

HYDROGEN PASSIVATION OF INTERSTITIAL IRON IN SILICON BY ANNEALING WITH PECVD SILICON NITRIDE FILMS

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ABSTRACT: This paper reports on the effective passivation of interstitial iron in p-type boron-doped silicon via annealing with plasma-enhanced chemical vapour deposited (PECVD) silicon nitride films. The concentration of interstitial iron was shown to reduce by more than 90% after a 30-minute anneal at 600 – 900°C with the silicon nitride films present. The most effective hydrogenation of iron was found to take place at 700°C, where more than 99% of iron was passivated after 30 minutes. Results show that the observed reductions in the interstitial iron concentrations are not likely to be caused by the precipitation of iron at structural defects by a hydrogen-enhanced diffusivity of iron, as has previously been suggested.

Keywords: hydrogen, iron, PECVD silicon nitride

1 INTRODUCTION

Iron is one of the most common and detrimental impurities in silicon. It is of great interest to investigate the mechanisms that reduce the harmful impact of iron in silicon, for example, via phosphorous and boron diffusion gettering, aluminium alloying and internal gettering. It has been reported in the literature by several authors that after hydrogen incorporation, the electrical activity of iron-related impurities is partially or fully passivated and the interstitial iron concentration is reduced [1-7]. However, the extent of the hydrogenation capability is unclear, and the underlying mechanism remains controversial. This work studies the hydrogen passivation of interstitial iron via annealing with PECVD silicon nitride films, by monitoring the concentration and distribution of interstitial iron in both multicrystalline and float-zone silicon wafers.

2 EXPERIMENT

Both directionally-solidified multicrystalline silicon with naturally high iron content, and float-zone silicon with uniformly implanted iron, are examined in this work. The samples have an initial interstitial iron concentration in the range of 10^{12} - 10^{13} cm^{-3} .

The wafers were grouped into two sets of samples – one with, and one without the hydrogen source present during the subsequent anneals. The set with hydrogen is passivated using PECVD silicon nitride (SiN_x) films, and the one without hydrogen is passivated with thermally grown silicon oxide (SiO_2) layers. The two sets of samples underwent the same thermal treatment prior to surface passivation. For the multicrystalline silicon samples, directly neighbouring wafers were chosen as pairs, in order to allow comparisons being made between wafers of the same structure and impurity distribution.

The pairs of the SiN_x and SiO_2 passivated samples were then annealed at a temperature in the range of 250 – 900°C for times from minutes to tens of hours. The SiN_x coated samples experienced severe surface degradation after annealing at 600 – 900°C, and were therefore re-passivated with fresh SiN_x films in order to measure the bulk lifetime and Fe concentrations. The extent of iron hydrogenation during the PECVD process itself was found to be small compared to the effect of annealing [8].

After each processing step, the concentration and the distribution of interstitial iron were measured, using both the quasi-steady-state photoconductance (QSSPC) lifetime method for the area-averaged values, and a high resolution ($25\mu\text{m}/\text{pixel}$) LIS-R1 photoluminescence imaging system from BTImaging [9, 10].

3 RESULTS AND DISCUSSION

Results show that the silicon nitride sample set (i.e. with hydrogen) consistently demonstrate much larger reductions in the interstitial iron concentration ($[\text{Fe}_i]$) compared to the silicon oxide samples (i.e. without hydrogen), for the entire annealing temperature range of 250 – 900°C. The quantitative interstitial iron concentrations are detailed in References [8, 11]. An example is shown in Figure 1 for the two neighbouring multicrystalline silicon wafers annealed at 700°C. The changes in $[\text{Fe}_i]$ for the no hydrogen sample set are consistent with the solubility-limit driven precipitation and dissolution of iron, which has been observed before on the same material [12], thus demonstrating the sole effect of temperature. The much more significant reductions in $[\text{Fe}_i]$ for the SiN_x passivated samples therefore indicate the effect of either hydrogen, or the PECVD silicon nitride films. The hydrogenation kinetics at 400°C from annealing with SiN_x films shows general agreement with the kinetics derived from other hydrogen incorporation methods, as detailed in Ref [8]. The hydrogen effect therefore seems more likely, at least at this low temperature. Further studies are underway to clarify this question.

The observed reductions in the $[\text{Fe}_i]$ were found to be not caused by the hydrogenation of the boron dopants in silicon [13], as revealed by monitoring the the resistivity of the samples, which remains the same throughout the annealing processes.

Similar hydrogenation kinetics are found for the multicrystalline and float-zone silicon wafers, by comparing the results in References [8, 11]. This shows that the $[\text{Fe}_i]$ reduction is not due to the presence of defects in multicrystalline silicon.

Figure 2 compiles the percentage of the passivated interstitial iron for the entire annealing temperature range, incorporating data from both multicrystalline [8] and float-zone silicon samples [11]. The most effective hydrogenation of iron is found to occur at 700°C, where

more than 99% of interstitial iron is passivated after a 30-min anneal. Significant reductions in $[Fe_i]$ are also found at high annealing temperatures of 800°C and 900°C, as shown in Figure 2. This has also been reported by other authors [2-4]. The iron solubility limits at 800°C and 900°C [14] are comparable or higher than the concentrations of Fe_i in the wafers, and thus Fe precipitation via a relaxation mechanism should not occur, consistent with the observations on the corresponding SiO_2 sample set [8]. The large $[Fe_i]$ reductions at high annealing temperatures therefore indicate that the reduced $[Fe_i]$ is not due to iron precipitation.

