Etch Pit Density Reduction in POCl₃ and Atmospheric Pressure Chemical Vapor Deposition-Gettered mc-Si

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Herein, the effects of gettering, temperature, dopant concentration, and metal contamination on the etch pit density (EPD) of an mc-Si material are studied. It is demonstrated that there is a reduction of EPD after gettering that is independent for varying etchants, thereby confirming the physical nature of this effect. The EPD analysis of wafers that are gettered on one wafer side, results in different EPD values for the two wafer sides. This finding constrains the possibilities for mechanisms of EPD reduction. The combined evidence of the experiments presented here supports the hypothesis that EPD reduction happens because the defect etching process for impurity-lean dislocations is different from dislocations decorated with impurities.

1. Introduction

The technique of atmospheric pressure chemical vapor deposition (APCVD) allows for cost-effective approaches to passivated emitter, rear totally diffused (PERT) and other advanced solar cell concepts. With the possibility of one-sided doping glass deposition and the separation of the doping glass deposition from the diffusion step, multiple high temperature steps can be combined into a single co-diffusion step. Co-diffusion gettering is known to increase the material quality of multicrystalline silicon,[1] and gettering[2] of the mc-Si material by means of phosphorous,[3,4] and boron-diffusion[5] are well researched. Although effects of phosphorous diffusion gettering on metallic contaminations have been studied and correlated with measurements of etch pit density (EPD),[6] there is a lack of literature on the interplay of gettering procedures with EPD measurements. While significant mobility of dislocations in the silicon crystal is expected only for temperatures much closer to the melting temperature[7] than what was used in the high temperature steps of this work, EPD seems to be affected by P-diffusion gettering processes.[8,9]

Findings presented here include evidence supporting the hypothesis that mobility of dislocations is not a requirement for an explanation of EPD reduction. With a combination of several experiments that demonstrate EPD reduction under variations of the diffusion gettering process on the one hand and EPD increase under certain conditions on the other hand, we aim to expand the knowledge on the working mechanism of defect etching and the interpretation of EPD measurements.

2. Sample Preparation

Two types of samples are studied here, both made from the same industry standard, boron-doped mc-Si with a resistivity of 1 Ω cm. By using wafers that, during wafering, are located right next to each other (so called sister wafers), we minimized systematic differences due to the change of the crystal and defect structure. The first sample type was prepared for measuring the effective minority charge carrier lifetime (τ eff) and interstitial iron concentration ([Fe i]),[10,11] and these results were combined with measurements of the EPD to obtain a complete picture of the material quality improvement due to the gettering step. These samples demonstrate a link between gettering and EPD reduction. With the second type of samples, the focus is solely on EPD; hence, surface passivation steps are skipped and preparation steps are modified on a per sample basis to study various possible influences on the EPD. Detailed aspects of the variations in sample preparation for these kinds of samples are discussed together with their associated results (Section 4).

Samples of the first type were subjected to wet chemical saw damage removal (9 μm per side), followed by a cleaning step in piranha solution (3 parts concentrated sulfuric acid, 1 part of 30% hydrogen peroxide) at 80 °C and a subsequent dip in diluted hydrofluoric acid. Samples destined for APCVD gettering were subjected to a deposition of a borosilicate glass (BSG) on one side, followed by a phosphosilicate glass (PSG) deposition on the other side using a roller-type APCVD from Schmid Group. Subsequently, a high temperature diffusion step at 840 °C for 75 min in nitrogen atmosphere was applied in a quartz tube furnace for creating the emitter and a p⁺ back surface field (BSF) in one single co-diffusion step. Doping glasses were removed in diluted hydrofluoric acid; the co-diffusion emitter and BSF were chemically removed as well (10 μm per side). After a further cleaning step, 70 nm of SiN:Hx were deposited via direct plasma-enhanced chemical vapor deposition (PECVD) on both sides of the wafers. After belt furnace firing at 850 °C peak set temperature, photoluminescence imaging characterization, calibrated via quasi-steady-state photo
3. EPD Analysis

