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Effect of Thermal History on Iron Precipitation in Crystalline Silicon

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Abstract

We have studied the effect of thermal history on iron precipitation behavior in intentionally contaminated Czochralski silicon wafers that contain well-defined precipitation sites for iron, oxide precipitates. Iron precipitation was studied at a temperature range between 600 °C and 700 °C for various times. The results indicate that iron precipitation is strongly affected by the thermal history of the wafers. Our results also explain the disagreement observed previously in iron precipitation behavior at low temperature anneals. Finally, we discuss how the results can be applied to gettering in multicrystalline silicon.

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1. Introduction

Low-temperature anneals are an effective way to reduce harmful dissolved iron contamination in solar cells. [1,2] The reduction is generally due to i) external gettering by emitter and ii) iron precipitation in the wafer bulk (internal gettering). Rinio et al. [3] found out that the external gettering dominates over internal gettering in their experiments. However, the experiments were made only with one thermal history, therefore, their conclusion cannot be necessarily generalized. In this work, our aim is to demonstrate that the iron precipitation rate can change dramatically depending on the thermal history of the wafers.

2. Experimental

In the experiments we used p-type 20-50 Ωcm CZ-Si with an initial interstitial oxygen level of 16 ppm (ASTM F 121-83 standard). We wanted to have well controlled precipitation sites for iron, therefore, oxide precipitates were chosen as precipitation sites. These were formed in the bulk by the typical three-step High-Low-High anneal: 4h@1150°C + 6h@550°C + 16h@1100°C. The total amount of precipitated oxygen, the difference between initial and final interstitial oxygen concentration, was measured to be around 9.3 ppm.

After formation of oxide precipitates the wafers were intentionally iron contaminated to the level of $2 \times 10^{13} \text{ cm}^{-3}$. At first the wafers were immersed in a SC1 solution containing 30 ppb added iron impurities. Iron was diffused into the wafers with a 55 min anneal at 850 °C. The remaining surface iron contamination was removed in a HF:H₂O₂:H₂O solution. Wafers were cleaned in the sequence of standard wafer cleaning solutions SC1 and SC2 including dip in diluted HF as the last step.

Two different kind of "thermal histories" were studied. In the first case, the wafers were slowly cooled (2 °C/min) from high temperature (850°C or 900°C) down to low temperature (600-700°C). These samples are named as UP. In the second case, the wafers were quickly pulled out of the furnace and air cooled to room temperature. These samples are named as DOWN. The "thermal history" was followed by low-temperature (LT) anneals at 600°C, 650°C or 700°C for annealing times up to two hours. Fig. 1 shows a summary of the thermal profiles of the experiments. The dissolution annealing starts with 20 min dry-oxidation followed by 20 minutes annealing in nitrogen ambient. The resulting thermal oxide layer has two functions, firstly, it minimizes iron precipitation to surface and secondly, it passivates the wafer surfaces for lifetime measurement. The dissolved iron concentration was measured by the microwave photoconductance decay (μ -PCD) technique using the well-known Fe-B light dissociation method [4].

