# Titanium-hydrogen defects in silicon

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Several titanium-hydrogen (TiH) complexes are generated in crystalline Si by wet chemical etching or a remote hydrogen plasma treatment. We identify two electrically active ($E_C-0.31$ eV, $E_C-0.57$ eV) and one electrically inactive TiH complex. The passive TiH complex dissociates at temperatures above 570 K, leading to an increase in the interstitial Ti concentration. [S0163-1829(96)52840-7]

## I. INTRODUCTION

Most transition metals in semiconductors introduce deep levels in the band gap and reduce the lifetime and diffusion length of minority carriers.[1] Examples are Ti and V which reduce greatly the efficiency of silicon solar cells, even in concentrations as low as $10^{12}$ cm$^{-3}$.[2] The use of $TiSi_2$ as contact material in device technology is also a potential source of Ti contamination.

Although Ti is believed to be predominantly on the interstitial site it diffuses slowly, which makes it difficult to get with standard techniques.[3] It exhibits an acceptor level at $E_C-0.09$ eV, a donor level at $E_C-0.27$ eV, and a double donor level at $E_V+0.25$ eV (see Ref. 1 and references therein). The tetrahedral interstitial site of Ti in the silicon lattice was observed by electron paramagnetic resonance (EPR).[4]

The interaction of Ti with hydrogen is a controversial issue. In a previous study hydrogen was found to have no passivating effect on the deep levels of Ti.[5] Woon *et al.*[6] calculated the barriers of Ti for diffusion and interaction with hydrogen. Their results disagree with the experimental findings. Titanium on both substitutional and interstitial sites should be possible traps for interstitial hydrogen. The authors point out that more than one hydrogen atom is needed to passivate the deep levels of Ti.[6]

In our paper we present evidence for hydrogen induced electrically active and inactive complexes in Ti doped $n$- and $p$-type silicon.

## II. EXPERIMENT

Samples are cut from Ti-doped single crystalline silicon grown by the Czochralski (CZ) or by the float-zone (FZ) technique. Phosphorus is used for $n$-type and boron for $p$-type doping. In both cases, we used two different shallow doping concentrations ($10^{14}$ cm$^{-3}$ and $10^{15}$ cm$^{-3}$).

Schottky diodes are formed by evaporation of aluminum for $p$-type and gold for $n$-type samples through a metal mask at room temperature. A eutectic InGa alloy is rubbed onto the back side of the samples to form the Ohmic contact.

The experimental setup used in this study is a computerized lock-in deep-level transient spectroscopy (DLTS) system. During the DLTS depth profiling[7] the sample is held at a constant reverse bias, while the filling pulse height is varied using pulses long enough to avoid incomplete trap filling.[8] The shallow dopant profiles are determined by CV measurements (1 MHz).

Cleaved samples were prepared by breaking the samples from the crystal rod and forming the contacts onto the surface without any surface treatment. Such a treatment results in Schottky diodes free of hydrogen.[9] Hydrogenation of the samples at room temperature is performed by wet chemical etching in a 1:2 mixture of HF and $HNO_3$. This etching step is used before the evaporation of the Schottky contacts and is sufficient to introduce the necessary amount of atomic hydrogen. Hydrogenation at higher temperatures is performed in a dc-driven hydrogen plasma. These samples are also wet chemically etched before they are mounted in the hydrogen plasma chamber. After the plasma etching, contacts are evaporated onto the samples without an additional wet chemical etch.

The samples are heated for the annealing studies up to 470 K on the sample holder. During the heat treatment a bias could be applied to the Schottky diode. Higher annealing temperatures were achieved in a furnace with the sample in Ar atmosphere. The samples could be illuminated with a laserdiode (HAM820/2428 from LASER 2000; $\lambda=820$ nm, 1–200 mW).

## III. RESULTS

After wet chemical etching a decrease of the net boron concentration close to the sample surface is observed. This well-known phenomenon is explained by the formation of neutral boron-hydrogen pairs.[10] Annealing the samples with a reverse bias applied to the Schottky contact [reverse bias anneal (RBA)] leads to a dissociation of the complexes and a reactivation of the shallow acceptors. The released positively charged hydrogen drifts in the field of the space charge region and forms new boron-hydrogen pairs at the edge of the depletion layer. In $n$-type samples, the formation of neutral P-H pairs close to the surface is detected directly after a wet chemical etch. After an RBA for 10 min at 400 K, we observe a reactivation of the phosphorus donors. However, no drift of hydrogen during RBA is observed in our samples. Therefore in $n$-type samples the depth distribution of the hydrogen is not controllable by RBA, as was found in $p$-type silicon.