Previous analyses of the EPD on mc-Si wafers have often relied on manual counting of etch pits in optical or scanning electron microscopy (SEM) images, if only small regions were of interest,[14] or EPD analyses relied on a calibration between EPD and the gray value of flatbed scanning images[8] or coherent light-scattering[9] for large-scale analyses. In this work, etch pits are detected and counted individually by high precision algorithmic analysis of optical microscopy image data of up to three large regions. The analysis code that is used here has made use (and extended the capabilities) of a previously published counting algorithm.[15] With this technique, the EPD in regions of mid and low EPD can be measured directly and with high spatial precision. Optical microscopy and SEM images taken from the same regions have demonstrated that the resolution achieved with the optical microscope is sufficient for the detection of individual etch pits (Figure 1); hence, EPD in mid and low EPD regions can be measured directly, i.e., without relying on a calibration process. Longer etching times lead to larger etch pits and higher contrast of etch pits in optical microscopy images. Since mc-Si material typically features regions of extremely high etch pit densities, even very briefly etched samples have regions in which individual etch pits are so close together that they overlap and form a single conglomerate structure. It is clear that it is not possible to count individual etch pits in such regions, containing no shapes that can be distinguished via their contrast (Figure 2). This clustering of etch pits results in a practical upper limit for EPD values that can be determined with the optical microscope. While regions of mid and low EPD can be measured calibration-free, this clustering of etch pits in practice requires that a calibration or a different means of constraining a degree of freedom has to be introduced for EPD measurements in regions of high EPD. EPD results presented here derive a calibration factor from an estimate of the expected size of etch pits after a certain defect etch process. Yet, the larger technical challenge for the analysis of high EPD regions is the distinction between structures that are grain boundaries and structures that are conglomerates of etch pits and, possibly, grain boundaries, too.

An etching time of 90 s with the Secco etch[13] combined with ultrasonic agitation at room temperature results in etch pits well suited for the detection in the optical microscope and subsequent algorithmic detection while not producing unnecessarily large...
etch pits. A good estimator for the lower EPD threshold of such clustered structures is obtained by uniformly distributing etch pits of a certain size (such as the median etch pit size) over the total area of the region, until it is completely covered. It is noteworthy that for comparison of samples with a different preparation history, e.g., a comparison between gettered and as-grown samples, this parameter, the expected etch pit size, should be a fixed value. If, on the contrary, expected etch pit size is derived from individual sample statistics, a change in measured EPD in high EPD regions would (likely) mean that the actual size distribution of etch pits has changed due to the preparation history. In fact, median etch pit size on a gettered sample and an as-grown sister sample can be significantly different.

Depending on the desired etch pit size (determined by the chosen etching time), etch pits begin to conglomerate for densities in the range of \(5 \times 10^6 \text{ cm}^{-2}\) to \(1 \times 10^6 \text{ cm}^{-2}\). However, etch pit size on mc-Si material is, among other things, grain dependent, and the distribution of etch pits is often far from uniform, so there is no hard limit on this value that applies for a large region of the same wafer. Here, the distinction criterion between individual etch pits and a conglomerate of etch pits is the size of a structure relative to the median size of all structures below a certain threshold. Conglomerates are weighted according to their relative size and thus counted as consisting of multiple etch pits of median size. The largest conglomerate structures in a wafer image are typically either a dislocation cluster (i.e., a region of extremely high EPD) or a grain boundary. Since EPD is typically used as a measure of dislocation density, it is important to identify grain boundaries and distinguish them from clusters. Several methods to do this have been tested, all of which start with dividing the largest structures into smaller pieces, which more often than not results in elongated line-like shapes for grain boundaries and round shapes for clusters. A distinction based on a threshold value on the eccentricity of a region is able to suppress most grain boundaries, and this method is used for grain boundary detection in this work.

It was noted that due to clustering of etch pits there is an upper limit for EPD values that are detectable after a certain etching time. It is noteworthy that the resulting images have a fixed lower limit of the EPD that depends on the bin size with which the density of etch pits is to be resolved. A physically meaningful bin size can be chosen using the minority charge carrier diffusion length as characteristic length scale for the bin width. However, in typical mc-Si material, there are regions of very high and low diffusion lengths in close proximity, so a compromise is necessary. If bins are very small (about the size of an etch pit), density calculation becomes meaningless. EPD plots in this work use square bins with a width of 62.5 \(\mu\text{m}\), corresponding to an area more than two orders of magnitude larger than the area of a single etch pit.