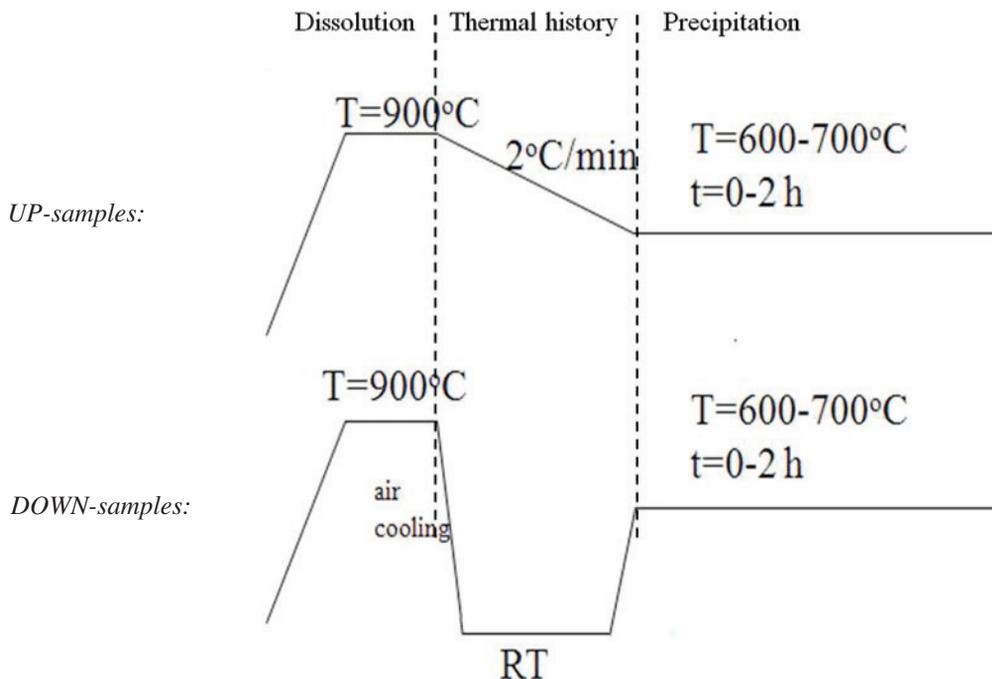


Fig. 1. Different thermal histories and following precipitation (LT) anneals.

3. Results and Discussion

The iron precipitation rate is directly proportional to *i*) the density of iron precipitates and *ii*) the diffusion constant of iron. The former is affected by the thermal history while the latter is determined by the temperature. At 850-900 °C we may suppose that all iron is in dissolved state (with given contamination level), which means that the density of iron precipitates is negligible, *i.e.* the thermal history is cleared.

Fig. 2 shows the dissolved iron concentration after LT anneals in case of two different thermal histories (2a and 2b). The effect of thermal history is very obvious from the figure. In all anneals the thermal history UP induces slower precipitation rate for iron. In these samples the iron nuclei are formed during the slow cooling and the following LT anneal. From the results we can see that the nucleation rate is very low above 700 °C (Fig. 2a). The rate increases when the temperature is lowered due to increasing supersaturation of iron. In other words, an increment in iron precipitate density dominates the precipitation over the decline in diffusivity. In case of the DOWN thermal history, the density of iron precipitate nuclei is much higher in the beginning of the LT anneal due to additional nucleation during RT ramps. Therefore, the precipitation rate is higher over the whole temperature range (Fig. 2b).

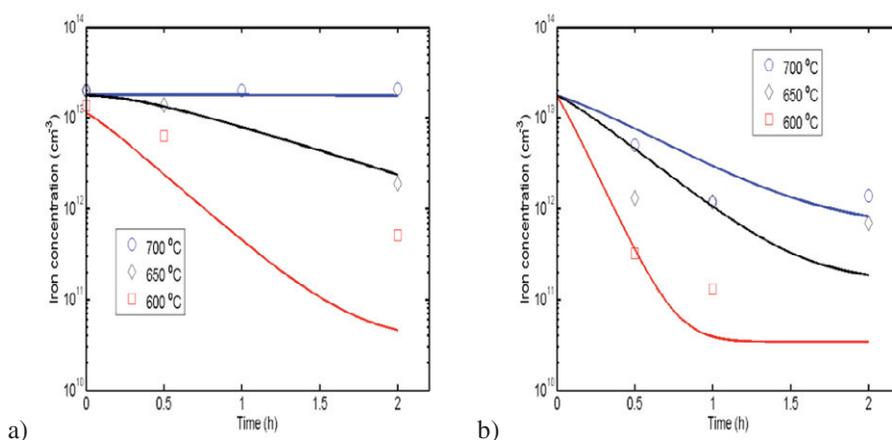


FIG. 2. The measured dissolved iron concentrations after similar precipitation treatments but with different thermal histories: a) UP-history and b) DOWN-history. The simulated results are shown by solid lines.

The experimental results were also compared to simulations, which were obtained using a model described in details in Refs [8,9]. In the simulations oxide precipitate density of $5.5 \times 10^9 \text{ cm}^{-3}$ with radius of 60 nm were used as input parameters as they fit nicely the 650 °C results with UP-history. Using iterative diffusion limited growth method [5] to fit oxygen loss during final Hi-anneal, we obtain oxide precipitate density $5.5 \times 10^9 \text{ cm}^{-3}$ and radius 70 nm. In this calculation the solubility and diffusivity values of oxygen were taken from Ref. [6] and SiO_2 phase was assumed. When simulating the DOWN history, the problem was unknown cooling and heating rates. However, it was observed by simulations that a slower heating rate close to the annealing temperature was needed to obtain the increasing precipitation rate with decreasing temperature.