A DLTS spectrum of an $n$-type sample after wet chemical etching is shown in Fig. 1(a). Four DLTS peaks $E(40)$, $E(150)$, $E(170)$, and $E(260)$ are detected. We label the

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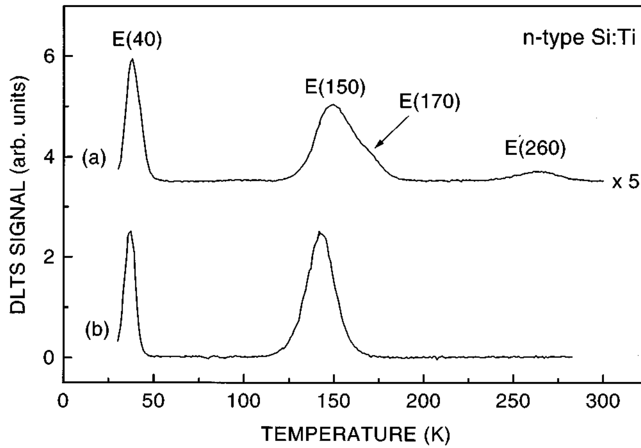


FIG. 1. DLTS spectra of Ti-doped $n$-type silicon taken (a) after wet chemical etching and (b) after an additional 3-h anneal at 570 K with zero bias (reverse bias = 2 V, filling pulse = 0 V, filling time = 1 ms, emission rate = 42 $s^{-1}$. Note that the DLTS spectrum in (a) is enlarged by a factor of 5.

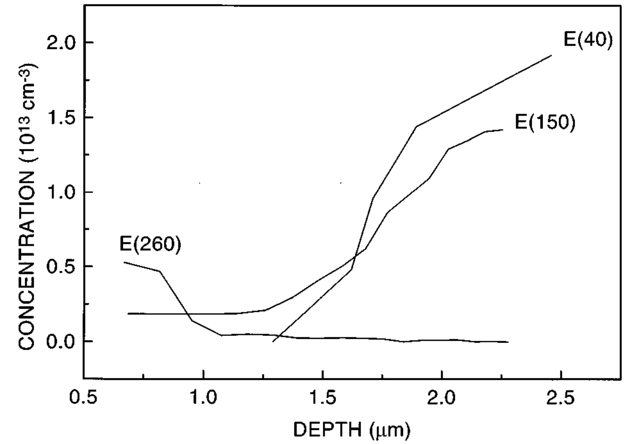


FIG. 2. Concentration depth profiles of traps $E(40)$, $E(150)$, and $E(260)$ after wet chemical etching (reverse bias = 10 V, filling pulse varied from 0 to 10 V).

DLTS peaks according to the temperature at maximum peak height (emission rate = 42 $s^{-1}$), where $E$ indicates electron emission and $H$ is the hole emission. Table I summarizes the electrical properties of the DLTS signals observed in Ti-doped silicon. The activation energies of the two major peaks $E(40)$ and $E(150)$ are in good agreement with the acceptor and donor levels of Ti.[1]

Varying the reverse bias while using the same pulse voltage leads to a change of the electric field and the width of the space charge region (SCR). The electric field has an effect on the emission rate from Coulombic centers. We observe a slight shift of $E(150)$ towards lower temperatures with increasing applied reverse bias. This small Poole-Frenkel effect for the Ti donor level is in agreement with the results reported in Ref. 11. The variation of width of the SCR enables us to study levels at various depths. At a reverse bias of $V_R = 10$ V only two peaks $E(40)$ and $E(150)$ are observable. Under this condition one studies the emission of centers placed within a depth of 1.2–3 μm. A reverse bias of $V_R = 2$ V shrinks the space charge region and allows us to observe the emission of centers within a region of 1.2–1.6 μm. In this region the two Ti levels are significantly reduced. However, two additional weak peaks $E(170)$ and $E(260)$ arise in the DLTS spectrum.

Annealing the sample in the temperature range from 300 to 450 K while applying zero or reverse bias to the Schottky contact does not significantly alter the DLTS spectra. However, annealing at 570 K with zero bias for 3 h leads to the disappearance of $E(170)$ and $E(260)$ [Fig. 1(b)] and at the same time to an increase of the Ti donor and acceptor peak by almost a factor of 5.

