

# GETTERING AND POISONING OF SILICON WAFERS BY PHOSPHORUS DIFFUSED LAYERS

D. Macdonald, A. Cheung and A. Cuevas

Department of Engineering, FEIT, The Australian National University, Canberra ACT 0200, Australia.

## ABSTRACT

The effectiveness of phosphorus gettering, and the possible re-injection of impurities from the gettering layer during subsequent annealing, has been studied through the use of float-zone samples deliberately contaminated with iron. Lifetime measurements reveal that phosphorus gettering, in this case at 880°C, initially removes more than 99% of the iron from the wafer bulk, to levels below  $1 \times 10^{11} \text{cm}^{-3}$ . However, upon further annealing at temperatures greater than the gettering temperature, some of the iron is injected back into the wafer. Annealing at 900°C caused a significant amount of this 'poisoning', with 7% of the pre-gettered iron returning to the bulk, resulting in a final Fe concentration around  $5 \times 10^{11} \text{cm}^{-3}$ . At 800°C there was no detectable re-injection of Fe within uncertainty. The results may have implications for optimising industrial metallisation fire-through processes for multicrystalline solar cells, which contain relatively high levels of iron and other metal impurities.

## 1. INTRODUCTION

Gettering of metallic impurities by phosphorus diffusion is a well-known technique for improving the carrier lifetime of silicon wafers, especially in relatively contaminated material such as multicrystalline or ribbon silicon. While such diffusions are primarily employed in industrial cells for junction formation, it is clear that their simultaneous gettering of impurities is an important contributor to the respectable efficiencies achieved by such devices. Provided that the contaminants remain tightly bound within the heavily diffused layer during subsequent processing, their impact on cell performance is minimised. However, it is possible to imagine the re-injection of these impurities back into the wafer bulk during subsequent high temperature steps, a process that has been referred to as 'poisoning'.

The work described in this paper reveals the extent to which such gettering and poisoning occurs for non-precipitated iron, a common contaminant in solar grade silicon. The results may have important consequences for industrial cell processing, especially considering the rapid uptake of fire-through metallisation schemes, which generally require relatively high firing temperatures. These thermal processes always occur after junction formation, and could potentially result in 'poisoning' of the cell.

Although these firing steps are usually fast, the diffusion length of Fe during a 1 minute anneal at temperatures between 800 and 900°C ranges between 65 and 90 microns [1], sufficient to cause contamination in the important region near the junction.

In this study, wafers with a known amount of Fe were prepared by ion implantation and annealing. After phosphorus gettering and etching the diffused layer, lifetime measurements revealed how much Fe was gettering from the bulk. Additional wafers, which were not etched after gettering, were annealed again, to reveal the extent of re-injection of the gettering Fe back into the wafer bulk.

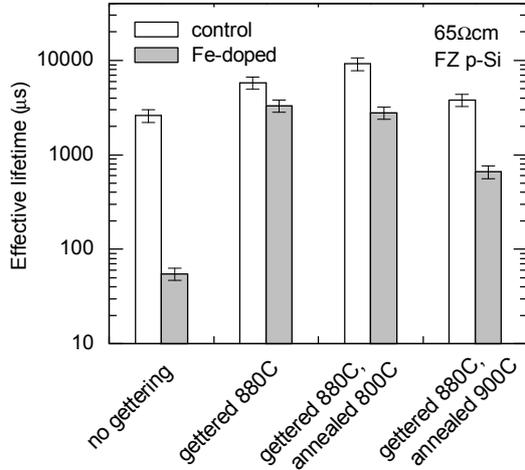
## 2. EXPERIMENTAL DETAILS

### 2.1 Sample preparation

Float-zone, *p*-type, boron-doped silicon wafers of 65Ωcm resistivity ( $N_A = 2 \times 10^{14} \text{cm}^{-3}$ ) and 400μm thickness were used in this study. This high resistivity was chosen because the plasma silicon nitride coating that is used for surface passivation is most effective on lightly doped wafers. This means that a large range of lifetimes can be measured (from 1μs to 10ms), allowing large changes in the Fe concentration to be detected.

