ABSTRACT: We have performed a systematic variation of the wet chemical oxidation and the subsequent oxide etching steps during the cleaning of Czochralski (CZ) single crystalline silicon wafers prior to surface passivation. The optimization of these preconditioning steps was carried out on saw-damage etched or textured Si wafers subsequently passivated by amorphous silicon nitride ($a$-SiN$_x$:H) or chemical passivation by an iodine ethanol (IE) solution. Measuring the carrier lifetime using the spatially resolved microwave detected photoconductance decay, we monitored the impact of the wet-chemical surface conditioning on the surface morphology and wafer base doping type. For damage etched surfaces in alkaline potassium oxide solutions and passivated by iodine ethanol, an optimum surface passivation is obtained by omitting the last water rinse (as used in the standard clean) and adding a hot water treatment as final step in the cleaning procedure. While this result was found for both $p$-type and $n$-type wafers, suggesting that the passivation mechanism is based on the saturation of dangling bonds, a strong dependence on the doping type was observed for the passivation by $a$-SiN$_x$:H. Prior to passivation by $a$-SiN$_x$:H, the best preconditioning for $n$-type was achieved by adding a hot water treatment and subsequent etching of the oxide by hydrofluoric acid (HF). For $p$-type however, no improvement was achieved with respect to the standard cleaning step. This dependency on the base doping type could be attributed to the passivation mechanism of $a$-SiN$_x$:H based on the field effect. By employing ammonium fluoride as final etching solution instead HF, followed by hot water treatment, compared to the standard treatment, an improvement of the lifetime can be observed for both surface structures, indicating that the surface micro-roughness can be reduced and the contamination can be removed.

Keywords: wet-chemical surface pre-treatment, interface state density, CZ silicon, surface passivation, damage etch, texture

1 INTRODUCTION

Czochralski (CZ) single crystalline silicon accounts for more than 40% of the photovoltaic market [1]. A decisive precondition to the development of economically attractive silicon solar cells is the wafer surface passivation. To prepare the surface of a silicon substrate for passivation, a saw damage layer has to be etched off. The result of this dependency on the base doping type could be attributed to the passivation mechanism of oxide by hydrofluoric acid (HF). For $p$-type however, no improvement was achieved with respect to the standard cleaning.

Two different substrate surface configurations were processed to investigate the influence of wet-chemical pre-treatment on surface passivation, (a) surface after saw damage etch and (b) textured surface. Aiming to minimize $D_i(E)$ and consequently the surface recombination velocity, we have investigated different cleaning procedures for boron doped $p$-type and phosphorous doped $n$-type CZ silicon wafers with (100) orientation by using a treatment in hot deionised water (DIW) as final oxidation medium or replacing diluted hydrofluoric acid HF (2%) by ammonium fluoride (NH$_4$F) as oxide etching solution. After surface passivation by $a$-SiN$_x$:H or chemical passivation by an iodine ethanol (IE) solution, the effect of surface pre-treatment on the interface passivation was characterized by spatially resolved microwave detected photoconductance decay ($\mu$W-PCD) [5]. The direct analysis of preparation-induced surface structures and their influence on $D_i(E)$ was carried out by means of scanning electron microscopy (SEM) and surface photovoltage method (SPV) [6].

2 EXPERIMENTAL

The investigations were carried out on different $n$-and $p$-type CZ Si wafers from different manufacturers. As $n$-type wafers we used phosphorous doped high-quality magnetic CZ (MCZ) silicon with a thickness of 300 µm and a resistivity of 2.5 to 3.0 Ωcm. This material is known to feature a low degree of contamination (e.g., oxygen and carbon) and hence a high bulk lifetime. The investigated p-type wafers were extracted either from the center and edge of a low quality solar-grade silicon ingot or from a standard ingot as used in the industrial CZ silicon solar cell manufacturing. The resistivity ranges between 3 and 6 Ωcm corresponding to a doping level from 1.3 to 4.7·10$^{15}$ cm$^{-3}$.

