HYDROGEN PASSIVATION OF IRON IN MULTICRYSTALLINE SILICON

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ABSTRACT

Concentrations of interstitially dissolved Fe can be measured by lifetime measurements before and after dissociation of FeB pairs. It allows the measurement of iron concentrations as low as 5×10^{10} cm^{-3}. The technique is applied to determine the change in Fe concentration after different solar cell process steps. In particular, hydrogen passivation of iron in multicrystalline silicon wafers is investigated. The results indicate that the passivation can be accurately followed with this technique.

1. INTRODUCTION

Impurities and defects determine the quality of crystalline silicon. Iron (Fe) is one of the most dominant metallic impurities in multicrystalline silicon (mc-Si) materials [1]. High Fe contamination leads to a dramatic decrease in the minority carrier lifetime. The contamination of ingots with Fe depends on several factors such as contamination of feedstock, the smelting environment, and growing methods.

A number of techniques are capable of detecting and measuring the concentration of Fe in silicon materials. Secondary ion mass spectroscopy (SIMS) and Rutherford backscattering can be used, however the detection limits of those techniques is higher than 5×10^{13} cm^{-3} [2]. Other techniques such as deep level transient spectroscopy (DLTS) or electron paramagnetic resonance (EPR) permit to detect Fe at lower concentrations (10^{11} cm^{-3}), but with a long measurement time. However, the technique based on measurement of the lifetime before and after illumination of the wafer, causing Fe-B pairs to dissociate, is very effective in determining very low Fe concentrations (as low as 5×10^{10} cm^{-3}). It has the advantages of being fast, non-contact, non-destructive and possible at room temperature.

In this paper we describe the application of this technique at high injection levels to multicrystalline silicon. A more elaborate discussion of the measurement technique will be published elsewhere [3].

The gettering of Fe has been studied with the FeB pair dissocation technique in some detail [4,5,6]. However, whether *hydrogen diffusion and passivation in mc-Si* can also be monitored with this technique has not been examined in literature before.

In this paper we present results which give a positive answer to this question. The incorporation of hydrogen into multicrystalline silicon materials is a very important industrial process step. It leads to a deactivation of certain impurities and defects and to a passivation of grain boundaries. However, it is challenging to monitor quantitatively the process. For example, SIMS measurements of deuterium have insufficient sensitivity [7] and FTIR measurements of PtH complexes require samples in which Pt is artificially in-diffused [8]. In contrast, virtually all multicrystalline materials contain already FeB in measurable concentrations. Therefore, FeB, if it is amenable to hydrogen-passivation and if this passivation can be measured conveniently, would be an ideal probe to study hydrogen passivation.

Kouketsu et al. [9] have reported the hydrogen passivation of Fe-B pairs and of iron-related hole traps in p-type silicon by DLTS and recombination lifetime measurements. In their study hydrogen ion implantation was used. In this paper hydrogen passivation of Fe in mc-Si material by hydrogen from remote PECVD SiNx coating layers is investigated [10].

2. Fe CONCENTRATION CALCULATIONS

Low-injection diffusion length measurements, made with the Surface PhotoVoltage (SPV) technique, have been used for many years for determining Fe concentrations in silicon. Zoth and Bergholz [11] showed that the Fe concentration is related to the diffusion lengths measured before and after dissociating the FeB pairs via:

$$[Fe] = A \times \left(\frac{1}{L_1^2} - \frac{1}{L_0^2} \right) = C \times \left(\frac{1}{t_1} - \frac{1}{t_0} \right)$$

Where L_0 and L_1 are the diffusion length and τ_0 and τ_1 the minority carrier lifetime respectivlly before and after illumination. This expression can also be written in terms of carrier lifetimes, as shown on the right. The critical point is knowledge of the pre-factors A or C (which are related through $A = D_n C$, with D_n the minority carrier diffusion coefficient).