After surface etching and thorough chemical cleaning, some samples were implanted with a dose of  $5 \times 10^{11} \text{cm}^{-2}$  70keV  $^{56}\text{Fe}$  isotopes while others were kept as controls. A relatively low energy was chosen to avoid excessive ion damage of the crystal structure. Following another cleaning step, all wafers (including the controls) were annealed at 900°C for 60 minutes in nitrogen to diffuse the Fe throughout the wafer. These conditions result in a diffusion length of around 700μm for the Fe atoms, which should provide a fairly uniform distribution with an average concentration of  $1.2 \times 10^{13} \text{cm}^{-3}$ . This is comfortably below the solubility limit of Fe at this temperature (around  $5 \times 10^{13} \text{cm}^{-3}$ ) [1].

Gettering was performed in a  $\text{POCl}_3$  atmosphere at 880°C for 60 minutes, resulting in a sheet resistance of 35Ω/square on both sides of the wafers. Subsequent anneals were performed at either 800 or 900°C for 60 minutes in nitrogen. These relatively long times were chosen to produce reasonably uniform Fe concentrations in the wafer bulk, which is important for accurate lifetime measurements. It also allows the equilibrium segregation conditions to be more closely approached, which would generally not occur for



**Fig. 1.** Effective lifetime measurements (at an excess carrier density of  $1 \times 10^{14} \text{cm}^{-3}$ ) for control and Fe-doped wafers after undergoing different treatments. The gettering layers remained intact during any subsequent annealing.

short anneals usually used for metal fire-through steps.

In all cases, pairs of samples with and without Fe implants were co-processed. Comparing the lifetimes of these pairs allowed a direct determination of the amount of Fe re-injected from the diffused region back into the wafer bulk.

Surface passivation was achieved with Plasma-Enhanced Chemical Vapour Deposited (PECVD) silicon nitride layers. These provide excellent passivation on high resistivity p-type silicon, as evidenced by the highest control lifetime of 9ms. The deposition is also performed at relatively low temperature ( $400^\circ\text{C}$ ), which should be sufficiently low to avoid further redistribution from the gettering layer to the bulk or vice versa.

Lifetime measurements were obtained with a combination of quasi-steady-state and transient photoconductance measurements [2]. All wafers were etched prior to passivation to eliminate the impact of the heavily diffused layer on the lifetime measurements. The uncertainty in the measured lifetime values is estimated to be approximately 15%.

## 2.2 Calculating the Fe concentration

Iron was chosen as the impurity in this study due to its prevalence in multicrystalline silicon, and also because of its well-known electronic properties. If a known amount of Fe is uniformly diffused through a wafer, it is possible to estimate the resulting lifetime using the Shockley-Read-Hall (SRH) model with considerable accuracy [3]. Conversely, by measuring the lifetime, one may infer how much Fe is in the wafer, provided it is possible to either exclude or subtract out the impact of other recombination mechanisms.

At a given excess carrier density  $Dn$ , the effective lifetime  $t_{Fe-doped}$  of an iron-implanted

**Table I.** Energy levels and capture cross sections of  $Fe_i$  and  $FeB$  pairs as used to calculate  $[Fe]$ .

|        | $E_T$ (eV) | $\sigma_n$ ( $\text{cm}^{-2}$ ) | $\sigma_p$ ( $\text{cm}^{-2}$ ) | Ref.  |
|--------|------------|---------------------------------|---------------------------------|-------|
| $Fe_i$ | $E_V+0.38$ | $5 \times 10^{-14}$             | $7 \times 10^{-17}$             | [1]   |
| $FeB$  | $E_C-0.23$ | $3 \times 10^{-14}$             | $2 \times 10^{-15}$             | [1,3] |

wafer contains terms related both to Fe and also other recombination mechanisms:

$$\frac{1}{t_{Fe-doped}} = \frac{1}{t_{Fe}} + \frac{1}{t_{other}}. \quad (1)$$

There is an implicit assumption in this relation that the action of the Fe-related centres is *independent* of the other processes. This is reasonable when the Fe concentration is low and there is no precipitation, as is the case in this study.