TABLE I. List of energy levels and assignments of deep levels in Ti-doped silicon.

| Level | Activation energy (eV) | Assignment |
|---|---|---|
| $E(40)$ | $E_C - 0.09 \pm 0.02$ | $Ti^{-/0}$ |
| $E(150)$ | $E_C - 0.27 \pm 0.01$ | $Ti^{0/+}$ |
| $E(170)$ | $E_C - 0.31 \pm 0.02$ | TiH |
| $E(260)$ | $E_C - 0.57 \pm 0.02$ | TiH |
| $H(180)$ | $E_V + 0.25 \pm 0.01$ | $Ti^{+/++}$ |

In Fig. 2 the DLTS depth profiles of the sample from Fig. 1(a) are shown. The concentrations of $E(40)$ and $E(150)$ increase towards the bulk. In addition, they agree over the investigated region within the experimental error which further supports the identification that $E(40)$ and $E(150)$ are indeed different charge states of the same center. The concentration of $E(260)$ has its maximum close to the surface and decreases rapidly towards the bulk. The depth profile of $E(170)$ cannot be determined, because this signal strongly overlaps with the signal of the Ti donor $E(150)$. However, DLTS spectra taken at different depths unambiguously reveal that both $E(170)$ and $E(260)$ are located only in the surface region (<2 μm). The annealed sample shows a homogeneous depth profile for the Ti acceptor and donor.

In addition, we cleaved one sample from the crystal rod with lower phosphorus concentration and evaporated contacts onto it without any further etching. In these samples we detect only the $E(150)$ level.

Finally, we treated an $n$-type sample for 3 h at 470 K in a hydrogen plasma. The DLTS spectrum of this sample is similar to the one shown in Fig. 1(a), except the $E(170)$ and $E(260)$ peaks are more pronounced.

A DLTS spectrum of a Ti-doped $p$-type silicon sample after wet chemical etching is shown in Fig. 3. One majority carrier DLTS peak at 180 K (emission rate 42 $s^{-1}$) and two minority carrier DLTS peaks are observed, which agree within experimental error with the signals $E(40)$ and $E(150)$. The electrical parameters for $H(180)$ are in good agreement with the Ti double donor[1] (see Table I).

The profile of the Ti double donor is flat and is not affected by the etching process [see Fig. 4(a), squares]. Zero bias annealing at 400 K for 35 min decreases the concentration of the Ti double donor near the surface [Fig. 4(a), dots]. The Ti double donor concentration follows the profile of the shallow boron acceptors, which were not passivated by hydrogen. The shape of the profile indicates therefore a com-

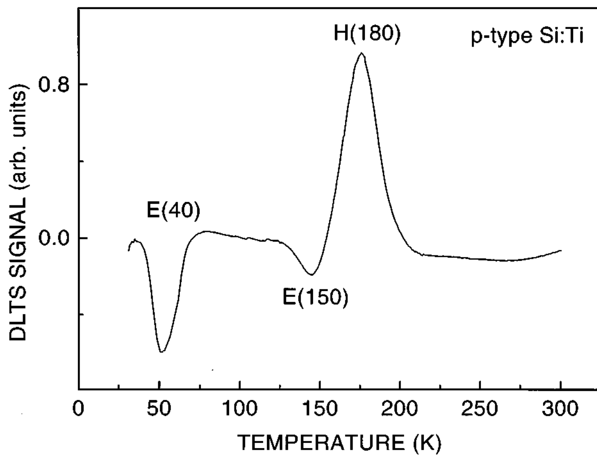


FIG. 3. DLTS spectrum of Ti-doped $p$-type silicon taken after a 2-min wet chemical etch (reverse bias = 2 V, filling pulse = 0 V, filling time = 1 ms, emission rate = 42 $s^{-1}$).

plexing of Ti with hydrogen. However, if we apply a reverse bias during the annealing at 400 K, we do not observe any change in the Ti concentration [Fig. 4(b)]. We studied the kinetics of the changes in the Ti double donor concentration. Due to the small variation in concentration (only 30% of the total concentration), we could not distinguish whether the kinetics follows first or second order. If we assume first order kinetics the rates $\nu$ exhibit an Arrhenius behavior with $\nu = \nu_0 \exp(E_a/kT)$ (attempt frequency $\nu_0$; activation energy $E_a$). A least squares fit to the measured data points gives an energy of $E_a = 0.77 \pm 0.15$ eV with an attempt frequency $\nu_0 = 2 \times 10^{6\pm1}\ s^{-1}$.