Figure 1: Overview of the wet-chemical pre-treatment steps following surface structuring with KOH or KOH/IPA prior to surface passivation by a solution of iodine ethanol or PECVD $a$-SiN$_x$:H.
damage etching using diluted potassium hydroxide (KOH) resulting in an etch removal of 12 to 15 µm on each side, and (b) surfaces textured with randomly distributed pyramids produced by etching in a solution of KOH and isopropanol (KOH/IPA). As a reference process we used the well known RCA cleaning process [7] consisting of the standard cleans SC-1 (NH4OH : H2O2 : H2O) and SC-2 (HCl : H2O2 : H2O). This was followed by two types of oxide etching solutions: (i) diluted HF and (ii) NH4F (48 %) at room temperature (RT). For some samples, an additional rinsing and oxidation step using hot DIW (80°C, 6 min) was added.

For surface passivation, we used either an iodine ethanol solution (I/E) solution or silicon nitride. For I/E, the pre-treated surfaces were spread with the solution and immersed in an airproofed plastic bag, as described in ref. [8]. Otherwise, to test the suitability of pre-treatment under technological conditions, the surfaces were passivated by means of the plasma-enhanced chemical-vapour deposition (PECVD) of Si-rich hydrogenated amorphous Si nitride (a-SiN_x:H) films on both wafer surfaces in an AK 1000 PECVD reactor [9]. The microwave detected photoconductance decay (µW-PCD) was used to determine the spatially resolved effective charge carrier lifetime [5] (referred to thereafter as lifetime). The SPV technique was utilised to measure \( D_\text{it}(E) \) as recently specified in ref. [3,6].

3 RESULTS AND DISCUSSION

3.1 Influence of surface morphology on the interface state density \( D_\text{it}(E) \)

The interface recombination velocity, which can significantly reduce the efficiency of solar cells, is mainly affected by the density and the character of interface states. These states are localized in an interlayer extended over only a few Ångstroms and result from Si dangling bond defects with different back-bond configurations. To gain insight into the relationship between preparation-induced structural imperfections at Si substrate surfaces and the distribution of interface states over the bandgap of silicon surface, \( D_\text{it}(E) \) was measured for (a) as-cut wafers, (b) after saw damage etch and (c) with alkaline texture. The morphology of these structures as visualized by means of SEM is shown in Fig. 2.

![Figure 2: SEM micrographs (tilted view) of (a) as-cut wafer, (b) wafer after saw damage etch and (c) wafer with alkaline texture.](image)

The energetic distributions of interface states \( D_\text{it}(E) \) obtained on these surfaces by field depended SPV measurements are given in Fig. 3. The minimum value of the energetic distribution of interface states \( D_{\text{it,min}} \) is commonly used in silicon device manufacturing, to characterize the electronic quality of surfaces and interfaces. The very high value of \( D_{\text{it,min}} \geq 2 \times 10^{13} \text{cm}^{-2}\text{eV}^{-1} \) (Fig. 3 curve a) obtained on the as-cut wafer surfaces, was significantly reduced by saw damage etching (Fig. 2b) to \( D_{\text{it,min}} \leq 2 \times 10^{12} \text{cm}^{-2}\text{eV}^{-1} \) (Fig. 3, curve b). As shown in Fig. 2b the KOH etched surface is characterized by flat, extended (20 to 50 µm) Si(100) structures.

![Figure 3: Interface state density on CZ Si solar cell substrates obtained by SPV measurements on (a) as-cut wafers, (b) after saw damage etch in KOH solution and (c) after texturization by anisotropic etching of pyramids in KOH/IPA.](image)

The alkaline texture generates randomly distributed pyramids on Si(111) crystal facets and obviously more roughness (Fig. 2c) increasing the density of states up to \( D_{\text{it,min}} \leq 5 \times 10^{12} \text{cm}^{-2}\text{eV}^{-1} \) (Fig. 3, curve c).

3.2 Effect of the pre-treatment on the performance of subsequent passivation of damage etched surfaces by I/E solution

Fig. 4 illustrates the influence of the surface pre-treatment steps on the passivation quality. The figure exemplifies histograms corresponding to 2D lifetime maps obtained on n-type CZ wafers passivated with I/E after different wet-chemical pre-treatment steps. The RCA treated interface without HF dip (V3) is characterised by high densities of states resulting from very aggressive oxidizing solutions, which produce defect-rich and often contaminated wet-chemical oxides [7]. The high interface recombination rate can be mainly reduced applying the standard procedure HF dip and subsequent short DIW rinse at RT (V5). Significantly higher values of lifetime were achieved, using a hot DIW treatment subsequent to the HF dip (V6).
In hot water, a non-aggressive layer-by-layer oxidation takes place resulting in a smoother, defect-poor interface with lower density of interface states [2]. Obviously, this is the best surface condition for subsequent passivation by I/E, which relies mainly on the saturation of dangling bonds. As also shown in Fig. 4, the final removal of the hot DIW grown oxide layer by a further HF dip (V7) leads to an H-terminated surface, which lowers the lifetime of I/E passivated interfaces.

