

HYDROGEN PASSIVATION OF IRON IN CRYSTALLINE SILICON

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ABSTRACT: Hydrogen passivation of iron in silicon is investigated by measuring the recombination-active FeB-concentration with the light-induced FeB-dissociation technique. Floatzone wafers were intentionally contaminated with iron. Hydrogen passivation by annealing of the wafers with an SiNx coating leads to a decrease of the FeB concentration with about a factor 3 (from $1.2 \times 10^{13} \text{ cm}^{-3}$ to about $4.5 \times 10^{12} \text{ cm}^{-3}$). Multicrystalline silicon wafers without an intentional iron contamination show a similar decrease of the measured iron concentration after annealing with SiNx coating. Based on these results, we conclude that the FeB defect is passivated by hydrogen in-diffusion after anneal of SiNx layers.

Keywords: iron, hydrogen passivation

1 INTRODUCTION

The incorporation of hydrogen into multi-crystalline (mc) silicon materials leads to deactivation of certain impurities and defects and to passivation of grain boundaries [1-3]. However, it is challenging to monitor the process quantitatively. Various attempts have been made in this direction. For example, FTIR measurements of PtH complexes can trace diffusion of hydrogen, but this technique requires samples in which Pt is artificially in-diffused and measurements at cryogenic temperatures [4]. SIMS measurements of deuterium (D) is a straightforward approach, but in many materials with relatively low defect density, too little D is trapped and this technique has insufficient sensitivity [5].

In this paper we present experiments which show that another impurity than Pt can be used to trace diffusion of hydrogen, namely Fe. Virtually all mc-Si materials already contain interstitial Fe in measurable concentrations. As is well known, the concentration of interstitial Fe, paired with B acceptors, can be measured sensitively via minority carrier lifetime measurements (shortly reviewed below). Therefore, if interstitial FeB pairs are susceptible to hydrogen-passivation, and if this passivation can be measured conveniently, it is an ideal probe to study hydrogen diffusion in silicon.

In this article we present results of hydrogen passivation of iron in silicon. These results extend our preliminary results published earlier [6]. Two types of materials are used for investigation: FZ-wafers which are intentionally contaminated with iron, and several types of mc-Si wafers with different iron concentration. The mc-Si wafers are not intentionally contaminated; they contain only the Fe present due to the feedstock and the growth process.

DLTS (deep level transient spectroscopy) measurements indicate that several iron-related states exist in silicon; levels at $E_v+0.1\text{eV}$ and $E_v-0.23\text{eV}$ which are attributed to the Fe-B pairs, and a level at $E_v+0.43$, which is related to the interstitial (Fe_i) [7]. Pearson et al reported that a hole trap at $E_v+0.4\text{eV}$ and $E_v+0.33\text{eV}$ was passivated by exposure to a hydrogen plasma [8]. While $E_v+0.33\text{eV}$ is assumed to be a complex of iron with oxygen [7], $E_v+0.4\text{eV}$ has not been assigned. However, they did not confirm the passivation of the interstitial state at $E_v+0.43\text{eV}$. Kouketsu et al. reported the hydrogen passivation of the FeB pair levels with implanted hydrogen [9].

While DLTS is a very sensitive technique, it requires significant sample preparation time, and results are often

difficult to interpret for multicrystalline silicon. However, the technique based on measurement of the minority carrier lifetime before and after light-induced FeB-dissociation is also very effective in determining very low FeB concentrations (as low as $5 \times 10^{10} \text{ cm}^{-3}$), and has been shown to work well on monocrystalline as well as multicrystalline material. Due to various sources of contamination, Fe is always present in multicrystalline silicon, usually with concentrations of interstitial Fe above $1 \times 10^{11} \text{ cm}^{-3}$, which is easily measurable. At room temperature the interstitial Fe is paired with boron acceptors forming FeB pairs. Strong optical illumination ($> 0.1 \text{ Wcm}^{-2}$) leads to the complete ($>99\%$) dissociation of the FeB pairs [10]. This dissociation causes significant changes in minority carrier lifetime. The FeB concentration can be found from the change in lifetime as:

$$[FeB] = C \cdot \left[\frac{1}{t_1} - \frac{1}{t_0} \right]$$

where τ_0 and τ_1 are the measured minority carrier lifetimes before and after the dissociation by illumination. The pre-factor C is known from literature and should be taken at the actual injection level where the minority carrier lifetime was measured. The measurement of FeB pairs via lifetime has the advantages of being fast, non-contact, non-destructive and possible at room temperature.

