INTERNAL GETTERING OF IRON AND CHROMIUM TO IMPROVE MULTICRYSTALLINE SILICON WAFERS

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ABSTRACT

Metallic impurities in interstitial form are one of the most important limiting factors for minority carrier lifetimes in p-type silicon. Interstitial impurities can be transformed into less harmful precipitates by annealing. In this way, it is shown that the minority carrier lifetime can be increased with one order of magnitude for iron and with two orders of magnitude for chromium.

Keywords:

Iron, Chromium, Internal Gettering

NOMENCLATURE

τ minority carrier lifetime [μs]
C   calibration factor
Δn   injection density [cm^{-3}]
N_D doping concentration [cm^{-3}]

INTRODUCTION

Multicrystalline silicon wafers are widely used for the manufacturing of solar cells due to the relatively low costs and good performance. Mc-Si is most commonly produced by directional solidification in coated quartz crucibles. High concentrations of impurities in the starting Si material (feedstock) and in the materials used in the crystallisation (e.g. crucible, SiN coating, furnace environment) cause relatively high concentrations of transition metal impurities in the Si ingot. The high recombination activity of interstitial transition metals, together with crystallographic defects (e.g. dislocations and grainboundaries), limits the efficiency potential of mc-Si.

For regions with low crystallograpic defects, the minority carrier lifetime is largely limited by metallic impurities in interstitial form. The most prevalent metallic impurity in solar grade silicon is iron, which has therefore received much attention in the past years. Chromium may be incorporated due to its presence in stainless steel which is often used as material for equipment. Both impurities have similar characteristics with respect to influences on lifetime, and diffusivity, but different energy levels (although both are donors) and capture cross sections which are two orders of magnitude larger for chromium.

Internal gettering (e.g. precipitation of impurities) of interstitial iron (Fe_i) at low temperatures has been demonstrated both for mono- and multicrystalline silicon wafers[1,2]. Henley and Ramappa concentrated on artificially contaminated floatzone material and found a reduction of 99% in [Fe_i] after an anneal of 90 minutes. Krain et al. concentrated on commercial multicrystalline material and found a decrease of 90% in [Fe_i] after an anneal of 1 hour. Interstitial Cr has not received as much attention as Fe_i, but the same situation may be expected to apply. However, since Cr_i diffuses at a much slower rate compared to Fe_i, an additional mechanism for gettering can be important.

EXPERIMENT

Intentionally contaminated multicrystalline silicon wafers with a high Fe_i concentration ($>10^{13}$ cm^{-3}) or high Cr_i concentration ($>10^{13}$ cm^{-3}), as well as reference wafers with normal Fe_i concentration ($\sim10^{11}$ cm^{-3}), were subjected to anneal steps. The chosen temperatures were 500 ^{o}C and 800 ^{o}C, because according to reference 1 in this range the most striking variation in effectiveness of internal gettering can be found. The anneal times used were 90 minutes and 180 minutes for both temperatures. Neighbouring wafers were used for the different temperatures.

The wafers were surface passivated by mw-PECVD silicon nitride (SiN_x), which yields a surface recombination velocity between 10 and 20 cm/s. A stable and low surface recombination velocity is important in order to measure bulk lifetime effects and changes thereof.

The effective minority carrier lifetime of the annealed wafers and their unprocessed neighbour wafers was measured with quasi-steadystate photo conductance (QSSPC) and microwave detected photo conductance decay (μWPCD).

At room temperature, in equilibrium, Fe_i is paired with substitutional boron. These pairs can be dissociated e.g. by illumination. Due to a large difference in recombination characteristics of Fe_i and FeB, different lifetimes are measured before and after illumination.

The Fe_i concentration can be calculated from these differences between dark and illuminated QSSPC measurements by[3]:

$$[Fe_i] = C(\Delta n, N_D) \times \left(\frac{1}{\tau_{dark}} - \frac{1}{\tau_{ill}} \right)$$

The lifetime measurements in this study were measured at injection level $\Delta n = 10^{15}$ cm^{-3}, to avoid both trapping and Auger recombination effects. The total error in lifetime measurements has been estimated to be 5% relative, which translates into the given errors in Fe$_i$.