Figure 4: Lifetime distribution (histograms) over the wafer surfaces (here n-type wafer after damage etch as example) after different sequences of wet-chemical steps and subsequent passivation with iodine ethanol solution (I/E).

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Figure 5: Effective lifetime $\tau_{\text{eff}}$ measured by µW-PCD on KOH etched p- and n-type substrates after various pre-treatments and subsequent passivation by I/E. The p-type wafers were extracted from the center and one edge of a CZ single crystal.

Fig. 5 plots the results of lifetime measurements obtained after various pre-treatments and subsequent passivation by I/E of n-type (MCZ) and p-type wafers. It is clearly seen that for both doping types the highest lifetime values can be obtained by hot DIW treatment (RCA + HF + hot DIW) prior to passivation (V6). The etching of the chemical oxide grown during hot DIW (V7) and the abandonment of SC-2 process (V1 and V2) decreases the lifetime values to the same degree. These results, obtained independently on the doping types confirm the assumption, that the passivation effect, utilizing I/E solution, is based on saturation of dangling bonds. Note that the simplification of the clean process through the replacement of the SC-2 by a hot DIW treatment also results in an acceptable passivation level with an environmental and economical benefit.

3.3 Comparison between the passivation behaviours of I/E and $a$-SiN$_x$:H films

The passivation by I/E is commonly used as an easy-to-handle technique for passivation during lifetime measurements, carried out to control wafer quality in the technological process. Since $a$-SiN$_x$:H is used for the same purpose and is furthermore the mostly used passivation layer used in the crystalline silicon photovoltaics, it is of primary importance to optimize the surface preconditioning of CZ silicon surfaces also for subsequent deposition of $a$-SiN$_x$:H. Fig. 6 summarises the results of lifetime measurements obtained on p-type wafers extracted from the center of the low quality silicon ingot used in the pre-
vius experiment as well as on n-type (MCZ) wafers. In this experiment all wafers were damage etched which leads to surfaces as illustrated in Fig. 2b. After repeating the same precondition steps as in Fig. 5, the wafers were subsequently passivated either by I/E or by a-SiN_x:H.

For p-type substrates, generally the highest lifetimes were obtained on a-SiN_x:H passivated interfaces after a completed RCA process. Although the best results were obtained by standard RCA + HF treatment, the omission of the last HF dip serving to etch the oxide grown during SC-2 resulted in a considerable improvement with respect to I/E passivation and this is also valid for n-type material. The further modification of this pre-treatment by hot DIW oxidation (V6) brought no beneficial effect on p-type and even a worsening the passivation quality on n-type substrates compared to standard RCA clean. This can be attributed to the very different passivation mechanism of a-SiN_x:H, which is based on the band bending at the substrate surface caused by fixed positive charges in the a-SiN_x:H film (field effect passivation). This positive charge is supposed to be strongly influenced by the unavoidable growth of a silicon oxide film, which turns to an oxinitride at the interface below the growing a-SiN_x:H film [10, 11]. The hot DIW grown oxide does not seem to provide the suitable charge properties required to generate the band bending. This can be confirmed by the fact that etching of oxides results in a better passivation of p-type silicon (compared to the unetched samples) and even in the best passivation of n-type by a-SiN_x:H (RCA + HF + hot DIW + HF).

The cancellation of SC-2 process (V1 and V2) leads to the lowest effective lifetime of p-type silicon, as we assume, due to the recombination losses caused by remaining surface contaminations. These contaminations due especially to metal impurities existing in the less pure feedstock or introduced during ingot and solar cell fabrication are known to impact severely the charge carrier lifetime in p-type silicon [12]. Since metallic impurities are known to be removed effectively by SC-2 process, this step is necessary for the preconditioning of p-type CZ silicon surfaces prior to any passivation mechanism. This effect has a less pronounced drawback on n-type silicon, which is known to be more resistant to this kind of contamination [13].