Zoth and Bergholz empirically determined A for the very low injection conditions achieved with SPV, and for the resistivity range 5-15 Ωcm. However, photovoltaic silicon is usually outside this range. It is also desirable to use faster lifetime measurement

techniques that do not require special sample preparation other than surface passivation (such as QSSPC, microwave-PCD, MFCA etc). These techniques must operate at moderate to high injection to overcome minority carrier trapping effects, an artefact that does not affect SPV measurements. At these injection levels the value of A or C is very different.
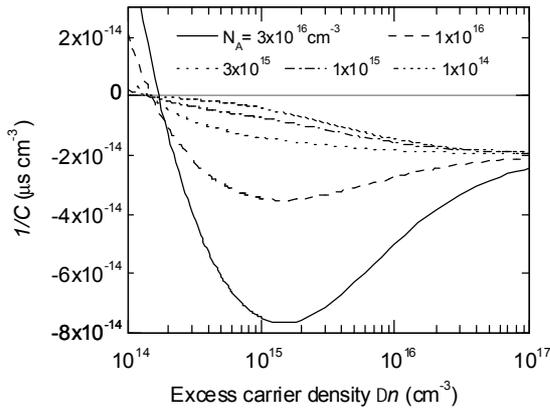

Fig. 1. Values of C for various doping levels

Fortunately, it is straightforward to calculate the factor C for any doping and injection level using the Shockley-Read-Hall model, provided that the recombination parameters are known for both interstitial Fe and FeB pairs. These parameters, specifically the energy level and capture cross sections for electrons and holes, may be found in the literature [12,13]. Fig 1 shows such calculated values for various doping levels.
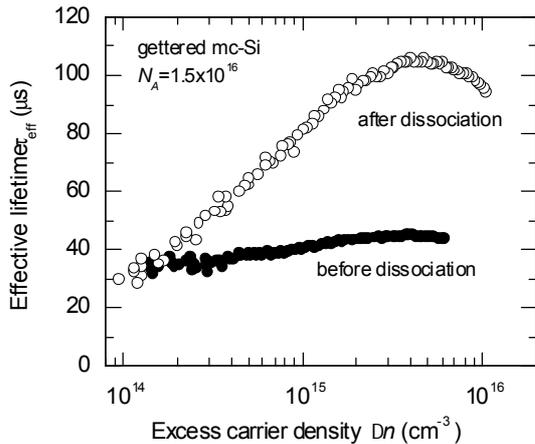

Fig.2. QSSPC lifetime curves before and after FeB dissociation by light soaking.

Fig 2 plots a typical pair of QSSPC lifetime measurements in multicrystalline silicon before and after FeB pair dissociation by light soaking for 5 minutes. Normally, a single value of Δn would be

chosen in order to calculate [FeB] with the corresponding value of C. Fig 3 however shows the resulting values of [FeB] calculated for *each* of the available values of Δn. The fact that the [FeB] values are independent of the choice of Δn gives confidence in the technique.

The uncertainty in [FeB], which is determined by the *difference* of inverse lifetimes, is less for higher values of Δn ($>10^{15} \text{cm}^{-3}$) where the lifetime curves are further apart. The error bars in Fig. 3, are based on an uncertainty in each lifetime measurement of 10%. From Figs. 2 and 3 it is clear that the statistical error (noise in the equipment) is much smaller than 10% for all but the lowest injection levels. However, there could be hidden systematic errors. For example, there is a trend visible in Fig. 3 of an increase of the calculated FeB concentration with injection level. These uncertainties are roughly represented by assuming a conservative 10% uncertainty in lifetime.

A more detailed description of this method, including justifications for assumptions regarding the extent of dissociation, will be published elsewhere [3].
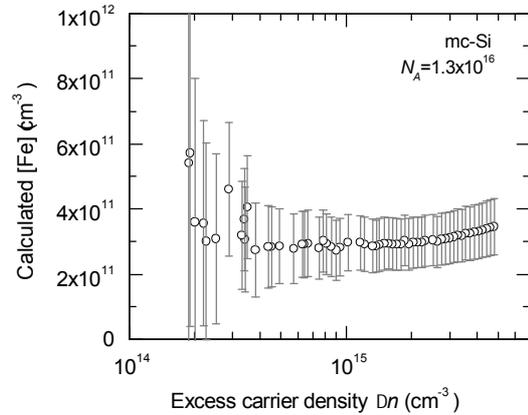

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Fig.3. FeB concentration calculated from curves in Fig. 2.