RESULTS

The τ_{eff} after annealing for 90 and 180 minutes are depicted in Figure 1 and Figure 2. The reference wafers were not positively affected by annealing. Although we used multiple wafers of reference material with varying concentrations of Fe$_i$, only one dataset (with the highest concentration, around 10^{12} cm^{-3}) is shown. The other reference wafers had minority carrier lifetimes of approximately 20 and 60 μs, with corresponding interstitial iron concentration of 6×10^{11} and 5×10^{10} cm^{-3}. In case of the iron contaminated wafers, the effect is stronger for longer annealing time, but only so at 500 ^{o}C. The chromium contaminated wafers show much improvement for 800 ^{o}C anneals, but we see no clear dependence on time for that temperature. For chromium, the effect of annealing at 500 ^{o}C improves with longer times.
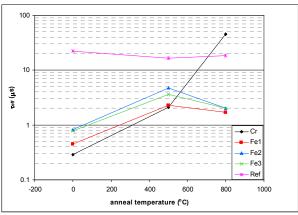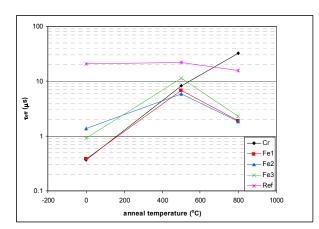

Figure 1: τ_{eff} after anneal of 90 minutes

Figure 2: τ_{eff} after anneal of 180 minutes

The [Fe$_i$] of the iron dominated wafers is depicted in Figure 3 and Figure 4. The [Fe$_i$] of the chromium contaminated ingot was not determined, because of the very low lifetime due to the CrB complex. The value for [Fe$_i$] is missing in some wafers, for instance Ref after 90 minutes anneal and Fe1 after 180 minutes anneal.. One of the characteristics of iron-boron dissocation is the cross-over point between the dark and illuminated lifetime-injectionlevel graphs. If this cross-over does not occur at ~2 × 10^{14} cm^{-3} injection level (for common wafer resistivities), the difference between the light and dark minority carrier lifetimes can not be attributed to the FeB complex[3]. Other effects, like trapping for instance, are equally strong, or stronger in wafers with a deviating cross over. Since we can measure Fe$_i$ in our samples when using a different process, we estimate that the [Fe$_i$] for the wafers missing from the graph 10^{11} cm^{-3} ± 10^{11}.

The references show mostly no effect of annealing on concentration of Fe$_i$. Only the reference with the highest concentration, shown in Figure 3, shows a decreased amount of Fe$_i$ after an anneal of 180 minutes at 500 ^{o}C, but this does not lead to increased τ_{eff}. The iron contaminated wafers show little response to the anneal at 800 ^{o}C, but the effect of an anneal at 500 ^{o}C is clear as suggested by Picket et al[4]. The [Fe$_i$] decreases approximately one order of magnitude after an anneal of 90 minutes, and approximately fifty times after an anneal of 180 minutes.
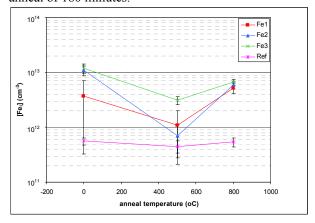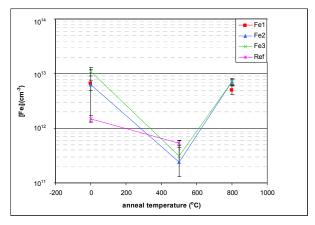

Figure 3: [Fe$_i$] after anneal of 90 minutes

Figure 4: [Fe$_i$] after anneal of 180 minutes

We measured μWPCD maps to see where the effect of the anneal step is strongest (see Figure 5). Note that we used a logaritmic scale between 0.1 and 100 μs in figure 5. The lifetime maps of Fe2 show homogenisation,

despite the fact that the QSSPC lifetime of Fe2 is very similar before anneal and after a 800 ^{o}C anneal. It is interesting to observe that some very low lifetime grains improve most strongly when annealed at 500 ^{o}C. This is even more clear in the difference map (see Figure 6).
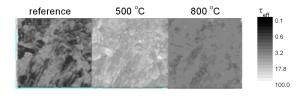

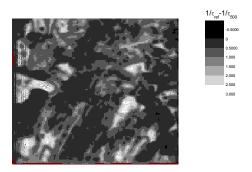Figure 5: τ_{eff} map of Fe2 after 180 minutes anneal