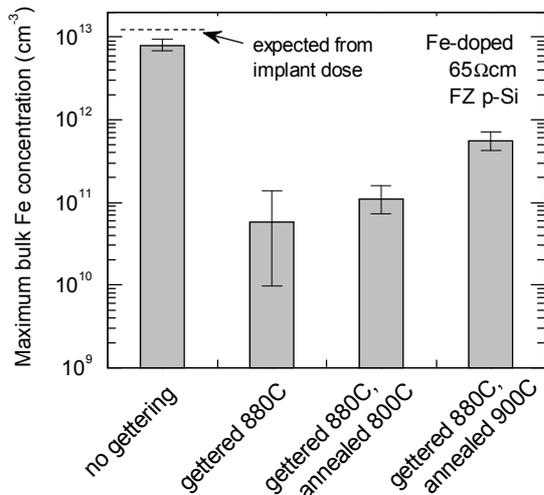
The term  $t_{other}$  incorporates surface and Auger recombination, as well as recombination due to any background contamination during processing. Therefore, if we take a pair of wafers that have received identical processing, apart from the intentional introduction of Fe in one of the wafers, we may use Eq. 1 to determine  $t_{Fe}$  at a given excess carrier density. In this case, the measurement of the non-implanted, or control wafer, is  $t_{other}$ .

There is one final consideration before we may use  $t_{Fe}$ , inferred from Eq. 1, to determine  $[Fe]$ . Assuming it is not precipitated, Fe in p-type silicon can be present in two forms [1,4]. When alone as interstitial Fe, it presents a deep level ( $E_V+0.38\text{eV}$ ) that has a strong impact on the lifetime at low excess carrier concentrations. On the other hand, if present as FeB pairs, the level is shallower ( $E_C-0.23\text{eV}$ ), and tends to dominate at higher excess carrier densities. Depending on the excess carrier density at which the lifetime is measured, these two centres will have a different relative impact on the lifetime [3]. Therefore, in general, it is essential to know what proportion of Fe is present interstitially and as FeB pairs.

Fortunately, there is a particular excess carrier density at which the lifetime *does not change* with the breaking or re-paring of FeB pairs. Above this carrier density, the lifetime will increase after pair dissociation, and below it will decrease. If the lifetime is measured near this 'crossover' point, the precise proportion as FeB pairs does not need to be known. It can be shown that this value of  $Dn$  is fixed at around  $1.5 \times 10^{14} \text{cm}^{-3}$  for any doping below  $5 \times 10^{16} \text{cm}^{-3}$  [5].

For the purposes of this work we assume 99.9% of the Fe is interstitial during measurement, since we first light-soaked the samples for several minutes to break the FeB pairs [4]. However, because we have measured the lifetime at an excess carrier density of  $1 \times 10^{14} \text{cm}^{-3}$ , the result does not depend strongly on this fraction.

The energy levels and capture cross sections from the literature of  $Fe_i$  and  $FeB$  pairs are summarised in Table I. Using these in conjunction



**Fig. 2.** Estimated maximum bulk Fe concentrations after different treatments.

with the Shockley-Read-Hall (SRH) model and the values of  $t_{Fe}$  from Eq. 1, we may then calculate [Fe] accurately after different process steps.

The uncertainties in the values of [Fe] were determined by assuming an uncertainty in each lifetime measurement of 15%. For pairs of lifetime which are relatively close (such as in the gettered case of Fig 1), the resulting uncertainty in [Fe] is much larger.