The influence of minority carriers on the formation of Ti-H complexes was studied in the following way. The Schottky contact was illuminated during the RBA annealing at temperatures between 360 K–400 K with the laserdiode. Depending on the laser power, we find two different effects on the depth profile of the Ti double donor [Fig. 4(c)]. High laser powers diminish the SCR, due to the high concentration of created minority carriers. There is no drift of $H^+$ under these conditions. The profile [Fig. 4(c), dots] is very similar to the profile shown in [Fig. 4(a), dots] for the zero bias anneal. With reduced laser power, a characteristic dip in the Ti double donor profile occurs [Fig. 4(c), triangles]. Under these conditions hydrogen drifts in the electric field of the reverse biased Schottky diode.

## IV. DISCUSSION

In a recent publication we demonstrated that cleaving a sample without any further chemical treatment results in Schottky diodes free of hydrogen.[9] In the cleaved sample of the present study only the Ti donor is found. The acceptor level cannot be observed in this sample due to a freezing out of the carriers below 60 K as the Ti acceptor compensates the shallow donors. The levels $E(170)$ and $E(260)$ are only observed in samples after wet chemical etching or hydrogen plasma etching. In addition, they are only detected near the surface where the hydrogen concentration has its maximum. Their occurrence is accompanied by a decrease in the concentration of the Ti donor and acceptor. This strongly suggests that $E(170)$ and $E(260)$ are titanium-hydrogen related deep levels.

But the concentrations of $E(170)$ and $E(260)$ cannot fully account for the decrease in concentration of the Ti levels (Fig. 2). After annealing at 570 K for 3 h the Ti acceptor and donor signals fully recover. Hence there must also be at least one electrically inactive TiH complex which concentration exceeds the concentrations of $E(170)$ and $E(260)$ by an order of magnitude.

The Fermi level in our samples at room temperature is below the Ti donor level ($E_C - E_F \geqslant 0.27$ eV). Therefore Ti is in its positive charge state ($Ti^+$). The charge state of hydrogen is less clear.[12,13] Still, we tentatively describe the formation of the TiH complex schematically as $Ti^+ + nH^+ + ne^- \rightleftharpoons [TiH_n]^+$. However, we are unable to distinguish whether the two TiH-related levels are different charge states of one TiH complex or are due to different TiH complexes differing in the position and/or in the number of bonded hydrogen atoms (TiH, $TiH_2$, etc.). We tentatively attribute these levels to different charge states of one electrically active TiH complex. In addition, there is another TiH complex yielding a passivation of Ti. After a 3-h anneal at 570 K the TiH-induced levels and the electrically inactive TiH complex disappear and the Ti concentration fully recovers.

The passivation of the Ti double donor in the dark only

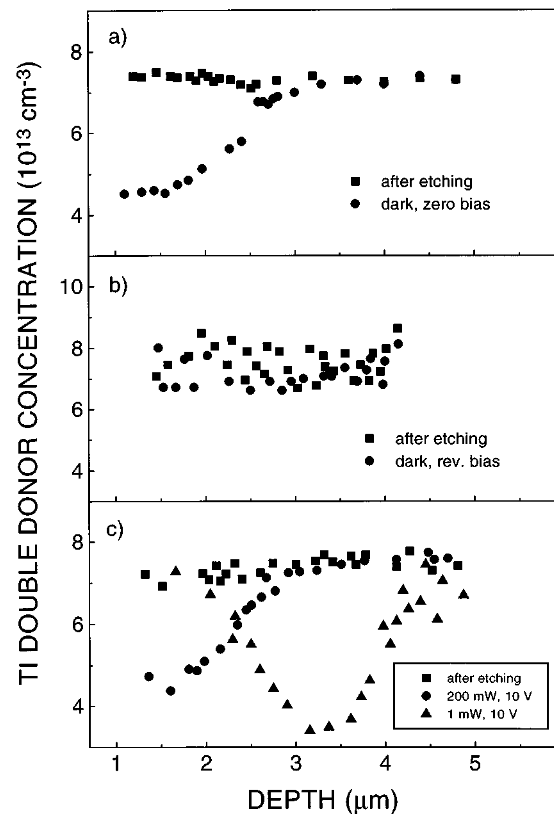


FIG. 4. (a) DLTS-depth profile of the Ti double donor after a 2-min wet chemical etch (after etching) and additional annealing at 400 K for 10 min with zero bias in the dark (dark, zero bias), (b) additional annealing at 400 K for 10 min with 10-V reverse bias in the dark (dark, reverse bias), and (c) additional annealing with 10-V reverse bias at 360 K for 10 min under illumination with different laser powers.