Figure 6: difference of the inverse lifetime maps of Fe2, reference versus 500 ^{o}C

Figure 7 shows the difference of inverse lifetime maps of the reference and the sample annealed at 800 ^{o}C in case of Cr. The grain boundaries do not improve as much as the grains.
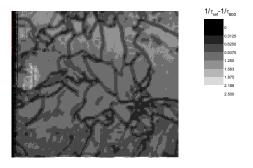

Figure 7: difference of inverse lifetime maps of Cr, reference versus 800 ^{o}C

Further experiments show that the result obtained by internal gettering is not maintained after treatment at high temperatures above 830 ^{o}C (see for example Figure 8). In particular, if internal gettering is followed by an industrial phosphorous emitter diffusion, the distinction between the annealed and non-annealed wafers disappears completely. Although the annealed wafers will probably still have a higher amount of precipitates as compared to the reference, neither the τ_{eff} measured by QSSPC nor the μWPCD maps show any effect on annealing.
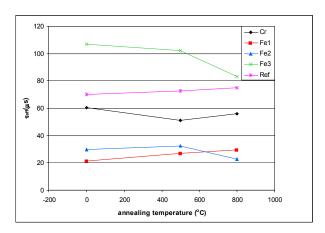

Figure 8: τ_{eff} after emitter diffusion of pre-annealed wafers. Shown on x-axis is the pre-anneal temperature (annealing time 90 minutes). Result after annealing only (before emitter diffusion) can be observed from Fig. 1

DISCUSSION

Since internal gettering is controlled by the diffusion of Fe_i, longer times are expected to yield better effective lifetimes and lower Fe_i. As the effects improve as an exponential over time, at some point the effect will saturate. Iron precipitates dissolve at 800 ^{o}C[5], so the increased growth of precipitates due to the increased mobility of the iron atoms is counter-acted by the dissolution process. The maximum precipitate growth has apparently been reached before 90 minutes, since we do not see any significant change in τ_{eff} or $[Fe_i]$ with longer times.

It is very likely that the internal gettering of Cr_i is dominated by a similar balance of diffusion precipitation and dissolution. The diffusion of Cr_i in silicon is slower than the diffusion of Fe_i[6], so it is expected that higher temperatures will improve gettering. Also, the dissolution of Cr precipitates apparently occurs at a higher temperature than the dissolution of iron precipitates, since at 800 ^{o}C we see no sign of Cr dissolution e.g. by a decrease of the lifetime. Rather, there is a strong effect of internal gettering.

Longer annealing times should yield better internal gettering results, under the assumption that internal gettering is the only phonomenon occurring. For the iron contaminated samples annealed at 800 ^{o}C this is not necessarily the case. This is probably due to the conflicting effects of precipitate growth and dissolution. Also the chromium contaminated sample shows no further improvement at an anneal of 800 ^{o}C for 180 minutes, relative to the 90 min anneal step. The mobility of Cr_i at 800 ^{o}C is higher than the mobility of iron at 500 ^{o}C [6], so it is expected that precipitate growth saturates faster for Cr_i at high temperatures.

Since the lifetime improvement of the wafers is mainly found in the intra grain areas, it seems that the interstitial metals are gettered to the grain boundaries. This is in agreement with the general consensus that the metals are gettered to crystallographic defects to form precipitates.

CONCLUSIONS

Fe_i and Cr_i can be transformed into precipitates by annealing treatments. This reduces recombination and enhances the minority carrier lifetime of the samples. We find an improvement of one order of magnitude for Fe-contaminated samples (but only so for samples with unusually high contamination), and two orders of magnitudes for Cr-contaminated samples. Most of the τ_{eff} improvement takes place in the intragrain areas, which supports the consensus that the interstitial metals are gettered to crystallographic defects to form precipitates.

In the case of Fe_i, an anneal temperature needs to be used at which the iron is highly mobile, but below a temperature where the iron precipitate dissolution becomes dominant. The same is probably true for Cr_i, but the mobility is lower and the dissolution temperature for precipitates is higher, so the optimum temperature for Cr_i is clearly higher than for Fe_i.

Unfortunately, most of the improvement from this internal gettering is lost after a subsequent phosphorous emitter diffusion.

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