4. Results

4.1. Co-diffusion Gettering and EPD Reduction

Measurements of \(\tau_{\text{eff}}\), \([Fe_i]\), and EPD are used to compare sister wafers in the as-grown state on the one hand and wafers that were subjected to gettering on the other hand and then with samples subjected to the temperature load of the gettering process (Figure 3). The co-gettering step results in typical improvements in \(\tau_{\text{eff}}\) and \([Fe_i]\). EPD measurements after Secco etch, executed on the P-gettered wafer side, show that low lifetime and high \([Fe_i]\) regions typically correlate with regions of high EPD and that such regions remain inferior to their surroundings after co-gettering. Apart from this well-known gettering behavior, we additionally observe that EPD in regions of mid and low EPD is reduced by about one third after APCVD gettering. Comparable results of EPD reduction after P-gettering have been observed in the past. The high temperature step without the presence of a gettering sink appears to have no influence on EPD results (Figure 3). It is especially noteworthy that no EPD reduction is observed when measuring the EPD on the boron-diffused wafer side instead of the P-gettered side. Details of the influence of one-sided P-gettering on EPD are discussed in Section 4.3. To study whether EPD reduction after boron diffusion can be observed with higher dopant concentrations, one-sided boron-diffused wafers after a boron diffusion with a higher temperature are studied (Section 4.2).

4.2. EPD of One-Sided Boron-Diffused Wafers

A comparison between the EPD before and after APCVD glass based boron diffusion has been carried out to check for effects of boron diffusion on the EPD separately from the influence of P-gettering. Three samples, an as-grown sample, a sample that was subjected to a one-sided APCVD B-glass deposition and a subsequent diffusion (920 °C peak temperature for 30 min) followed by chemical removal of the emitter (10 \(\mu\text{m}\) material per wafer side), and a third sample that was only subjected to the temperature load of this boron diffusion, have all shown similar EPD levels after defect etching with the Secco etch (samples not shown). Based on the idea that the surface dopant concentration could contribute to the effect of EPD reduction, this boron diffusion was not optimized for its gettering performance but was chosen because of the resulting emitter structure. On the one hand, the depth of the doping profile is similar in depth to the emitter of the P-gettering processes that was used throughout this article. On the other hand, significantly higher surface concentrations of boron atoms (in the range of \(4 \times 10^{19} \text{ cm}^{-3}\)) compared to the co-diffusion process studied previously are achieved with this diffusion. Hence, a more meaningful comparison to the phosphorous diffusion with surface concentrations of around \(2 \times 10^{18} \text{ cm}^{-3}\) is achieved. However, regarding the gettering performance, minority charge carrier lifetime measurements of passivated samples from this boron diffusion have even shown a reduction of \(\tau_{\text{eff}}\) compared to the as-grown state. The finding that this boron diffusion did not result in a reduction of the EPD is slight evidence for the hypothesis that the impurity concentration (and hence the gettering efficiency) is contributing to the EPD reduction effect.

4.3. EPD Reduction after One-Sided P-Gettering

Experiments featuring one-sided deposition of phosphorous doping glasses with the APCVD and subsequent EPD analysis of both wafer sides have shown that EPD reduction occurs only on that side of the wafer on which the doping glass has been deposited (Figure 4b,c). The EPD of the wafer side that was
not covered by a doping glass during diffusion remains unchanged compared to the as-grown state (Figure 4a). This one-sided EPD reduction is an evidence that strongly constrains possible explanations for the mechanism of EPD reduction, as is discussed in Section 5. Naturally, this finding suggests that the distance between the highly doped region and the EPD measurement surface might be an important variable, comparable to results that show EPD reduction limited to

Figure 3. Overview of the gettering efficacy and corresponding EPD measurements for an as-grown, a temperature reference, and an APCVD-gettered sample. APCVD gettering shows considerable improvement in $\tau_{\text{eff}}$ and [Fe$_i$], while the effects of the temperature load without a gettering sink are minute in comparison. The number of etch pits after defect etching with Secco etch is reduced strongly in regions of mid and low EPD after gettering, but unaffected by the temperature process.