The injection level-dependent lifetime curves of FeB and Fe_i recombination centres show characteristic behaviour (their shape, and the existence of a so-called cross-over point) which is can be used for identification [10]. The results obtained in multicrystalline material as well as intentionally contaminated monocrystalline material in this paper showed such behaviour.

Finally, it should be noted that our experiment only uses the FeB measurement to monitor the hydrogen passivation process. We have not quantitatively determined which changes in the Fe-related levels (position, cross section) occur due to passivation.

2 EXPERIMENT

FZ wafers with a p-type resistivity of $1\Omega\cdot\text{cm}$ were contaminated by immersing in FeCl_2 solution for about 10min. After drying with N_2 , the wafers were annealed in a furnace at 900°C for 40 minutes. After anneal, the wafers were rapidly cooled down to room temperature. This cool-down rate is estimated to be $120^\circ\text{C}/\text{sec}$, enough to avoid precipitation of interstitial iron in the critical region ($500\text{-}600^\circ\text{C}$) [11]. $30\mu\text{m}$ was removed from each side of the wafer to avoid any later effects of the Fe-contaminated surface layer. This procedure resulted in a range of $1\text{-}2\times 10^{13}\text{ cm}^{-3}$ in Fe.

Multicrystalline wafers were not intentionally contaminated; instead, their already present Fe concentrations (lower than in the contaminated FZ wafers) were used. Multicrystalline Si is also known to contain other impurities (such as O, C, Cu, Ti etc...) and various crystal defects. In this experiment, multicrystalline silicon samples were chosen from the top and middle of one ingot (called material A and B, respectively). The distribution of impurities is not homogeneous along the ingot. The concentration of iron-boron pairs in the material A as-received is $6.5\times 10^{11}\text{ cm}^{-3}$, for material B it is $3\times 10^{11}\text{ cm}^{-3}$. The concentration of carbon and oxygen are 3.5 (carbon at position B), 8.5 ppma (carbon at position A) and 2.6 ppma (oxygen at position B) versus 1 ppma (oxygen at position A), respectively.

These wafers were processed as described in Fig.1 and Fig.2. The experiments are divided in two parts. In the first part, the effect of hydrogen diffusion on the contaminated FZ and mc-Si was investigated. In the second part the effect of phosphorus diffusion on subsequent hydrogen passivation was inspected.

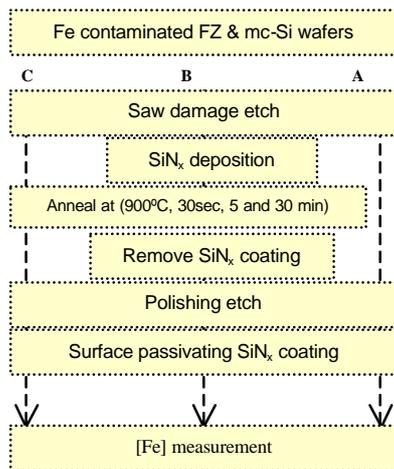


Fig.1: Schematic of processing group 1

Three different process schemes A-C sketched in Fig.1 were used to investigate the hydrogen passivation of Fe in the first group. Process A served to measure the as-cut minority carrier lifetime and the starting FeB concentration in the wafers. Group B served to monitor the effect of the hydrogen on the Fe in the materials. SiN_x layers for bulk passivation were deposited by PECVD on both sides of wafers in group B. Hydrogen diffusion into the wafers of group B was accomplished by a high-temperature (900°C) anneal step for different times. Group C served to monitor the effect of the anneal step, done without SiN_x coating on wafers.

