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Dissociation of iron-related centers in Si stimulated by hydrogen

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Abstract

The interaction of hydrogen with Fe-related centers in p-type Si was investigated by deep level transient spectroscopy (DLTS). After wet chemical etching (WCE) of iron diffused Si samples the interstitial iron concentration exceeds the equilibrium concentration close to the surface. The iron depth profiles exhibit an exponential dependence with a characteristic length identical to the hydrogen penetration depth, which is about ten times larger than the iron diffusion length. On the other hand, after reverse bias annealing (RBA) the iron profile deviates clearly from the exponential distribution. Our results give evidence for a release of iron by a hydrogen-stimulated dissociation of iron-related defects. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: DLTS; Chemical etching; Silicon; Iron; Hydrogen; Iron–boron pairs

1. Introduction

With decreasing dimensions and increasing complexity of highly integrated circuits the tolerable concentrations of detrimental impurities have to shrink considerably. In particular, a contamination due to transition metals with their high diffusivity is critical for all Si technology processes. Iron is considered to be the most important impurity since it is a main constituent of the technological equipment and a common contaminant in chemicals [1]. Therefore, many investigations have been devoted to the properties of iron in Si and to the development of technological processes in order to suppress its effect on electrical properties of devices.

Hydrogen passivation is usually proposed to eliminate the harmful effect of defects on the electrical properties of semiconductors and it seems to be timely to study the hydrogen interaction with Fe and Fe-related centers. These investigations should also clarify the influence of hydrogen during various processing steps, which are known to introduce hydrogen unintentionally into the samples [2]. Recent investigations have shown [3,4], that hydrogen interaction with transition metals is a rather complex process and it is necessary to check and re-understand the results obtained in previous studies. In spite of the importance of iron in recent silicon technology there are only a few reports on the interaction of hydrogen with iron and iron-related complexes in Si. In Refs. [5–7] the binding of hydrogen with iron related deep level centers is reported and possible passive or electrical active Fe–H complexes are proposed. Other interactions with hydrogen were reported, e.g. a hydrogen stimulated dissociation of iron related centers in [8]. At present, a clear evidence for a hydrogen passivation of the interstitial Fe_i [6,7] is missing and in general the influence of hydrogen on iron related centers is not understood.

In the present study, wet chemical etching (WCE) was used to introduce hydrogen into Fe-diffused Si. In p-type samples most of the interstitial iron is paired with boron. We will show that chemical etching leads to the reactivation of interstitial iron within the penetration depth of atomic hydrogen. The interstitial iron is generated by a hydrogen stimulated Fe–B pair dissociation.

2. Experimental

The experiments were carried out on p-type Si samples grown by the Czochralski (Cz) and floating zone (FZ) methods with boron concentration of $\sim 10^{15}$ cm^{-3}. No differences in the results obtained on Cz and FZ samples were observed in this study. The samples

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were dipped in a $FeCl_3$ water solution, dried and then annealed at 950°C for 3 h. After the diffusion process the samples were quenched to prevent iron precipitation. Afterwards, the samples were chemically etched in an acid mixture of $HF:HNO_3 = 1:7$ and the Schottky barriers with a diameter of 2 mm were formed by thermal evaporation of Al. The ohmic contacts were made by scratching an Al–Ga alloy onto the back-side of the samples. Annealing was carried out with or without reverse bias applied to the Schottky diodes. The concentrations of Fe–B pairs and interstitial Fe and their depth profiles were studied by standard deep level transient spectroscopy (DLTS) technique with a lock-in amplifier as correlator. The depth distribution of electrically active boron was determined from the free carrier concentration measured by the capacitance–voltage (C–V) method at room temperature.

