Interaction between hydrogen and the Fe-B pair in boron-doped p-type silicon

C. K. Tang,[a] L. Vines, B. G. Svensson, and E. V. Monakhov
University of Oslo, Physics department/Center for Materials science and Nanotechnology, P.O. Box 1048 Blindern, Oslo N-0316, Norway

The effect of hydrogen incorporation into iron-contaminated boron-doped Cz-Si has been investigated using deep level transient spectroscopy. In-diffusion of hydrogen by wet chemical etching followed by reverse bias annealing of Al, Schottky diodes result in the appearance of the defect level characteristic to interstitial iron (Fe_i), and the concentration of iron-boron pairs (Fe-B) decreases correspondingly. Quantitative observations from various defect concentration versus depth profiles imply strongly that H promotes dissociation of Fe-B releasing Fe_i whereas no detectable passivation of Fe-B or Fe_i by H occurs. © *2011 American Institute of Physics.* [doi:10.1063/1.3619848]

Iron in silicon is well known for its effect in degrading the performance of devices, such as in integrated circuits and solar cells.[1] Significant reduction in minority carrier lifetime, even at low iron concentration, is one of the main issues in solar cells based on p-type multicrystalline silicon. The efficiency of lifetime recovery by reducing the concentration of electrically active iron-related defects through gettering or passivation has frequently been investigated.[2–5] For the passivation, especially hydrogen has been studied. However, experimental reports on the effects of hydrogen on the iron behavior have shown various results. On one hand, passivation of iron by hydrogen was concluded through lifetime measurement.[4] On the other hand, deep level transient spectroscopy (DLTS) studies have observed an increase in the lifetime killing interstitial Fe (Fe_i) as possibly due to stimulated dissociation of the Fe-B pair by hydrogen.[6,7] In the latter reports, wet chemical etching (WCE) was performed to introduce H at the surface which resulted in an increase of Fe_i in the region where B-H was formed. Annealing under reverse bias led to an increase in the Fe_i signal in the depletion region and an indication of a small peak at the depletion edge where B-H reached its maximum concentration. Two mechanisms for release of Fe_i were discussed in Refs. 6 and 7. The first one involves a change in the Fermi-level position and changing the charge state of Fe_i from positive to neutral, which reduces the binding energy between Fe and B^- and quenches the formation of Fe-B.[8] The second one involves hydrogen in a reaction with Fe-B forming Fe_i and B-H but no decrease in Fe-B equivalent to the increase of Fe_i as a function of depth has been verified yet.

The interaction between Fe_i, Fe-B, and H has recently been predicted through *ab-initio* calculations using Vienna Ab-initio Simulation Package (VASP) and Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) by Sanati *et al.*[9] The stability of various *a priori* configurations was estimated in different charge and spin states. In the case of Fe-B and H, it was predicted that the most stable configuration consists of an isolated $^{3/2}Fe_i^+$ and $^0B\text{-}H^0$ with 3/2 and 0 spin state, respectively. The gain in

energy was 0.25 eV compared to $^{3/2}Fe\text{-}B^0$ and $^0H_{BC}^+$ (H in bond centered configuration). In addition, a stable configuration was also predicted between Fe_i and H, in the case of $^1Fe_i^0$. The gain in energy varied with the H reactant in $^{1/2}H_{BC}^0$ and $^0H_{BC}^+$ states to be 0.82 and 0.40 eV, respectively. The resulting Fe-H pair exhibits a deep donor level at 0.36 eV (SIESTA: 0.42 eV) above the valence band edge (E_V) and a deep acceptor level at 0.26 eV (SIESTA: 0.30 eV) below the conduction band (E_C). However, an additional H could release the Fe from Fe-H by forming Fe_i and H_2.

The charge state of Fe_i can easily be modified in a diode structure by applying an external bias which moves the Fermi-level and interchange Fe_i^+ to Fe_i^0. Such an experiment provides the opportunity for examining possible reaction between Fe_i^0 with H^+ which should appear in a specific region and give rise to new energy level positions, as predicted theoretically.