In the industry SiN_x deposited on wafers serves as an ARC coating and as a source of hydrogen for passivation. The hydrogenation process step takes place during metallisation in a short time (about 20sec). Anneal at 900°C has the advantage that no iron precipitates form at this temperature [12].

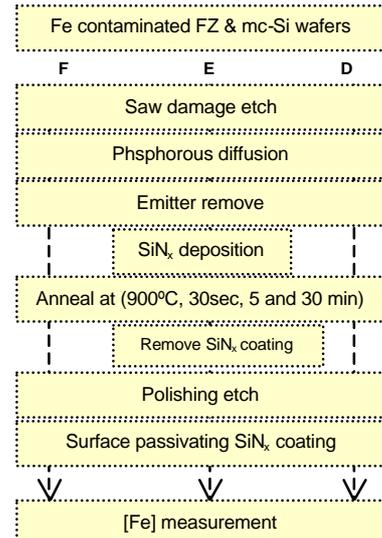


Fig.2: Schematic of processing group 2

In the second part of the experiment, neighbouring wafers are used to those used in the first part. Three different processing schemes D-F shown in Fig.2 were used to investigate hydrogen passivation of iron after phosphorous gettering. Group D served to monitor the effect of gettering on iron in the materials. Group E served to monitor the effect of hydrogen passivation of Fe after gettering, and the last group (F) monitored the effect of the anneal step without SiN_x on the wafers.

After annealing steps, the wafers of all the groups were etched to remove $20\mu\text{m}$ from the surface, and a surface passivating SiN_x was deposited by PECVD on both sides of the wafers. This allowed measurement of the bulk minority carrier lifetime.

3 RESULTS AND DISCUSSION

3.1 Contaminated FZ wafers

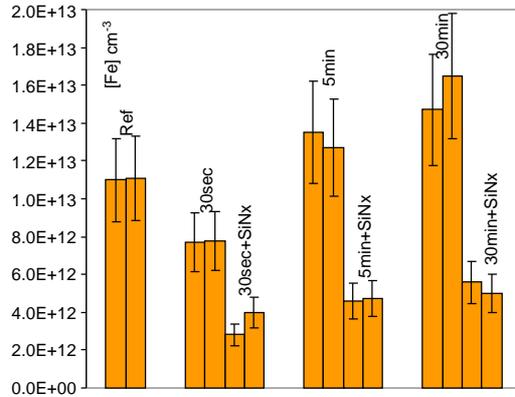


Fig.3: Iron concentration of contaminated FZ-wafers after different processing steps. The first two columns correspond to wafers annealed at 900°C without nitrides.

The contamination results in $1.2 \times 10^{13} \text{ cm}^{-3}$ iron. When the wafers were annealed for different durations without SiNx coating, the concentration of iron increases with anneal time. This may be due to the dissociation of iron-agglomerates, which are formed during the contamination. The results indicate that 30sec is not sufficient for dissociation of these agglomerates.

On the other hand, anneal of not-contaminated FZ wafers without SiNx coating in the furnace reduces slightly the minority carrier lifetime of these control samples (data not shown). Analysis of the data show that the reduction of measured minority carrier lifetime is not due to the iron contamination, which means that the furnace is clean enough.

However, when wafers are annealed with SiNx coatings on both sides, the concentration of measured iron decreased compared to those processed without SiNx layer. This decrease in iron concentration is surely due to hydrogenation and not to precipitation; otherwise iron would also be precipitated in the wafers that were annealed without SiNx coating. Note that for the wafers with SiNx, a slight increase in Fe concentration was observed for longer annealing times. However, taking into account the error bars no significant change is recorded. The error bars are based on an uncertainty in each lifetime measurement of 10%, mainly due to the systematic uncertainty of the equipment.