3. HYDROGEN PASSIVATION OF FE

3.a Experiment

Samples were chosen from different positions from bottom to top in the central columns of p-type mc-Si ingots. The concentration of Fe is quite different for those positions due to segregation and solid-state diffusion from the crucible. Four different process schemes A-D (Fig. 4) were used to investigate the effectiveness of hydrogen passivation of FeB. Process **A** served to

measure the as-cut minority carrier lifetime and the starting FeB concentration in the material. After saw damage removal, a phosphorus emitter was diffused in a belt furnace at 890°C on groups **B** through **D**, resulting in a 45Ω sheet resistance. SiNx layers were deposited by PECVD on the front side of groups **C** and **D**. Wafers in group **D** were also coated with Al at the rear surface. Subsequently, the SiNx coated wafers of groups **C** and **D** were fired with standard metallisation firing-through conditions at ECN. Finally, nitrides, emitters and Al BSF were removed and new surface passivating nitrides deposited on both sides of the wafers. This allowed measurement of the bulk minority carrier lifetime. The measurement of the interstitial FeB concentration was based on the measurement of the minority carrier lifetime as presented in part 2.
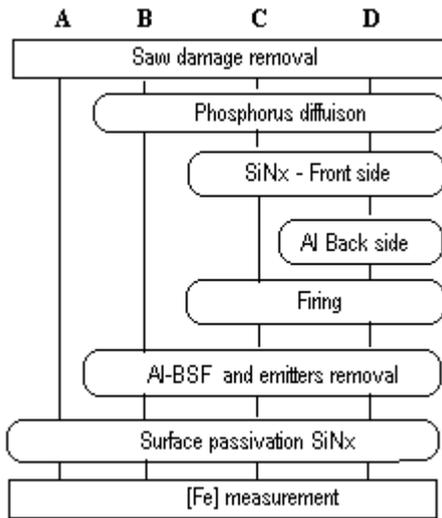

Fig.4. Schematic of the processing groups

3.b Results

Fig. 5 shows for three different ingots the FeB concentrations in the wafers of group **B** and **C**. The effect of phosphorus gettering (group **B**) is to reduce excessive Fe contamination in top and bottom of ingot (as described previously in [6]). By subsequently firing a SiNx coating (group **C**), the measured FeB concentration is significantly reduced, compared to the concentration after phosphorus gettering. It is unlikely that the rapid firing (only a few seconds above 800°C) has actually strongly changed the FeB concentration. It is more likely that the in-diffused hydrogen has passivated a large fraction of the FeB pairs. Remarkably, the top and bottom wafers of the ingots do not show a clear reduction due to SiNx firing.
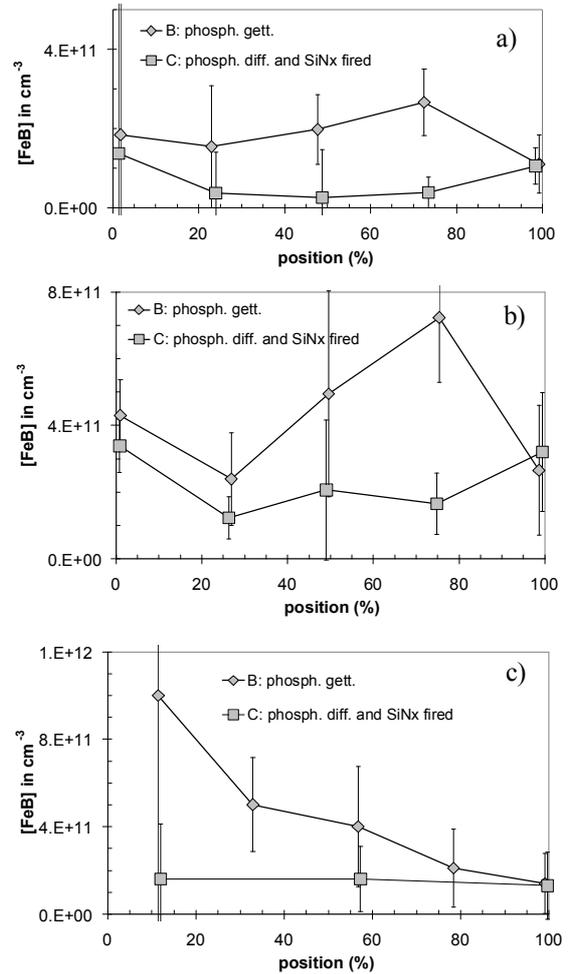