In this study, we have incorporated hydrogen in iron-contaminated p-type silicon through wet chemical etching and investigated its effects on iron. The results of different defect concentration versus depth profiles strongly favour dissociation of Fe-B in the presence of H, where the absolute loss in the concentration of Fe-B is accompanied by a corresponding gain in the concentration of Fe_i. In addition, our results show no detectable passivation of Fe_i and Fe-B by H.

Samples were cut from as-grown Czochralski Si wafers of p-type with a boron doping concentration of $\sim 1.3 \times 10^{14}$ cm^{-3}. Iron was introduced by ion implantation on the back-side of the samples with energy and dose of 700 keV and 7×10^{11} cm^{-2}, respectively. Heat treatment was thereafter performed at 900 °C under nitrogen flow for 1 h in a tube furnace to distribute the Fe homogeneously in the samples. After the heat treatment, the samples were quenched rapidly in water to room temperature (RT).

WCE was performed for 30 s (7:5:2, HNO_3:HF:CH_3COOH) on one set of samples in order to introduce hydrogen at the surface.[7] Reference samples, which did not undergo WCE, were dipped in HF. All samples were, thereafter, further cleaned in RCA3 (H_2O, HCl, H_2O_2, 5:1:1, at 80 °C). Schottky barrier (SB) contacts were realized by thermal evaporation of Al through a metal mask on the front-surface
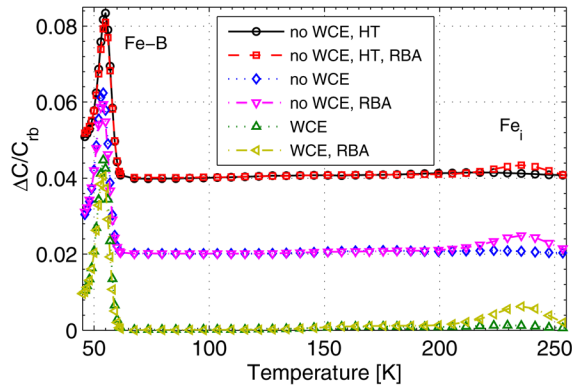
[a] Electronic mail: c.k.tang@smn.uio.no.

FIG. 1. (Color online) DLTS spectra before and after RBA on iron-contaminated samples with/without WCE treatment. The curves are taken with a rate window of $(40 \text{ ms})^{-1}$. An offset in $\Delta C/C_{rb}$ has been applied to the data for samples without WCE for clarity.
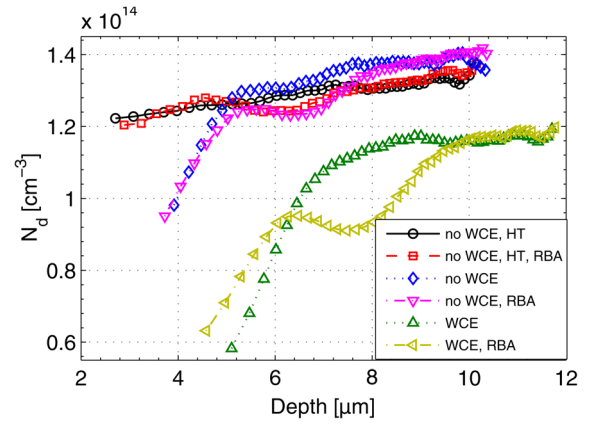

FIG. 2. (Color online) Charge carrier concentration vs depth profile before and after RBA on samples with/without WCE treatment. It reveals the passivated region, which results from the formation of B-H, and can be related to the concentration of hydrogen.

and Ohmic contacts were achieved by applying silver-paste on the back-side. Since the sample processing steps may introduce unintentional hydrogen at the surface, one set of the reference samples were heat treated (HT) at 180 °C for 30 min to distribute any accumulated hydrogen into the sample. Reverse bias annealing (RBA) was performed at 350 K for 30 min with a reverse bias voltage (V_{rb}) of 4 V.