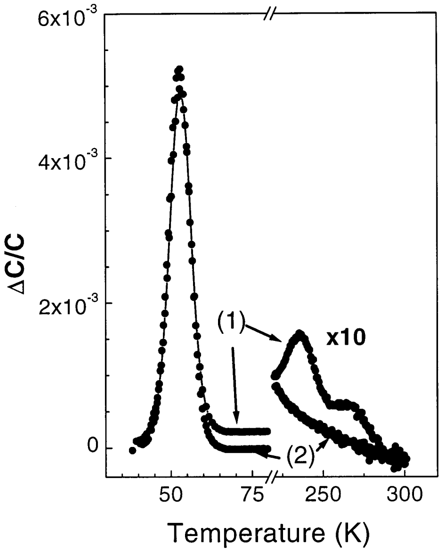

Fig. 1. DLTS spectra on p-type Si doped with iron after WCE, measured at a depth of 1.4–2 μm (1) and 2.8–3.4 μm (2).

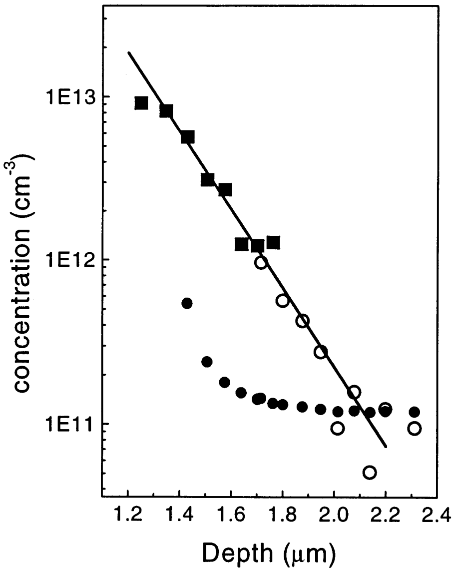

Fig. 2. Depth dependence of the Fe_i (solid squares) and B-H pair (open circles) concentration in Fz p-type Si after WCE. The B–H concentration was divided by 200 to scale with the Fe_i concentration. The Fe_i profile presented by small solid circles was calculated according to Eq. (2).

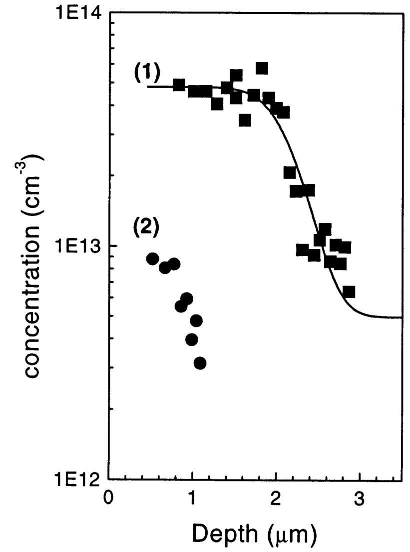

Fig. 3. Fe_i depth profile in p-type Si after annealing at 380 K for 10 min with 5 V applied reverse bias (1) and without bias (2). The simulated Fe_i profile is presented by the solid curve.

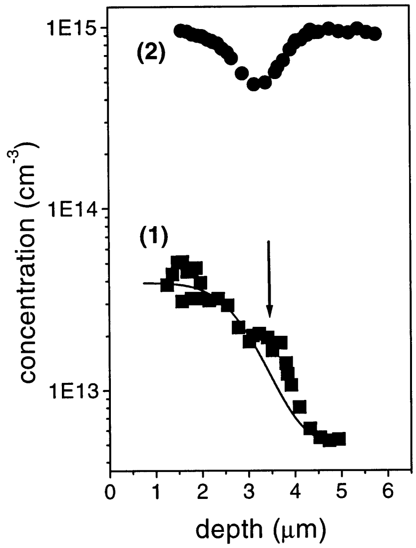

Fig. 4. Fe_i (1) and isolated boron (2) depth profiles in p-type Si after annealing at 380 K for 30 min with applied reverse bias of 5 V. The simulated Fe_i profile is presented by the solid curve.