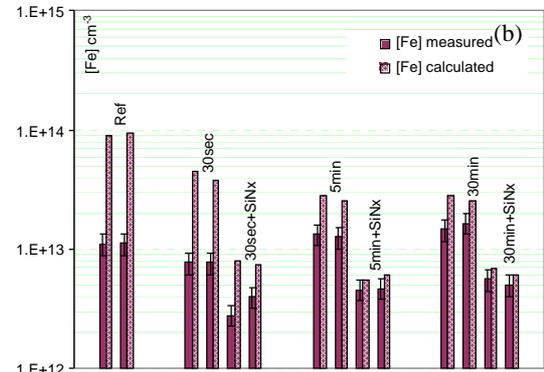
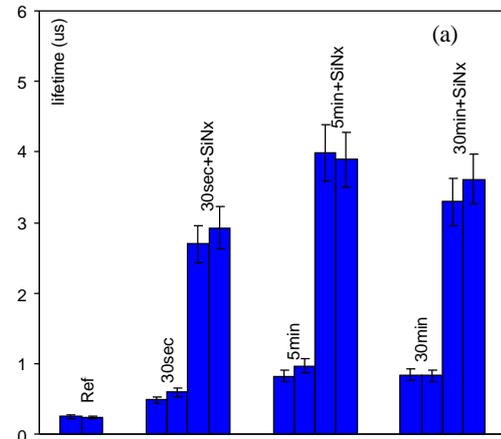


Fig.4: (a) Minority carrier lifetime of contaminated FZ wafers after different processing steps. (b) theoretical iron concentration which correspond to measured minority carrier lifetime.

The measured lifetime of $0.2 \cdot \text{s}$ corresponds theoretically to a concentration of iron equal to $8 \times 10^{13} \text{ cm}^{-3}$ while the experimentally determined iron concentration is equal to only $1 \times 10^{13} \text{ cm}^{-3}$ (Fig 4a). This observed difference may be caused by introduction of other types of contaminants or defects in the material during the intentional contamination with Fe. However, after hydrogenation the theoretically calculated iron concentration coincides perfectly with the measured values (Fig.4 (b)), meaning the wafers are then indeed dominated by Fe. This result can be interpreted as partial passivation of the iron and almost complete passivation of the other introduced defects. The calculation of lifetime based on iron concentration is described in detail in ref [10].

3.2 Multicrystalline wafers

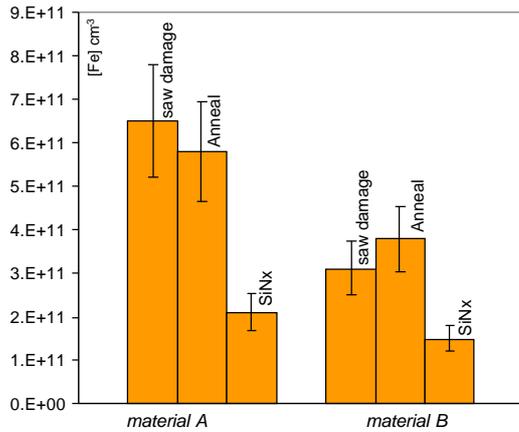


Fig.5: Iron concentration of mc-Si wafers after different processing steps (annealing at 900°C for 30sec).

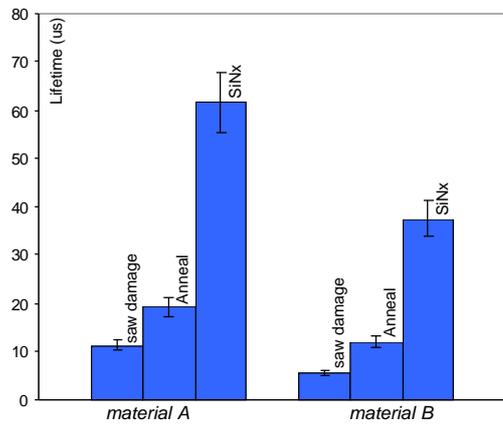


Fig.6: Minority carrier lifetime of mc wafers after different processing steps

Fig.5 shows the iron concentration in materials A and B after different processing steps. Annealing wafers with SiNx coating leads to the reduction of the measured iron concentration in both materials. After hydrogenation the minority carrier lifetime increases strongly (Fig.6) compared to the reference wafers. Similar to the situation for the FZ wafers, however, this increase of lifetime cannot necessarily be attributed to passivation of iron only because mc-Si wafers contain various defects and impurities.