DLTS measurements were performed with a V_{rb} of 8 V, pulse bias of −8 V, and pulse width of 50 ms in the temperature range of 40 to 300 K. The DLTS signal was extracted using a lock-in weighting function, and six rate-windows ranging from $(5 \text{ ms})^{-1}$ to $(160 \text{ ms})^{-1}$. The first DLTS measurements were performed after two weeks of storage at room temperature after the sample preparation.

Figure 1 shows DLTS spectra before and after RBA on samples with and without WCE treatment. Before RBA, one dominant peak can be observed at 55 K in all samples, with a defect concentration of 1.2×10^{13} cm^{-3}. From the result from the different rate windows, the energy level position and apparent capture cross-section were deduced to be $E_V + 0.10$ eV and 4×10^{-15} cm^2, respectively. The obtained values are in good agreement with the identification of the peak as Fe-B.[1] After RBA, a second peak appeared at 242 K with energy level position at $E_V + 0.40$ eV and apparent capture cross-section 3×10^{-16} cm^2, in good agreement with previous identification of Fe$_i$.[1] During storage at RT, the Fe$_i$ peak decreased in all samples while the Fe-B peak increased correspondingly. The evolution of the peaks is due to the (re)association of Fe$_i$ with B forming the Fe-B pair. This behaviour is a well known characteristic of Fe in boron-doped silicon, where the stable Fe-B pair can dissociate in a reversible reaction into Fe$_i$ by thermal treatment, illumination or minority carrier injection.[10] Although all samples experienced the RBA, the samples treated in WCE showed a higher DLTS signal of Fe$_i$ than the samples without WCE. In particular, it can be noticed that the HT sample exhibits a weak Fe$_i$ signal. However, from the Fig. 1, it can be misleading to conclude on a direct interaction between hydrogen and Fe, since changes in the charge carrier concentration (from RBA) can affect the DLTS signal.

Figure 2 shows the charge carrier concentration versus depth measured by capacitance-voltage measurement for the corresponding samples in Fig. 1. The charge carrier concen-

tration can be related to the hydrogen concentration due to the formation of the B-H pair which is electrically inactive.[11] Accordingly, Fig. 2 unveils a considerable concentration of hydrogen in the near-surface region in the reference and the WCE-treated samples, while no change in carrier concentration is observed in the HT samples. Interestingly, a small concentration of hydrogen in the WCE samples has penetrated beyond 12 μm, seen as a reduced carrier concentration in the WCE samples compared to samples without WCE. The effect is also observed in other methods for hydrogen incorporation[12] and shows a large migration length of H despite efficient trapping by B. After RBA, a larger degree of passivation of B by H can be observed, causing a carrier concentration minimum, except for the HT sample which remains only slightly affected. The minimum in carrier concentration occurs at the depletion edge and is due to the electric field in the depletion region forcing/drifting the H$^+$ to the depletion edge, resulting in an accumulation of hydrogen.[13] It should also be mentioned that the debonding process of B-H has been reported to occur at a much higher rate within the depletion region compared to the quasi-neutral region.[14]

Figure 3 shows the concentrations of FeB and Fe$_i$ versus depth profiles for WCE samples and HT samples. The appearance of Fe$_i$ and the correlated loss in Fe-B, observed in Fig. 1, originates from a distinct layer, defined by RBA, within the DLTS depletion region.

As mentioned previously, one possibility for the release of Fe$_i$ is a change in the charge state of Fe$_i$ from positive to neutral which has been shown, by Kimerling and Benton,[8] to extinguish the pairing of Fe$_i$ and B$^-$. Since the applied reverse bias during RBA raises the Fermi-level above the level of Fe$_i$ (transferring it to the neutral state), the resulting defect profiles may be caused by the Fermi-level effect within the depletion region. It should be emphasized that the region where Fe changes the charge state is not located at the depletion edge but a distance closer to the surface, due to the so-called lambda-length.[15] Thus, release of Fe$_i$ should not occur at the depletion edge.

