the two levels EII(150), which is the difference of the two profiles E(150) and E(270), and E(70) is easily determined from Fig. 2. A ratio of  $2.2 \pm 0.4$  is found for the two different penetration depths. We tentatively ascribe E(70) to a Rh-H<sub>1</sub> complex and EII(150) to a Rh-H<sub>2</sub> complex.

The thermal stability of the complexes were investigated by isochronal annealing at different temperatures. Level E(90) is strongly reduced after annealing at 380 K for 1 h (not shown) and the level has completely vanished after an anneal for 1 h at 400 K (see Fig. 1(c)). This behavior provides further evidence for the attribution of E(90) to the C-H donor. After the 400 K anneal it can also be seen that the intensity of E(270)

decreases further, which shows that additional rhodium is converted into hydrogen-rhodium complexes, when H is liberated from the C-H complex. Annealing at 600 K partially restores peak E(270), while E(70) is substantially decreased (Fig. 1(d)).

### 3.2. p-type Silicon

No levels attributed to rhodium in p-type silicon have been reported so far. In our cleaved sample a level H(200) at the energy of  $E_V + 0.37$  eV was observed. The concentration of this level was enhanced by further hydrogen incorporation and we have found that H(200) was not homogeneously distributed throughout the sam-

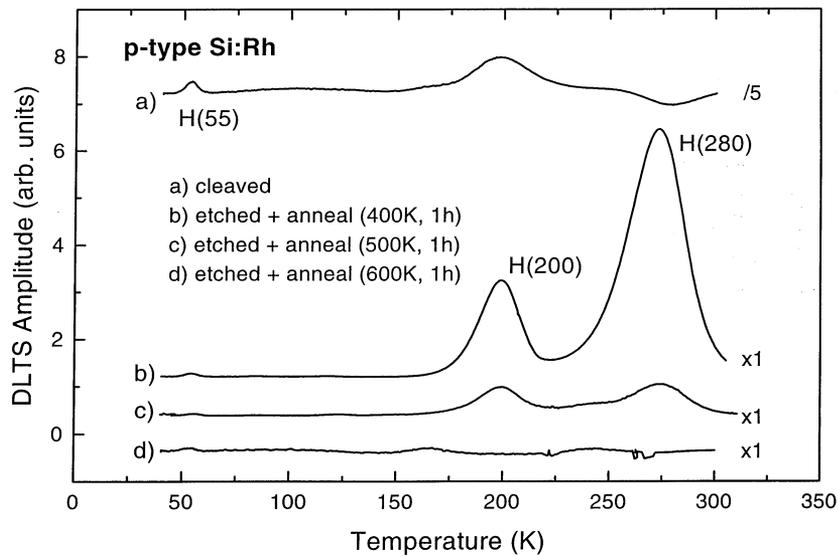


Fig. 3. Deep-level transient spectroscopy spectra of floating zone p-type Si:Rh: (a) cleaved sample; (b) etched sample; (c) etched sample after 400 K anneal for 1 h; (d) after additional 500 K anneal; (e) after additional 600 K anneal.

ple (see Fig. 4). Similar to the behavior of the n-type samples we propose that H(200) is hydrogen related and was already present in the as grown samples.

The wet-chemical etching leads to a strong passivation of the shallow boron acceptors consistent with previous observations [7]. Annealing at 400 K for 1 h reactivates the boron acceptors and leads to the formation of the levels H(200) and H(280). The passivation and subsequent reactivation of the shallow dopants was measured using C–V profiling (1 MHz). Fig. 4 shows the depth-profiles of levels H(200) and H(280). The ratio of the two penetration depth profiles is  $\approx 2$  ( $1.8 \pm 0.3$ ). Applying again the model of Feklisova and Yarikin we tentatively ascribe H(280) to a Rh–H<sub>1</sub> complex and H(200) to a Rh–H<sub>2</sub> complex.