3.3 Phosphorous-gettered multicrystalline wafers

Phosphorus gettering is known to remove metallic impurities from silicon materials. It has been used here to reduce the iron concentration in the neighbour wafers of those investigated in the first part of our experiment.

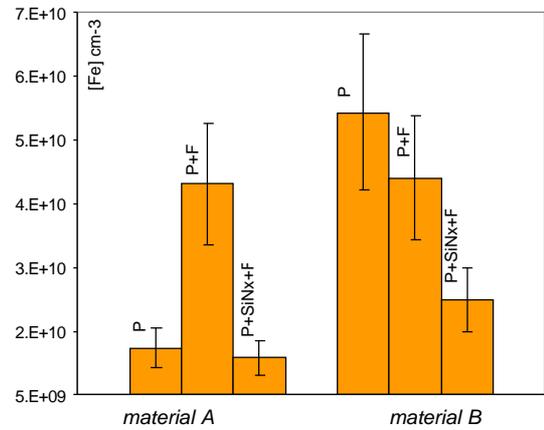


Fig.7: Iron concentration of mc-Si wafers after: (p): phosphorous gettering, (p+F): phosphorous gettering followed by anneal and (p+SiNx+F): phosphorous gettering followed by anneal with SiNx on wafers.

Fig.7 shows that due to gettering the iron concentration is dramatically reduced in both materials (from $6.5 \times 10^{11} \text{cm}^{-3}$ to $1.6 \times 10^{10} \text{cm}^{-3}$ and from $3.1 \times 10^{11} \text{cm}^{-3}$ to $5.4 \times 10^{10} \text{cm}^{-3}$ respectively for A and B). Annealing without nitrides leads to an increase in iron concentration, which is probably due to release of the iron from precipitates in the material A. But this is not the case for the material B. After hydrogenation, the iron concentration decreases further to its detection limit and the minority carrier lifetime increases (Fig.8).

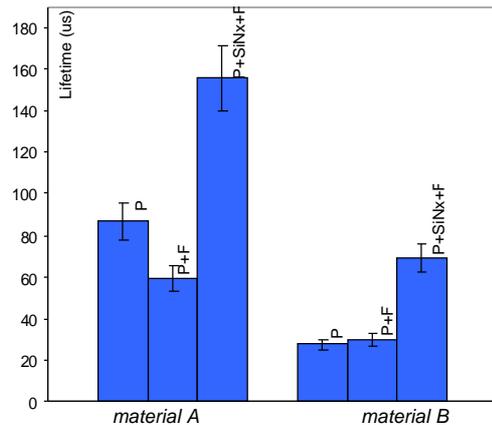


Fig.8: Minority carrier lifetime of mc-Si wafers -shown in Fig.7- after phosphorous gettering

3.4 Outlook

As a further step, the application of these techniques can lead to a clearer understanding of the hydrogen diffusion in silicon. The benefits of using this technique are the simplicity of both sample preparation and measurement of the iron concentration. Experiments have been started in this direction. Iron will be passivated by diffusion of hydrogen with varying parameters. Measurement of the iron concentration before and after removal of a surface layer will indicate to which depth is the hydrogen is diffused.

4 CONCLUSION

This investigation shows the capability of hydrogen passivation of iron in silicon and of detecting this by measuring the recombination-active FeB-concentration with the light-induced FeB-dissociation technique. Hydrogen passivation of intentionally contaminated Floatzone wafers with iron leads to a decrease of the FeB concentration with about a factor 3 (from $1.2 \times 10^{13} \text{ cm}^{-3}$ to about $4.5 \times 10^{12} \text{ cm}^{-3}$). Multicrystalline silicon wafers without an intentional iron contamination show a similar decrease of the measured iron concentration after annealing with SiNx coating. Thus Fe can be a possible candidate to study hydrogen diffusion in silicon.

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