3. Results

DLTS measurements on iron diffused samples reveal two deep levels with energies at 0.42 and 0.1 eV from the valence band. The first level is the interstitial iron Fe_i level and the second one originates from Fe–B pairs [1]. The concentration of electrically active iron measured as a sum of interstitial Fe_i and Fe–B pair concentrations is $\sim 10^{14}$ cm^{-3}. The Fe_i concentration was found to decrease during room temperature storage with a rate of $\sim 4 \times 10^{-5}$ s^{-1}. The same behavior was observed earlier [9] and could be associated with the Fe–B pair formation. After a few days storage at room temperature the concentration of interstitial iron decreased to a negligible value. Subsequent chemical etching of these samples led again to the appearance of interstitial iron in the samples. The Fe_i peak is observed only close to the surface (Fig. 1, curve 1) and is undetectable in deeper regions (curve 2). The concentration of interstitial iron after chemical etching is always lower than that of Fe–B pairs (30 times lower in the spectrum presented in Fig. 1) and differs from sample to sample in a wide range. The depth profile of interstitial iron after wet chemical etching is presented in Fig. 2. The profile is given by

$$[Fe_i(x)] \sim \exp(-x/x_0)$$

with $x_0 = 0.18$ μm. In the same figure the profile of the boron–hydrogen pairs is included, their concentration had to be reduced however by a factor of 200 to allow a direct comparison. The concentration of the boron–hydrogen pairs was obtained from $[B\text{–}H] = [B_{bulk}] - [B(x)]$, where $[B_{bulk}]$ is the boron concentration far from the etched surface and $[B(x)]$ the concentration of electrically active boron at depth x, measured by the C–V method. Both profiles show the same characteristic length x_0, but the Fe_i concentration is about 200 times lower than that of [B–H].

After reverse bias annealing (RBA) at 380 K the Fe_i profile forms a plateau in the depletion region and decays in the bulk to a constant concentration of $\sim 5 \times 10^{12}$ cm^{-3} (Fig. 3, curve 1). The width of the plateau depends on the bias and correlates with the depletion layer width. For comparison, the Fe_i profile is given after annealing under the same conditions but without bias. The decay of the Fe_i profile under both annealing conditions is similar and seems to follow a simple diffusion process. The boron concentration after an RBA treatment increases inside the depletion region due to the dissociation of B–H pairs and the drift of hydrogen to the edge of the depletion region. With an increase in annealing time the boron concentration reaches its bulk value. As a result, the hydrogen concentration increases near the edge of the depletion region and leads there to a decrease of the isolated boron concentration (Fig. 4). In some samples with a higher hydrogen concentration (revealed by the deeper minimum in the free carrier concentration at the edge of depletion region) a small peak in the Fe_i concentration was observed, at a position which correlates with the minimum in the electrically active boron concentration (indicated in Fig. 4 by the arrow).

4. Discussion

The Fe–B pairs break up under electron injection, illumination or heating [2,9] and lead to an increase in the Fe_i concentration. Reference samples were prepared to study the possible effect of sample heating or illumination during contact preparation. After etching the samples were stored for a few days at room temperature. Afterwards, the contacts were prepared and no interstitial iron in noticeable concentrations could be observed. The results indicate that the chemical etching itself is responsible for an appearance of interstitial iron and the storage at room temperature leads to a decrease of its concentration.

Interstitial iron Fe_i could be created during WCE at the surface due to some surface contamination or could be introduced from the contaminated etchant. The distribution of Fe inside the sample can be estimated from the diffusion equation with a moving boundary (due to the chemical etching) [10,11]. The Fe distribution reaches a stationary distribution after a few minutes of etching which can be described as $[Fe_i] = A \exp(-x/L_{eff})$, with

$$\frac{1}{L_{eff}} = \sqrt{\frac{1}{D_{Fe}\tau} + \left(\frac{V}{2D_{Fe}}\right)^2} + \frac{V}{2D_{Fe}} \tag{1}$$

where D_{Fe} (cm^2/s) $= 1.3 \times 10^{-3} \exp(-0.68/kT)$ [1] is the iron diffusivity, τ the lifetime in s determined by iron trapping, V (cm/s) is the etching velocity (at 300 K and ≈ 3 μm/min). Even if iron trapping is neglected ($1/\tau = 0$), L_{eff} would be 1×10^{-5} μm, several orders of magnitude smaller than the experimentally obtained value of 0.18 μm.

