Physical mechanisms of boron diffusion gettering of iron in silicon

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We have studied the boron diffusion gettering (BDG) of iron in single crystalline silicon. The results show that iron is gettered efficiently by electrically inactive boron, which leads to gettering efficiencies comparable to phosphorus diffusion gettering (PDG). In addition we discuss the different physical mechanisms behind BDG. We also consider the possibilities of using boron diffusion gettering in solar cell fabrication and discuss the role of boron and iron concentration in the optimization of gettering efficiency.

1 Introduction Most of the silicon solar cells fabricated today have a p-type base with an n-type emitter. However, recently the use of n-type silicon as a base material for solar cells has received considerable attention [1–3]. It is well known that n-type silicon has some superior characteristics over p-type, including the absence of light induced degradation [4]. Moreover, the recombination activity of common metal impurities, such as iron, is lower in n-type, which often results in higher bulk lifetimes of charge carriers [5, 6]. The lifetime of an n-type substrate can also be further improved by conventional PDG, similar to a p-type substrate [7].

The formation of the emitter in an n-type silicon solar cell is often realized by boron diffusion. Typically the temperature needed in boron diffusion is higher than for phosphorus. The higher temperature leads to a higher risk of external contamination and dissolution of metal precipitates. The contamination can become a problem since the gettering capability of the boron doped area is not very high during a typical emitter formation [1]. As a consequence, the boron emitter formation can result in lifetime degradation in the material.

In this letter we present results which, in contrast to previous studies, show that with specific anneals a diffused boron emitter can be used as an effective gettering sink for iron, thereby resulting in a drastic increase in the base lifetime. We also discuss various physical mechanisms behind BDG, possibilities to use boron diffusion gettering in solar cell fabrication and the role of boron and iron concentration in the optimization of gettering efficiency.

2 Experimental Silicon wafers used in the experiments were boron doped p-type, $\langle 100 \rangle$-oriented Czochralski-grown wafers with a diameter of 100 mm. The wafers had a low initial oxygen level (7–9 ppma MCz). The thickness of the wafers was 400 μm and the resistivity was in the range of 2.7–3.0 Ω cm.
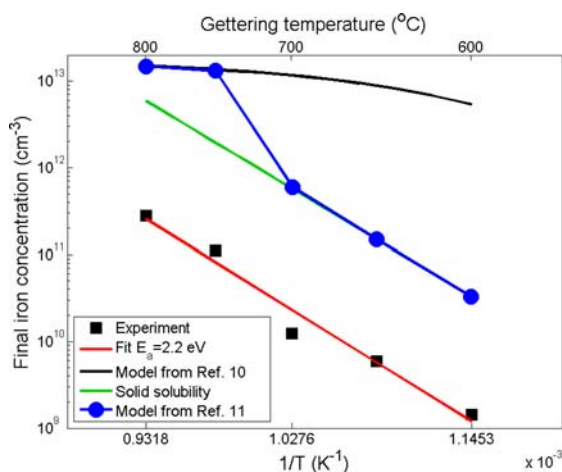
As a first process step all the wafers were intentionally iron contaminated to the level of 2×10^{13} cm^{-3} by the procedure described in detail in [8]. After contamination the wafers were dry oxidized to a thickness of 27 nm for surface passivation and the initial iron concentration was verified by surface photovoltage (SPV) measurements. Prior to BDG anneal, the oxide was removed from the front side of the wafers by etching in BHF. Boron spin-on-dopant, Filmtronics Boron Film B-154, was applied on the front side of the wafers and the wafers experienced different BDG anneals consisting of a high temperature diffusion and a low temperature tail. The high temperature boron in-diffusion was carried out at 930 °C for 60 min in an atmosphere containing 95% of nitrogen and 5% of oxygen. The in-diffusion step was followed by a slow cool down to the lower temperature in nitrogen atmosphere. The low-temperature anneals used were: 2 h at 800 °C, 3.5 h at 750 °C, 5.5 h at 700 °C, 8 h at 650 °C and 15 h at 600 °C. The annealing times were chosen in such a way that ac-

cording to simulations [9], a steady state iron concentration was reached in a 525 μm wafer.
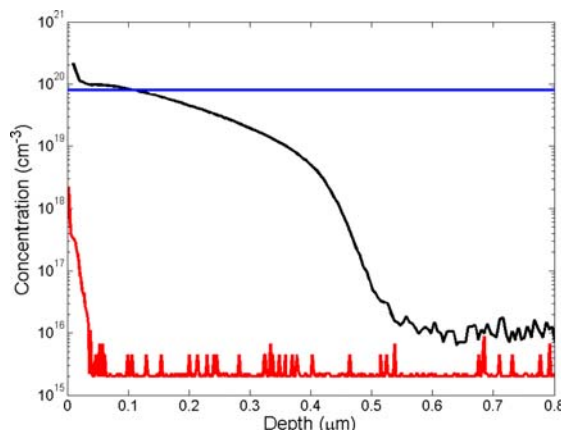
After the low temperature gettering anneal the remaining spin-on-dopant was removed in BHF and the wafers were SC-1 cleaned. Finally the remaining interstitial iron concentrations were measured by SPV method. In addition both boron and iron profiles close to the boron diffused surface were measured by Secondary Ion Mass Spectrometry (SIMS).

3 Results Figure 1 presents the measured average iron concentration in the bulk of the wafers after different low temperature anneals. It also shows the simulated values obtained using the well known solubility model [10] that takes into account the segregation of iron due to high boron doping concentration (black line). In addition, simulation results of the recently proposed model [11] that takes into account both segregation and the heterogeneous precipitation of iron to the surface of the wafer are shown (blue line). As can be seen from Fig. 1, the measured iron concentrations are well below the expected values.