3.5 Influence of surface texture on the efficiency of surface pre-treatment

The aim of wet-chemical pre-treatment is the removal of damaged surface layers and the further decrease of surface micro-roughness on the atomic scale. The influence of various sequences of wet-chemical cleaning, oxidation and oxide removal steps (which are summarized in Fig. 1) on lifetime distribution was investigated for both surfaces, saw damage etched in KOH as well as textured in KOH/IPA.

Fig. 7 depicts results of lifetime measurements obtained on p-type wafers with the two surface structures after different sequences of wet-chemical steps and subsequent passivation with I/E solution or PECVD a-SiN_x:H. The effect of different sequences of wet-chemical pre-treatment steps on saw damage etched and textured CZ p- and n-type solar silicon wafers prior to surface passivation by iodine ethanol solution was investigated by µW-PCD and SPV measurements.

For the passivation by iodine ethanol solution (I/E), it was shown that the quality of surface passivation can be mainly improved by an optimized wet-chemical pre-treatment. First of all, the substitution of the last water rinse at room temperature by a hot water treatment subsequent to SC-2 process, results in improved surface passivation of damage etched p- and n-type wafers, contrast, on textured surfaces the omission of DIW rinsing leads to lower lifetimes. Both can be explained by the counteracting effects of two processes caused by DIW rinsing: the removal of chemical reaction products, which leads to a clean, hydrogen-terminated surface and the subsequent initial oxidation of this clean surface. On the pyramids of textured substrates, a clean surface with higher lifetime can only be achieved by DIW rinsing. On the comparatively flat surface of KOH etched substrates however, the rinsing leads to oxidation-induced defects, higher density of states and lower lifetime values. In order to decrease surface micro-roughness on the atomic scale, for the first oxide removal step the HF-dip was replaced by NH_4F treatment. Without rinsing in DIW this treatment RCA + NH_4F (V8) results in a drastic decrease of the lifetime probably due to surface contamination by ammonium salts [14]. To dissolve these contaminations the substrates were subsequently treated in hot water for 6 min (V9) followed by a HF-dip to remove the water-induced surface oxide (V10). The highest values of lifetime were obtained applying these treatments followed by a final short DIW rinsing at room temperature: RCA + NH_4F + hot DIW + HF + DIW (V11).

Figure 7: Lifetime distribution over the area of representative p-type samples from the investigated ingots obtained on wafer with the two surface structures - shown in Fig. 2b and Fig. 2c - after different sequences of wet-chemical steps and subsequent passivation with iodine ethanol solution.

4 CONCLUSION

The effect of different sequences of wet-chemical pre-treatment steps on saw damage etched and textured CZ p- and n-type solar silicon wafers prior to surface passivation by iodine ethanol solution or PECVD a-SiN_x:H was investigated by µW-PCD and SPV measurements.
evidencing the assumption that the passivation is related to the saturation of dangling bonds.

Comparing as-damage etched with textured surfaces, first results show a significant effect achieved on saw damage etched p- and n-type substrates by omitting the last water rinse at room temperature (DIW) which is known to generate oxides with higher defect density. On textured surfaces, however, the omission of the water rinsing step after HF-dip results in a strong decrease of the lifetime as the macroscopic surface roughness impeded the complete removal of HF solution and reaction products from the last oxide etching process. An additional improvement of lifetime was achieved on saw damage etched and textured p-type substrates after the cleaning sequence RCA + NH$_4$F + hot DIW due to reducing the micro roughness of the surface during the NH$_4$F treatment. Subsequently, the rinsing in hot water solves and removes the ammonium salts formed during the reaction of the oxidized wafer surface with NH$_4$F.

As to the surface passivation by a-SiN$_x$:H, the impact of the pre-conditioning steps depends strongly on the doping type. While no improvement in the surface passivation of p-type has been reached with respect to the standard clean (RCA + HF), n-type responded very positively to the step V7 (RCA + HF + hot DIW + HF). In addition, the replacement of SC-2 by hot DIW resulted in the same effect as standard clean (RCA + HF) with the exception for mostly all configurations (exception: I/E passivated p-type)

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