In our experiments the Fe_i distribution correlates well with that of the B–H pairs (Fig. 2). Hydrogen is known to be introduced from the acid mixture [12,13] and its depth distribution in p-type Si can be easily monitored by the measurement of the B–H depth profile. The concentration of the B–H pairs is directly proportional to that of hydrogen. The direct correlation between Fe_i and B–H pairs gives evidence that the appearance of Fe_i is associated with hydrogen. Hydrogen seems to stimulate the dissociation of iron related complexes. The results indicate that only one hydrogen atom is participating in the dissociation reaction which creates one Fe_i. The most trivial example of such reactions is the indirect influence of hydrogen on the Fe–B pair dissociation via the formation of H–B pairs. The equilibrium Fe_i concentration pro cm^{-3} is described by [9]

$$[Fe_i] = 10^{23}([Fe\text{–}B]/[B]) \exp(-0.65\ \text{eV}/kT) \tag{2}$$

A decrease of the isolated B concentration due to formation of B–H pairs should lead to an increase in Fe_i concentration. The Fe_i depth distribution calculated according to Eq. (2) is compared with the measured Fe_i depth profile in Fig. 1. It is clear that the experimentally determined Fe_i concentration and the depth profile are not in agreement with the calculated concentrations. We have to assume that hydrogen directly stimulates the dissociation of Fe–B pairs or some other iron related complexes.

The rate of Fe–B dissociation at elevated temperatures is rather high, therefore the Fe–B pair concentration at any temperature results from the dynamic equilibrium between the formation and dissociation of Fe–B pairs. Inside the depletion region Fe_i is neutral, which leads to a much lower rate of Fe–B formation in this region than that in the bulk. For this reason the stationary Fe_i concentration inside the depletion region is about one order of magnitude higher than that in the bulk and approaches the total Fe concentration (Figs. 3 and 4). Under the assumption that during RBA the Fe_i concentration inside the depletion region is constant (i.e. it approaches the equilibrium value rather fast) the Fe_i distribution can be calculated and used to fit the experimental curves. The results are presented in Figs. 3 and 4 by solid curves. The agreement between simulated and experimental depth profiles is good. The obtained diffusion coefficient correlates well with that of Fe_i at 380 K. In the sample which was annealed without RBA we find a similar good fit with the same value of the diffusion coefficient. In all the annealed samples it is not necessary to assume that the formation of the iron profile is affected by hydrogen.

However, the peak in the Fe_i concentration at the edge of the depletion region (marked by the arrow in Fig. 4 curve (1)) can not be explained by the diffusion of Fe_i. The peak correlates well with the maximum in the hydrogen concentration, which is revealed by a decrease of the electrically active B concentration (Fig. 4 curve (2)). Similar to the Fe profile after WCE, the decrease in isolated B concentration is too low to explain the observed Fe_i peak by the Eq. (2). Therefore, the Fe_i depth profile after RBA also indicates that hydrogen stimulates the dissolution of some iron related centers. It should be noted that a similar reaction was observed in [14], where hydrogen stimulated the dissolution of vacancy related radiation defects in Si.

The simplest explanation for our results seems to be a direct mechanism, where hydrogen dissociates the Fe–B pairs by forming B–H pairs and generates Fe_i. Unfortunately, such a process is difficult to verify. The concentration of released iron is usually much lower than that of Fe–B pairs, therefore it is not feasible to compare the decrease of the Fe–B concentration with the concentration of released iron. If indeed the Fe–B dissociation is the reason for the generation of Fe_i the stability of the Fe–B complex has to be smaller than that of the B–H complex. The binding energy of the Fe–B pair is 0.65 eV [9], the dissociation energy which includes the activation energy for hydrogen diffusion of the B–H pair is 1.28 eV [15]. Taking into account the activation energy for hydrogen diffusion, the B–H pair binding energy is indeed larger than that of Fe–B pair and the process discussed can be considered as a possible source of interstitial iron.

5. Conclusion

Wet chemical etching of Fe contaminated p-type Si leads to the appearance of interstitial Fe in the near surface layer of the sample. The most probable reason for this behavior is the direct dissociation of Fe–B pairs by hydrogen, which leads to the formation of B–H pairs and interstitial Fe. The detailed mechanism of the hydrogen stimulated dissociation is subject of further studies.

Acknowledgements

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