### 3. RESULTS AND DISCUSSION

A bulk Fe concentration of  $1.2 \times 10^{13} \text{ cm}^{-3}$  yields, via the SRH model, a predicted lifetime of  $35 \mu\text{s}$  at an excess carrier density of  $10^{14} \text{ cm}^{-3}$  with 99.9% of the Fe interstitial.

Figure 1 shows that the lifetime in the Fe-doped wafer that was not gettered was measured to be  $55 \mu\text{s}$ , in contrast to the control wafer which gave  $2600 \mu\text{s}$ . This figure is a little higher than the calculation of  $35 \mu\text{s}$  above, and is slightly outside the range expected from uncertainties attributable to dose variation ( $\pm 10\%$ ) and uncertainty in lifetime measurement ( $\pm 15\%$ ). The discrepancy is likely to be due to the loss of the slightly Fe-rich region near the front surface, which was etched after post-implant annealing. The measured lifetime of  $55 \mu\text{s}$  implies a bulk Fe concentration of  $8 \times 10^{12} \text{ cm}^{-3}$ , as shown in Fig. 2.

#### 3.1 Efficiency of phosphorus gettering

After phosphorus gettering at  $880^\circ\text{C}$ , the amount of Fe in the wafer bulk is massively reduced. The Fe-doped wafer improved to become close to the control wafer ( $3300$  compared to  $5800 \mu\text{s}$ ), revealing that almost all of the Fe was trapped in the gettering region, which was removed before lifetime measurement. Using this pair of lifetime values yields  $[\text{Fe}] = 6 \times 10^{10} \text{ cm}^{-3}$  after gettering. This suggests that more than 99% of the

Fe is removed by gettering, or, alternatively, implies a segregation coefficient of less than 0.01. It is important to note that the error bars shown in Fig 2 suggest that the segregation coefficient could actually be significantly smaller, due to the small difference between the measured lifetimes with and without Fe.

A further point of interest is that the gettered control lifetime is twice the non-gettered control in Fig 1. This suggests that the gettering has removed some native impurities in the FZ material, whether they are Fe or other mobile impurities. If specially grown solar-grade FZ material becomes available in the future, such gettering steps might be very useful in improving performance.

#### 3.2 Poisoning by subsequent anneals

Annealing the wafers after gettering, but with the gettering layer intact, resulted in a reduction in the lifetime for the Fe-doped wafers relative to the controls. This can be attributed to the re-injection of some Fe back into the wafer bulk. The extent of this 'poisoning' effect was significant only for the  $900^\circ\text{C}$ , 60 minute anneal, for which 7% of the original Fe concentration was injected back into the bulk (resulting in a concentration of  $5.5 \times 10^{11} \text{ cm}^{-3}$ ). In contrast, the  $800^\circ\text{C}$  anneal apparently resulted in less than 1.5% re-injection ( $1.0 \times 10^{11} \text{ cm}^{-3}$ ). This lies within the uncertainty limits of the pre-anneal Fe concentration, and so should be interpreted as implying very little or no change.

There are several mechanisms that may play a role in the re-injection of impurities from the gettering layer. Firstly, there is the capacity of the gettering layer itself to hold impurities, which could be expressed as an effective solubility limit, and how this may change with temperature. The corresponding equilibrium solubility limit of Fe in the wafer bulk will also increase with temperature. The segregation coefficient, or gettering efficiency, will then be related to the ratio of these solubilities. There is some evidence that the solubility of metals in a phosphorus diffused layer does not increase as rapidly with temperature as the bulk solubility [6]. This would then be a driving force for poisoning at higher temperatures, as observed here for the  $900^\circ\text{C}$  anneal.

A further consideration is the fact that the diffusion profile itself will be altered during high temperature anneals. The peak surface concentration would be reduced, and the solubility limit of the gettering layer for metals would probably decrease, while that of the bulk would not change. This would also drive the equilibrium distribution towards greater concentrations in the wafer bulk.

Both mechanisms would occur for the  $900^\circ\text{C}$  anneal, while only the second could produce poisoning for the  $800^\circ\text{C}$  anneal. However, at this lower temperature the diffusion profile is not expected to change dramatically. It therefore seems reasonable that we have observed poisoning for temperatures greater than the gettering temperature, but practically none for lower temperatures.