Figure 4. EPD maps (top row) and histograms of EPD (bottom row) after Secco etch. Columns (b) and (c) display results from the front and back sides of the very same wafer after one-sided gettering with an APCVD-based phosphorous doping glass. The side of the wafer on which the doping glass was deposited exhibits EPD reduction (c), while the opposite wafer side that was blank during diffusion does not display EPD reduction (b) in comparison to the as-grown sample (a). As discussed in Section 4.6, sample (d) has been treated in an RTP furnace before the defect etch process, but was otherwise treated identically to (c). The resulting increase in EPD due to the RTP furnace treatment is interpreted as a result of contamination, as discussed in Section 5. Only data in the regions corresponding to the dashed rectangle in the EPD map (a) have been used in the creation of the bottom row histograms, to avoid the influence of regions affected by wafer breakage (column a) or suboptimal surface preparation (column b).
a region close to the sample surface after high temperature annealing.\cite{17}

### 4.4. EPD Measured at Varying Distances to Phosphorous Emitter

It was shown that one-sided P-gettering and emitter removal result in one-sided EPD reduction. By skipping the emitter removal, EPD measurements closer to the region of high phosphorous concentrations are possible. It turns out that the reduction in EPD on the side containing the phosphorous doping glass is not changed, regardless of whether the EPD is measured close to the phosphorous-doped surface or whether 10 μm of surface material is removed before the EPD measurement.

Sample preparation for polishing requires glueing the wafer to a sample holder surface, which often results in a slightly twisted wafer surface after glueing. Thus, a typical polishing process does not affect the whole surface of the wafer at the same time, but rather some areas are polished first, and with more polishing time, these polished areas grow to cover the whole wafer. On a further sample, this circumstance has been used to analyze the EPD as close as possible to the emitter by stopping the mechanical polishing process as soon as the first regions of the wafer have been successfully polished. On areas that are close to the unpolished regions on this partially polished wafer, a minimal amount of material for a successful EPD analysis has been removed. In these regions, the EPD is measured as close as possible (with the method described here) to the emitter structure, although it has to be noted that a typical polishing process removes material in excess of the emitter depth.

Neither in the case of low or mid EPD regions nor in the case of clustered regions of high EPD do results from surface close regions differ from results in sister samples, for which the EPD was measured at least 10 μm further below the surface. EPD reduction is of similar strength when measured close to the emitter surface and 10 μm below.

In a different attempt to maximize the dopant concentration on the surface, an APCVD glass was deposited on a sample with an already polished surface. However, polishing is a process for which metallic contaminations cannot be avoided, so the high temperature diffusion step could not be carried out in the clean environment of a standard quartz tube diffusion furnace. While EPD results after Secco etch show some EPD reduction for this sample, when compared with an as-grown sister, EPD reduction is noticeably less than after diffusion in a clean environment. These results are discussed in more detail in Section 4.6.

### 4.5. EPD Reduction for Various Defect Etch Solutions after POCl₃ Gettering

To exclude that EPD reduction is a feature specific to a certain defect etch solution, a comparison of EPD reduction on sister wafers under variation of the used etch solution (Secco,\cite{13} Schimmel,\cite{18} Sopori,\cite{19} and Wright etch\cite{20}) has been carried out. Etch times of 60 s for the Secco etch, 90 s for the Schimmel etch, 240 s for the Wright etch, and 80 s for the Sopori etch were used. The Secco and Sopori etches have been subjected to ultrasonic agitation. The Sopori etch was cooled to 0 °C with an ice bath before and during the etching process. A time series experiment with these etch solutions has demonstrated that a minimal etching time is necessary to reveal a stable number of etch pits in mid and low EPD regions. Increased etching times yield constant EPD results in mid and low EPD regions until an increase by a factor of 1.5 or 2 in etching time. As the area fraction of clustered regions increases with larger etch times, the aforementioned etching times are chosen to be about 20% above the previously mentioned minimum value.