The depletion edge and the significance of the lambda-length are highlighted in Fig. 3 with added lines. The depth of the depletion region is determined from the capacitance that
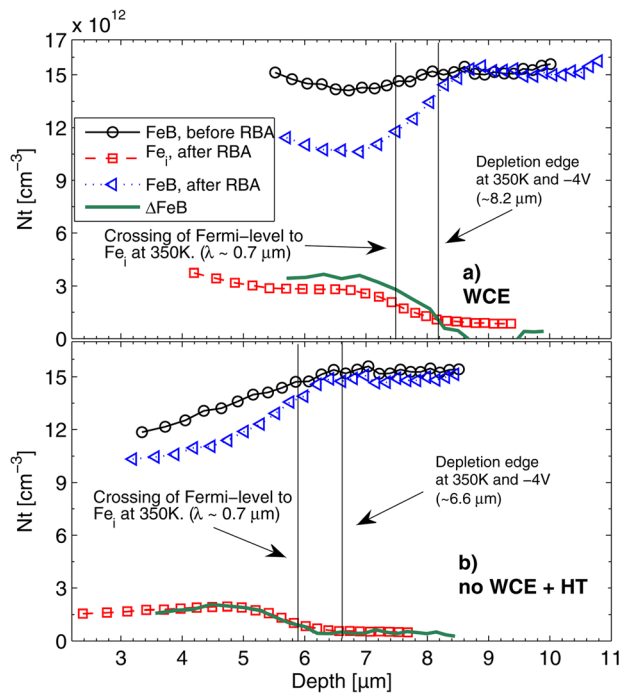
FIG. 3. (Color online) Defect concentration vs depth profile for Fe-B and Fe_i measured on (a) samples with WCE and (b) HT samples without WCE.

was recorded continuously during the RBA at 350 K. Due to the H re-distribution, a change in the capacitance takes place during RBA; it amounts, however, to only 0.3%, i.e., ~20 nm in the depletion edge depth and can be neglected.

The characteristics of a release of Fe_i by the Fermi-level effect are fulfilled in the HT samples where the influence of H is small. The depth profile in Fig. 3(b) shows that the increase of Fe_i occurs close to the charge state transition region (as highlighted by the vertical lines). However, in the WCE samples, a significant release of Fe_i can be observed not only in the region with Fe_i^0 but also in the part of the depletion region where Fe_i^+ exists. Moreover, the concentration of released Fe_i in the depletion region is higher by a factor of 1.5-2 in the WCE sample as compared to the HT sample. This demonstrates the significance of the mechanism, where Fe_i is released due to a direct dissociation of Fe-B promoted by H: Fe-B + H → B-H + Fe_i.

It may be argued that Fe_i released close to the surface has in-diffused to such an extent that it could account for the measured defect profiles. However, the gain in concentration

of Fe_i as a function of depth agrees closely with the loss of in concentration of Fe-B, implying that no significant net diffusion has occurred in the measured region.

As mentioned in the introduction, an interaction of H with Fe^0,[9] may be expected in the depletion region. However, based on our quantitative observations, we can not confirm formation of Fe-H complexes under the present experimental conditions; indeed, if hydrogen is to passivate Fe_i or Fe-B, a dissimilar concentration change between the two defects should occur. In addition, no new level in the vicinity of 0.3–0.4 eV above E_V, predicted for a donor state of the Fe-H pair, is observed. Thus, no evidence for passivation of Fe_i or Fe-B by H is obtained.

In conclusion, hydrogen has been incorporated into iron-contaminated boron-doped Cz-Si and demonstrated to interact with the Fe-B pair. By monitoring the absolute concentration of Fe-B and Fe_i versus depth before and after RBA, strong evidence of hydrogen-induced dissociation of the Fe-B pair into Fe_i and B-H are found confirming previous tentative experimental findings and recent theoretical predictions. In addition, no detectable passivation of Fe_i by hydrogen is observed.

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