The peak height of H(200) increases relative to H(280) upon annealing at 500 K, showing that the Rh–H<sub>2</sub> complex has a higher thermal stability. Between 500 and 600 K both complexes dissociate and no significant peaks can be detected in the DLTS spectra (see Fig. 3(d)).

In all the DLTS spectra of Fig. 3 there is a small peak located at 55 K. The activation energy of this peak is  $E_A = 0.10$  eV and the free carrier capture cross-section is  $\sigma_p = 6.5 \times 10^{-15}$  cm<sup>2</sup>. The intensity of H(55) is too small for a careful study of its properties.

#### 4. Conclusion

In Rh doped samples, we observed two hydrogen–rhodium related levels in n-type silicon and two in p-type silicon, which are formed after wet-chemical etching. From the spatial distribution of the levels we associate them with different hydrogen–rhodium com-

plexes. A complication is introduced by the circumstance that in n-type silicon a rhodium level and a hydrogen–rhodium level have very similar energy lev-

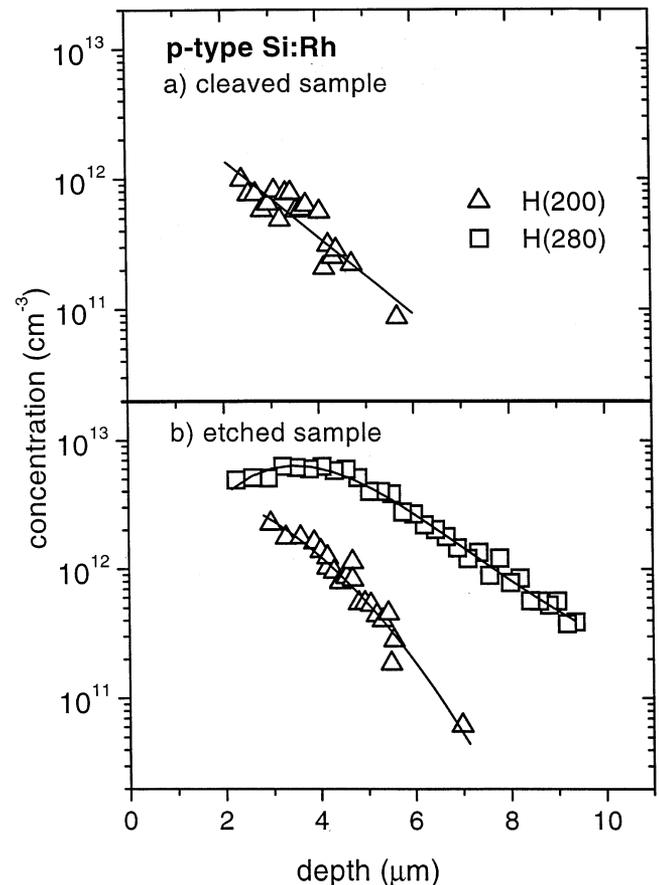


Fig. 4. Depth profiles in p-type Si:Rh: (a) cleaved sample; (b) etched sample after 400 K anneal for 1 h.

els. However, the defects have very different capture cross-sections and were separated by varying the filling pulse duration. In n-type samples we tentatively assign the level E(70) to a Rh–H<sub>1</sub> complex and EII(150) to a Rh–H<sub>2</sub> complex. In p-type samples we assign the level H(200) to a Rh–H<sub>2</sub> complex and H(280) to a Rh–H<sub>1</sub> complex. We have obtained no evidence for an electrically passive complex. In n-type samples we also observed the level E(90), which we attribute to the C–H donor.

All hydrogen–rhodium complexes in p-type samples are dissociated after annealing at 600 K, generating the rhodium-acceptor and -donor levels. In the case of n-type samples the level E(90) dissociates between 380 and 400 K while the hydrogen related levels E(70) and EII(150) can still be detected in low concentrations after a 600 K anneal.

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