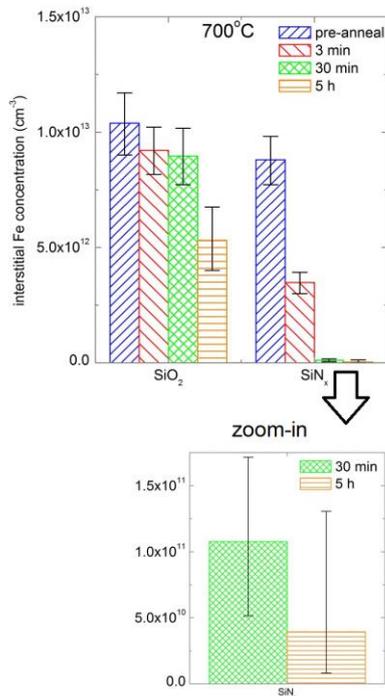


Figure 1. Interstitial iron concentration of two neighbouring multicrystalline silicon wafers annealed at 700°C for various times, with different surface passivation – one with SiO_2 , which contains no hydrogen; and the other with SiN_x , which is known to release hydrogen during annealing.

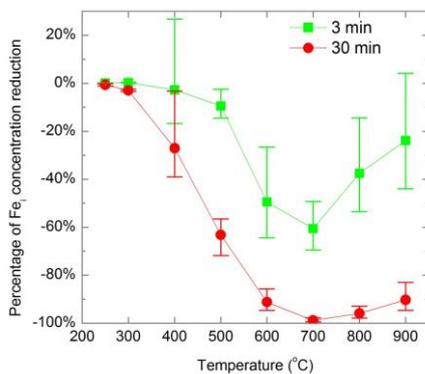


Figure 2. Percentage of the passivated interstitial iron after annealing with SiN_x films for 3 minutes (green) and 30 minutes (red), at various annealing temperatures.

The Fe images of the SiN_x coated multicrystalline silicon wafers annealed at various temperatures all show that the reductions of $[Fe_i]$ occur quite homogeneously across the mc-Si wafers. An example is shown in Figure 3. Note that the images become more smeared out after hydrogenation, due to the increased minority carrier diffusion length. The homogeneous reduction is different from the effect of Fe precipitation, where the denuded zones of reduced $[Fe_i]$ near grain boundaries and dislocations can be clearly seen on the Fe images, as demonstrated in Ref [12]. This is an additional indication that the greater reductions in $[Fe_i]$ of the SiN_x coated wafers are not caused by the gettering of Fe by the crystal defects, accelerated by hydrogen-enhanced Fe diffusivity, as some authors speculated [5, 15].

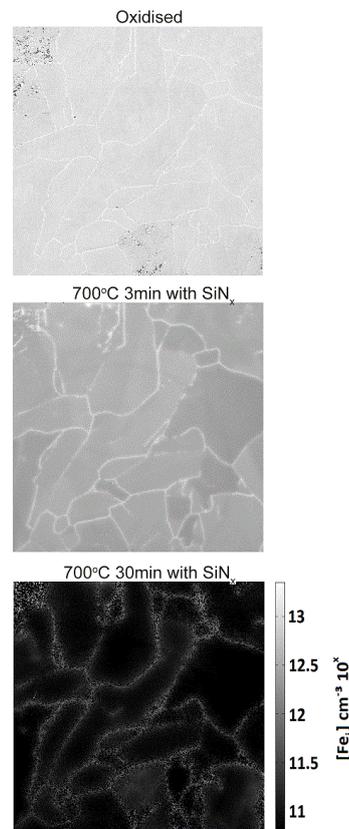


Figure 3. Interstitial iron concentration images, obtained using the PL imaging technique, of the same wafer before (top) and after hydrogenation at 700°C for 3 minutes (middle) and 30 minutes (bottom). Note that the interstitial iron concentration colour bar is in logarithmic scale.

Therefore, by comparing the changes in the interstitial Fe concentrations of the SiO_2 and SiN_x coated wafers annealed for a wide temperature range, for both multicrystalline and float-zone silicon samples, and by examining the spatial changes in $[Fe_i]$ across the multicrystalline wafers, it is clear that the observed decreases in $[Fe_i]$ of the SiN_x set are not due to hydrogen-enhanced Fe precipitation.

The mechanism for the apparent hydrogenation of iron remains unknown at this stage. If the passivation effect is assumed to be caused by some reaction of

hydrogen and iron, it is likely to involve the majority charged species of positive hydrogen and neutral iron [11]. Whether the actual reaction involves a direct bonding of hydrogen to iron, thereby reducing its recombination activity, or whether the hydrogen merely catalyses some other change of state of the iron, remains unclear at this stage. Further study is underway to try to solve this mystery.

4 CONCLUSION

Experimental evidence is presented for the hydrogenation of interstitial iron in silicon, upon annealing with PECVD silicon nitride films. Results show that the significantly reduced interstitial iron concentrations are not caused by the hydrogen-enhanced precipitation of iron.

5 ACKNOWLEDGEMENTS

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