The Arrhenius fit of the gettering results (represented by the red line in Fig. 1) gives an activation energy of about 2.2 eV. This value fits quite well to the activation energies of 2.1 eV [12] and 2.27 eV [13] obtained previously for iron gettering by electrically inactive boron and B–Si precipitates, respectively. This, together with the fact that the deactivation of boron most likely occurs by precipitation [14], implies that the high gettering efficiency of BDG observed here is due to the formation of B–Si precipitates. The SIMS results of boron and iron concentrations after the BDG anneal of 2 h at 800 °C presented in Fig. 2 further support this conclusion, as iron seems to be

Figure 2 (online colour at: www.pss-rapid.com) Iron (red line) and boron (black line) concentrations at the diffused surface measured by SIMS after the BDG anneal of 2 h at 800 °C. The boron solubility at 930 °C [15] is shown as a vertical blue line.

collected to the region close to the surface, where the boron is supersaturated, e.g., the concentration significantly exceeds its solubility value at 930 °C [15].

4 Discussion

4.1 Gettering mechanisms Figure 1 shows the three different mechanisms that can take place during the boron diffusion gettering. At first sight, it seems that the B–Si precipitate gettering mechanism has the highest potential to be efficiently utilized e.g. in silicon solar cell fabrication. In B–Si precipitate gettering, the iron concentration decreases below the solubility, which is a clear finger print for the segregation based mechanism. It is proposed that the segregation in this case is due to chemisorption of some metals, like Fe, Cu and Co, to solution sites within the B–Si precipitates [13]. For iron, the sinks at the solution sites within the B–Si precipitates remain unsaturated and therefore the gettering is quantified by the temperature dependent equilibrium coefficient [13]. Overall, it should be kept in mind that efficient gettering requires that the boron concentration exceeds its solubility at the annealing temperature for a sufficiently long time, otherwise, the nucleation and growth of B–Si precipitates are substantially diminished and this mechanism is no longer effective.

If the boron concentration remains lower than the solubility, surface precipitation and conventional segregation induced by the solubility difference become the dominating mechanisms during BDG [11]. The surface precipitation mechanism (blue line in Fig. 1) and the conventional segregation mechanism (black line in Fig. 1) are actually related to each other as follows: Segregation to the p$^+$ layer increases the concentration of mobile iron near the wafer surface, which enhances the iron precipitation rate in the p$^+$ layer as compared to a bare silicon surface. This kind of gettering is robust since the iron concentration can always be reduced to the solubility limit [11], provided that the iron supersaturation is sufficiently high. This is a clear

Figure 1 (online colour at: www.pss-rapid.com) Measured iron concentration in the bulk (black squares) after low-temperature anneals and fitted Arrhenius relation with an activation energy of 2.2 eV (red line). Black line represents iron concentrations calculated by using the solubility model [10] and blue spheres represent iron concentrations calculated by using the model including both segregation and precipitation [11].

benefit compared to pure segregation gettering, in which the final iron concentration depends on the initial iron concentration.

As mentioned above, iron does not precipitate to the surface if the supersaturation of iron at the boron emitter is not high enough for the nucleation of iron precipitates. Obviously, this is the case if the initial iron concentration is too low or the temperature is too high. The latter one is demonstrated in Fig. 1, in which the significant nucleation occurs only at temperatures below 750 °C. It is important to note that also in a very low temperature range (<400–450 °C), the iron supersaturation remains too low due to the limited diffusion of iron from the bulk [11]. This was the case e.g. in the experiments of MacDonald et al. [16], who observed that only 65% of the iron concentration was gettered by BDG from the wafer bulk during boron diffusion and a following 40 min anneal at 400 °C. Since the surface precipitation of iron is negligible in their experiments, their results can be entirely explained by the conventional segregation model.

4.2 Recombination at the emitter B–Si precipitate gettering requires high boron concentration at the emitter. The high boron concentration increases the Auger recombination which, in the case of solar cells, leads to increased emitter saturation current. On the other hand, in the case of a moderately doped emitter a similar problem can occur: The emitter saturation current is now increased due to the dissolved iron that is gettered at the emitter [16]. However, in the latter case, the increased recombination (due to dissolved iron), can be reduced by employing the previously mentioned surface precipitation gettering technique. The precipitation treatment can be relatively short, even just a modified firing step, as instead of collecting iron from the bulk the purpose is only to transform the iron at the emitter to a less recombination active precipitated state. In principle this is the same method which can be used to minimize the detrimental effect of iron at boron doped bases [17]. Overall, it seems that instead of getting rid of iron related problems in an n-type base, the problems are only transferred (at least partially) to the emitter.

4.3 Back-surface field formation In a solar cell process, in addition to the formation of an emitter in n-type cells, boron can also be used to form a back-surface field (BSF) in p-type cells. In this case gettering by B–Si precipitates is not a good choice since the doping needed for the formation of B–Si precipitates is too high for an optimal surface passivation due to the increased Auger recombination [18]. However, the surface precipitation gettering can again be used to improve the bulk lifetime if the annealing time is sufficiently long.

5 Conclusions We have shown that during boron diffusion, the formation of B–Si precipitates can result in a drastic increase in the iron gettering efficiency. However, the utilization of B–Si precipitate gettering is not that straightforward as long annealing times and high boron concentrations are needed. We have also discussed various physical mechanisms behind BDG and propose the dominant mechanism under different conditions.

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