Fig. 3 shows a comparison of the results presented here with previously published data in FZ- [7] and CZ- [8] Si at nearly the same contamination level and comparable annealing times. The lines show the apparent hysteresis in iron precipitation rate induced by the thermal history. Notice that we have also shown earlier that iron at this contamination level can remain completely in dissolved form even after 12

hours annealing at 600 °C. [9] In that study the wafers were low oxygen CZ-wafers with thermal oxide on both surfaces. The result clearly indicates that the nucleation rate of iron precipitates is very small with passivated surfaces and in the absence of bulk defects even at 600 °C, i.e., in general, homogeneous iron precipitation has only a negligible effect to experimental results.

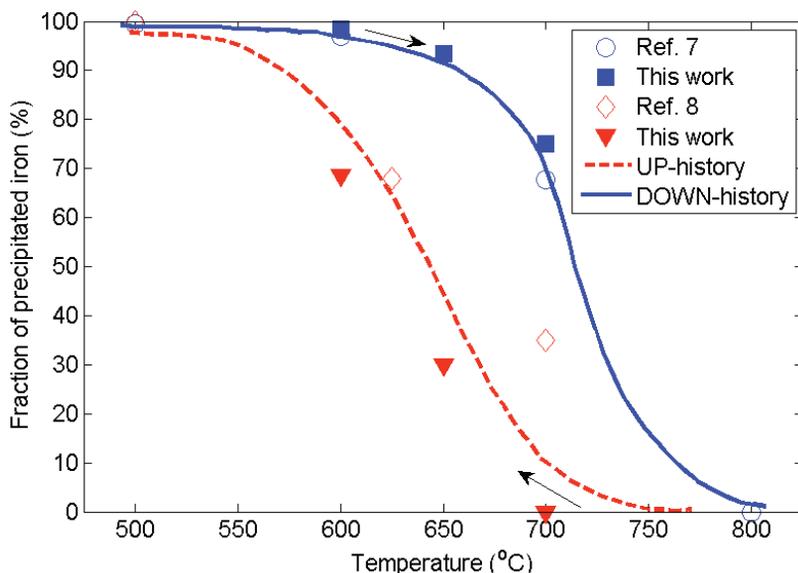


FIG. 3. Effect of thermal history on the nucleation rate of iron at the contamination level $\sim 10^{13} \text{ cm}^{-3}$. The lines are only guides for the eye.

All these results [7,8] indicate that the iron precipitation rate has a maximum around 500-600 °C at the contamination level between $5 \times 10^{12} - 8 \times 10^{13} \text{ cm}^{-3}$. These observations are in disagreement with the result of Zeng et al. [10], who reported that the iron precipitation rate increases when temperature increases from 300 °C to 700 °C in as-received CZ-Si. However, Zeng et al. [10] performed low temperature annealing at 200 °C for 10 minutes before the actual precipitation anneal (for breaking iron-boron pairs). This of course changes the starting conditions for precipitation (=thermal history) as we have shown and most probably explains the observed difference. It has been reported that during annealing at 200 °C iron nucleates to nearly all available precipitation sites [11] and therefore the density cannot much increase in later anneals. This means that in their experiments, the precipitation rate is increased with temperature as the increment in diffusivity dominates over small change in iron precipitate density.

The results of Rinio et al. indicate that external gettering dominates over internal gettering during LT-annealing. [3] However, the results in Fig. 2 clearly show that even at the same temperature the internal gettering varies greatly depending on the thermal history. We can compare the precipitation time constants (a reduction of iron to the factor 1/e) from Fig. 2 and the time constant ($\approx 0.4 \cdot w^2 / D_{\text{Fe}}$ [12]) for similar reduction due to strong external gettering. From the comparison (using $w=260 \text{ }\mu\text{m}$) we can conclude that internal gettering (precipitation) should be significantly weaker or only comparable to external gettering with all UP-histories and also with DOWN-history of 700 °C. As the wafers in the experiments of Ref. 3 were taken from the cast ingot, which generally exhibits slow cooling, the observation of dominating external gettering is not surprising. On the other hand, in case of DOWN-histories followed by anneal at 600 °C or 650 °C, internal gettering should dominate over external gettering. This could be the case e.g. for the fast cooled (ribbon) mc-Si. The change in dominating

gettering mechanism was observed also by simulations in our previous study [13], but the conclusion has not yet been verified by direct experimental results.

4. Conclusions

We have shown that the thermal history can greatly affect the precipitation behavior of iron due to fast nucleation of iron precipitates at low temperatures. Our results can also explain the discrepancies reported in the past related to iron precipitation behavior in silicon. Thermal history can also affect the dominating gettering mechanism (external vs. internal) in low temperature anneal in multicrystalline silicon.

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