For gettering, here, an industry standard POCl₃ diffusion was used, whose gettering properties on this material are well known\cite{18,19}. Results show a comparable overall EPD for all the different etching solutions as well as similarly strong EPD reduction for all etchants (Figure 5). EPD reduction as an artefact of a specific defect etching solution can thus be excluded. In addition, this demonstrates that EPD reduction occurs for POCl₃, as well as for APCVD-based gettering. Upon closer inspection, some differences between the results of the various etching solutions can be observed. While some of these differences are due to specifics of the processing or analysis (i.e., regions show lower EPD due to contact with the sample carrier during etching or other technicalities), some of the observed differences are possibly due to the different behaviors of the various etchants. Yet, EPD reduction is apparent for all tested etchants.

### 4.6. Contamination Experiments and EPD

#### 4.6.1. Reversing EPD Reduction via Contamination

A sample that was polished first, and only then an APCVD PSG was deposited on the polished surface, was subjected to a high temperature step in a rapid thermal processing (RTP) furnace to facilitate a diffusion gettering process. Unlike the quartz tube diffusion furnace, this RTP furnace has been routinely used for metallized samples of all kinds. Its use here is required, since mechanical polishing releases finely dispersed iron. The total time in the RTP furnace amounts to 155 min of treatment in nitrogen atmosphere and consists of 30 min ramp up from 620 °C to a peak of 840 °C, held for about 75 min, followed by a ramp down to 620 °C over the course of 50 min. These process times imitate a typical diffusion gettering process. This RTP furnace–treated wafer, compared with an as-grown reference, exhibits slight EPD reduction after Secco etch, mainly in regions of low EPD in the as-grown state. However, EPD reduction here is much less than what is seen after a similar diffusion in a clean environment.

A further experiment uses an APCVD P-gettered sample prepared identically to the sample shown in Figure 4c, except that after mechanical polishing of the getter wafer side, the sample was treated in the aforementioned RTP furnace process. This sample shows considerably less EPD reduction (Figure 4d) in contrast to the otherwise identically processed sister wafer (Figure 4c). As the isolated influence of this high temperature step, when performed in a clean environment, does not change the EPD from the as-grown state (Figure 3), either the contaminated environment of the RTP furnace or some difference in the behavior of gettered and as-grown material during temperature treatment must be causing the observed increase in EPD. A further experiment yields results similar
to this finding: A P-gettered sample that has already been subjected to an EPD analysis was placed in the RTP furnace for contamination and subsequently subjected to a second defect etching and EPD analysis. This resulted in a considerable amount of newly formed etch pits observable under the optical microscope. However, this process damaged the wafer surface considerably so that a software-based analysis was not possible afterward.

4.6.2. Increase of EPD via Contamination

The EPD of an as-grown sample was compared with the EPD of a sample that was placed in the previously described RTP furnace process, resulting in an increase of EPD over the as-grown values (Figure 6). As temperature treatment in a clean environment has not resulted in changes of the EPD (Figure 3), we interpret the increase in EPD after RTP furnace treatment reported in all of Section 4.6 as a consequence of contamination.

4.6.3. Etch Pit Details after Contamination

It has to be noted that some of the etch pits in regions of increased EPD after contamination in the RTP furnace appear different from etch pits of samples that have not been treated in the RTP furnace (Figure 7). Using focused ion beam (FIB) ablation, cross-sections of these two types of etch pits have been analyzed, confirming that the two types of etch pits differ in depth by about a factor of 4–5.