took place during zero bias annealing, but not during an RBA. Meijer *et al.*[14] showed that in a Schottky diode minority carriers are injected. The injection occurs only close to the sample surface region, i.e., the diffusion length of minority carriers is small. Certainly, the diffusion length of the minority carriers is not increased by applying a reverse bias to the Schottky diode. During zero bias annealing, both hydrogen and minority carriers are located at the surface region, where the passivation of Ti occurs. In contrast, during RBA hydrogen drifts to the end of the SCR, whereas the minority carriers remain close to the surface region. Under these conditions no passivation of Ti is detected. The situation completely changes, when the sample is illuminated during RBA. Passivation of Ti occurs only where the hydrogen is available [Fig. 4(c)]. These results support the explanation that minority carriers are involved in the formation of the TiH complexes. The attempt frequency for the passivation of Ti is $2\times10^6$ s$^{-1}$. This value is typical for a capture of carriers accompanied by multiphonon emission.[15] The CV measurements after RBA reveal that hydrogen is in the positive charge state. The Ti is also predominantly in the positive charge state ($E_F=E_V+0.35$ eV) during the RBA at 400 K. The formation of the TiH complex can again be written schematically as $\mathrm{Ti}^+ + n\mathrm{H}^+ + ne^- \rightleftharpoons [\mathrm{TiH}_n]^+$. The complexing of Ti with H in $n$-type silicon is more pronounced as in $p$-type, due to the lack of Coulombic repulsion between hydrogen and Ti in $n$-type silicon.

## V. CONCLUSION

The interaction of hydrogen with titanium in Si was investigated. Two new electron traps induced by TiH complexes at $E_C-0.31$ eV and $E_C-0.57$ eV were observed in the surface region of Ti-doped $n$-type silicon. In addition, there exists at least one electrically inactive TiH complex. In $p$-type silicon the passivation of Ti seems to occur only if minority carriers are available. The TiH complexes dissociated at around 570 K, leading to an increase in the interstitial Ti concentration.

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[1] K. Graff, *Metal Impurities in Silicon-Device Fabrication* (Springer, Berlin, 1995).
[2] J. T. Borenstein, J. I. Hanoka, B. R. Bathey, J. P. Kalejs, and S. Mil'shtein, Appl. Phys. Lett. **62**, 16 151 (1993).
[3] K. Leo, R. Schindler, J. Knobloch, and B. Voss, J. Appl. Phys. **62**, 3472 (1987).
[4] D. A. van Wezep and C. A. J. Ammerlaan, J. Electron. Mater. **14** A, 863 (1985).
[5] R. Singh, S. J. Fonash, and A. Rohatgi, Appl. Phys. Lett. **49**, 800 (1986).
[6] D. E. Woon, D. S. Marynick, and S. K. Estreicher, Phys. Rev. B **45**, 13 383 (1992).
[7] H. G. Grimmeiss, E. Janzén, B. Skarstam, and A. Lodding, J. Appl. Phys. **51**, 6238 (1980).
[8] S. D. Brotherton, Solid-State Electron. **26**, 987 (1983).
[9] W. Jost, J. Weber, and H. Lemke, Semicond. Sci. Technol. **11**, 22 (1996).
[10] T. Zundel and J. Weber, Phys. Rev. B **39**, 13 549 (1989).
[11] D. Mathiot and S. Hocine, J. Appl. Phys. **66**, 5862 (1989).
[12] N. M. Johnson, C. Herring, and C. G. Van de Walle, Phys. Rev. Lett. **73**, 130 (1994).
[13] C. H. Seager, R. A. Anderson, and S. K. Estreicher, Phys. Rev. Lett. **74**, 4565 (1995).
[14] E. Meijer, L. Å. Ledebo, and Z. G. Wang, Solid State Commun. **46**, 255 (1983).
[15] A. Chantre and D. Bois, Phys. Rev. B **31**, 7979 (1985).