Fig. 5. Reduction of FeB concentration by SiNx firing. Shown are FeB concentrations measured on wafers from three ingots after phosphorus gettering (group B) and after phosphorus gettering followed by SiNx coating and firing (group C). The ingots are from two different manufacturers. Lines are guides to the eye.

Fig. 6 shows that the reduction of measured FeB concentration is not due to an Al rear side metallisation: The reduction of FeB concentration is not significantly different, whether the Al rear side metallisation is present (**D**) or not (**C**).

In the results of Figs. 5a-b and 6a-b, the emitter diffusion for group **B** was not performed in the same process batch as for groups **C** and **D**. Therefore a varying effectiveness of phosphorus gettering would be an alternative explanation for the difference of [FeB] between **B** and **C/D**. However, in Figs. 5c and 6c all wafers were phosphorus gettered in the same batch. Those results confirm the results of Figs. 5a-b and 6a-b.
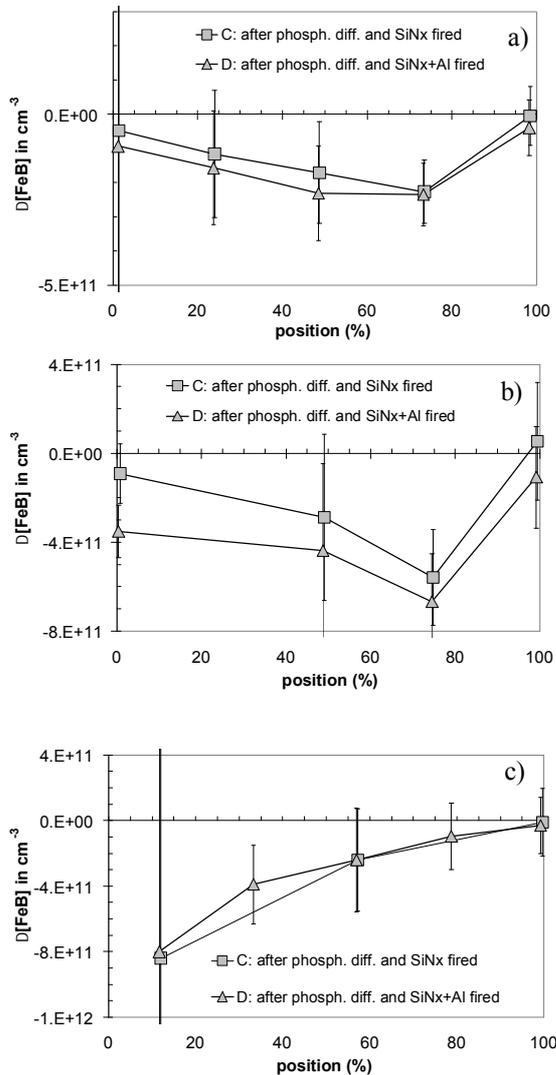
Fig. 6. Effect of Al rear side coating. Shown are changes in concentrations of FeB after firing of SiNx coating, without (C) and with (D) Al rear side metallisation, relative to concentration after phosphorus gettering only. a), b), c) correspond to Fig. 5. Lines are guides to the eye.

Further experiments are in progress to clearly confirm these results, and to apply them to the study of hydrogen passivation.

5.   CONCLUSIONS

In conclusion, we have described how lifetime measurements can be applied to the determination of FeB pair concentrations in multicrystalline silicon.

As one application of this technique, we have presented preliminary results which show that FeB can be used as a probe of hydrogen passivation. This opens the way to a new sensitive technique to study hydrogen diffusion in common multicrystalline materials.

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