5. Interpretation

P-gettering reduces the number of etch pits only on that side of the wafer that is covered by a gettering sink during diffusion, whereas on the opposite wafer side, EPD remains unchanged. This is strong evidence against the hypothesis that dislocations could be mobile in the applied thermal conditions, a behavior expected only for temperatures much closer to the melting point...
of silicon than what was used here during high temperature diffusions (840 °C and 920 °C). Isolation of these high-temperature steps does not result in EPD changes. Large areas of grains of mid and low EPD of the ungettered side of the wafer are reduced to a measured EPD of zero on the gettered wafer side. If it is assumed that these grains contain dislocation lines that go along the direction of crystal growth, i.e., the same dislocations contribute to the EPD on both wafer sides, then it can be excluded that dislocation mobility and subsequent pairwise annihilation of dislocations with opposite burgers vector is the cause for EPD reduction, since only one wafer side is affected by EPD reduction. One-sided EPD reduction after one-sided P-gettering clearly suggests that the phosphorous doping source has some influence on either defects and dislocations in the crystal or on the process of defect etching itself. This influence can be either the removal of substances from the wafer (the gettering process) or it can be the addition of new substances into the wafer (the in-diffusion process). Candidates of substances that are introduced to the wafer are phosphorous, oxygen, or silicon self interstitials. The finding that EPD reduction occurs with phosphorous doping but not with boron doping excludes oxygen or silicon self-interstitials from causing the EPD reduction effect, since both species are present in comparable amounts in both cases (the number of silicon self-interstitials is assumed to be proportional to the amount of boron or phosphorous entering the silicon wafer). EPD reduction is observed despite the removal of at least 10 μm of surface material on both sides of the wafer. This is some evidence against the notion that the presence of phosphorous plays a role in the EPD reduction effect. The absence of differences in EPD when comparing phosphorous-diffused wafers, for which the EPD was analyzed as closely as possible to the emitter surface, with regions that are at least 10 μm below the emitter, is further evidence against phosphorous itself playing a role in the EPD reduction effect. However, a faster diffusion of phosphorous along dislocation lines could in principle facilitate a very localized accumulation of phosphorous in high depths in or around dislocations. But the observation that EPD reduction does not happen in high EPD regions is further evidence against phosphorous playing a direct role in this phenomenon. All the results discussed earlier agree with the following hypothesis: Dislocations that are lean of impurities are not significantly etched by the applied defect etch solutions, but only dislocations that are decorated with impurities are revealed by defect etching. One-sided EPD reduction would thus be a consequence of lower contamination close to the gettering sink. The boron diffusion sample exhibits no EPD reduction because no

Figure 7. SEM in-lens detector image of Secco etch pits in a region that has shown an increase in EPD after RTP furnace treatment. While the region marked “A” contains etch pits typical of a Secco etch, similar to what is shown in Figure 1, the etch pits contained in the region marked “B” have a comparatively stronger SEM signal in the center. Cross-sections of etch pits from these regions have shown that etch pits similar to those shown in region “A” are 4 to 5 times deeper than etch pits from region “B.”

Figure 6. EPD maps (top row) and histograms of EPD (bottom row) of an as-grown (left) sample and an RTP furnace treated, but otherwise identically processed, sample (right) after Secco etch. Regions of low EPD in the as-grown wafer appear as regions of mid EPD (consisting of nonclustering, individual etch pits) after RTP furnace treatment. An increase in the area fraction of regions with EPD between 1 × 10⁵ cm⁻² to 8 × 10⁵ cm⁻² together with a decrease in low and zero EPD regions is observed.
significant gettering effect was achieved. The finding that temperature treatment in a metal-contaminated RTP furnace reduces the EPD reduction effect on P-gettered wafers is explained by re-contamination/decoration of dislocations, either due to the contaminated environment of the RTP furnace (external contamination) or due to redistribution of the (ungettered) back side of the wafer (internal contamination). The increase of EPD in the as-grown sample after similar RTP furnace treatment suggests the presence of some impurity-lean dislocations in the as-grown material and is strong evidence for external contamination. EPD reduction not happening in regions of high EPD can be interpreted as a failure to reduce the metal concentration to a level as low as in regions exhibiting an EPD that is an order of magnitude lower.

6. Conclusion

It was shown that phosphorous gettering goes along with a reduction of the etch pit density. EPD reduction has been observed for four different defect etching solutions and for both, POCl$_3$ as well as APCVD-based P-gettering, demonstrating that this effect is a consequence of P-gettering and an effect not specific to a certain defect etchant. The evidence from the various experiments presented suggests that EPD reduction is not a mechanism that actually removes dislocations from the crystal. Rather, the evidence supports the hypothesis that only dislocations that are decorated with impurities can be revealed by the applied defect etch reactions; hence, EPD reduction after getting is a consequence of the removal of impurities from dislocation sites and the defect etching process itself. Following this reasoning, EPD reduction observed after defect etching could also be used as a tool for measuring gettering efficacy that, unlike the metric of minority charge carrier lifetime, distinguishes true external gettering from internal gettering at defect sites within the wafer.

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Conflict of Interest

The authors declare no conflict of interest.

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