### 3.3 Relevance for industrial multicrystalline silicon cells

It would be of great benefit if phosphorus gettering could be as effective at removing Fe in mc-Si as it is for the FZ wafers of this study. However, other studies of phosphorus gettering in mc-Si have revealed considerably less efficient gettering. POCl<sub>3</sub> gettering by Ballif *et al.* [6] at 900°C reduced the free Fe concentration in mc-Si by only a factor of 3, although it was for a shorter time than used here. Similar reductions were reported by Geerligts *et al.* using a belt diffusion [7]. On the other hand, Neutron Activation Analysis [8] has shown that the total Fe concentration can be reduced by up to an order of magnitude in mc-Si, although this of course includes impurities removed from precipitates as well. Taken together, this information strongly suggests that precipitates act as a constant source of free Fe within the mc-Si wafers, resulting in a higher equilibrium Fe concentration in the bulk than we observed for the FZ samples in this study.

There are also possible implications of the poisoning findings in this work for industrial mc-Si cells. Of course, such wafers are usually more heavily doped than the FZ samples used here. Fortunately, it is possible to use the SRH model to determine the impact of a given level of iron contamination in differently doped material. For 1Ωcm material, an Fe concentration  $5.5 \times 10^{11} \text{cm}^{-3}$ , as occurred after the 900C poisoning, would limit the bulk lifetime to around 25μs at 1 sun illumination. This represents quite a stringent limitation that would be significant in modern SiN-based mc-Si cells.

It is important however to consider the fact that industrial fire-through processes are generally much shorter, typically only a few minutes, than the poisoning times used in these experiments. This would tend to reduce the extent of poisoning, considering that Fe diffuses rather slowly at these temperatures. On the other hand, even within just a few minutes a significant amount of Fe could be re-injected into the near-junction region, where it can do the most damage. In fact it is likely that the equilibrium concentration of Fe, as determined by the segregation coefficient, would be approached rather quickly near the front surface. Longer poisoning times would simply allow this level of contamination to spread deeper into the cell. For short anneals, any possible gettering action by the rear Al BSF can not be expected to help in this regard, since it is simply too far from the front surface to sink much Fe.

Another factor to consider is the magnitude of Fe contamination before gettering. A recent study using Neutron Activation Analysis [8] suggested that the *total* Fe concentration in typical non-gettered mc-Si wafers can be as high as  $10^{14} \text{cm}^{-3}$ . Of course much of this must be present in precipitates, otherwise the lifetime would be extremely low. Nevertheless, in that study, a large proportion of this Fe was sunk in the surface phosphorus layer during gettering. This means that

the amount of Fe in the diffused layer may be as much as an order of magnitude higher than in this current study. For a fixed segregation coefficient, this would of course result in greater poisoning, even for fast anneals.

### 4. CONCLUSIONS

Phosphorus gettering is extremely effective at reducing the Fe concentration in FZ material that does not contain precipitates. However, when annealing again at temperatures higher than the gettering temperature, the increased segregation coefficient, or solubility ratio, tends to drive Fe back into the wafer. When annealing at lower temperatures, such poisoning does not occur, provided that the phosphorus diffusion profile is not altered too much. However, in mc-Si, metallic precipitates act as a slow, constant source of mobile Fe atoms, and would most likely result in higher bulk iron concentrations after similar gettering treatments.

The poisoning results may have relevance for industrial fire-through processes, since even a small amount of re-injection near the front surface could be detrimental to cell performance. It seems that lower temperature metallisation firing steps are desirable, at least from the point of view of maintaining effective gettering by emitter diffusions. Of course this needs to be balanced against the need for good electrical contact and sufficient bulk hydrogenation. A double-diffusion process, in which the initial gettering diffusion is etched away, is one possible approach to reducing such poisoning effects.

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