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Metal Surface Contamination during Phosphorus Diffusion

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Abstract

We present work on the impact of surface contamination before phosphorus diffusion on solar cells and life-time samples. Metal surface contamination on KOH / IPA textured Cz wafers was measured by the Sandwich-Etch ICP-MS technique. High surface contamination, especially of Cu, was found directly after texturing, which is attributed to low solubility of metals in diluted, non-oxidizing alkaline solution. Different contamination levels were reached by applying standard cleaning procedures such as HCl / HF dip sequences and the piranha etch. The emitter profiles that were tested ranged from heavy diffusions of 45 $\Omega$/sq to shallow diffusions of 120 $\Omega$/sq. It was found that threshold values which obviously impact life-times and solar cell performance (Voc) were much higher than expected.

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1. Introduction

Metal surface contamination is well-known to play an important role in semiconductor processing. [1] However, no studies on threshold values for surface contamination on silicon surfaces before standard industrial high temperature processes for solar cell processing, such as diffusion and surface passivation exist. To find limiting concentrations on solar cell performance the influence of surface metal contamination on the diffusion process was investigated.

2. Design of the Experiments

In order to vary contamination levels KOH / IPA textured Cz wafers were cleaned using different cleaning procedures (see Fig. 1).

Fig. 1. Cleaning sequence used in both experiments (DI water dips in between every step). Groups were separated at 1., 2., and 3.

High surface concentrations were obtained right after texturing. HCl / HF dips and piranha clean were used to reduce these concentrations. The surface concentrations of the different groups were measured using the Sandwich-Etch ICP-MS technique. [3] Two experiments were carried out (Fig. 2 (a) and (b)). In the first experiment the influence of the different cleaning procedures on symmetrical lifetime samples and standard screen-printed solar cells was measured. Three differently cleaned groups of KOH / IPA textured p-type 1.6 Ωcm Cz wafers were diffused in three consecutive 65 Ω/sq diffusions in a diffusion tube furnace. To ensure comparability of the three diffusions the wafers were placed in the same boat positions, and wafers for sheet resistance measurements were placed at the beginning, in the middle, and at the end of each batch. The PSG was removed in a batch process using 2 % HF. The cleaning step after PSG etching was applied to remove potential back-contamination from the PSG etching (HCl / HF), and to etch back (piranha clean) the emitter. The etch-back was thought to be necessary to remove – at least parts of – the potentially metal-rich dead layer, and therefore, to distinguish between surface effects and the effect of contamination in the emitter region. In addition to the solar cells, lifetime samples were prepared similar to Experiment 2.

Fig. 2. (a) Process flow of Experiment 1; (b) process flow of Experiment 2
In Experiment 2 the influence of high metal surface concentration on four different diffusion profiles (45, 55, 80 and 120 Ω/sq) was compared. For this purpose symmetrical life-time samples (SiN x – n⁺ – p-type base – n⁺ – SiN x) from 0.8 Ωcm KOH / IPA textured wafers were prepared. For each emitter group a reference diffusion with cleaned wafers at the two ends of the diffusion boat (Fig. 2 (b)) was followed by a test diffusion with cleaned reference wafers also at the gas inlet and non-cleaned samples at the gas outlet in order to avoid potential cross contamination. Again the PSG was removed and the HCl / HF and piranha clean were applied.

3. Results

3.1. Surface concentrations

High metals surface concentrations were measured right after the KOH / IPA texturing (Fig. 3). The high concentrations are attributed to the low solubility of most metals in diluted KOH [2]. We assumed that most of the contamination resulting from the wire sawing process precipitates on the surface of the wafer during the etching process. Highest concentrations are found for Cu ranging from 7E13 – 2E14 atoms/cm². Fe, Ca and Al are also found in relatively high concentrations in the range of 1E12 atoms/cm². Comparing the two experiments it can be stated that concentrations differ by a factor of five in the case of Cu and by a factor of about two for the other elements with the higher concentrations in Experiment 1. Al differs widely between samples and experiments – a fact that has been observed in previous experiments and cannot be explained so far.

After the HCl / HF clean, surface concentrations have been reduced significantly, by a factor of 60 for Cu and 50 for Fe. The other elements are also reduced, yet much less drastically. Most of them are still well over the detection limit of 1E10 atoms/cm². After the piranha cleaning sequence almost all elements in both experiments are reduced to 1 – 12E10 atoms/cm². Many elements, such as Cr, Ti, and Mn are reduced to less than the detection limit of 1E10 atoms/cm².

The reason for the difference in initial metal surface concentration between the two experiments is most likely that material from different suppliers was used. It is assumed that either different kinds of sawing wires and / or different cleaning processes were used after wire sawing. When comparing the concentrations of the two experiments after the piranha clean it becomes obvious that the effectiveness of the piranha clean – as it is implemented at our institute – differs over time.
3.2. Life-time and cell results of Experiment 1

Comparing the sheet resistances of the three different diffusions no significant difference can be found, therefore the groups can well be compared. The life-time samples reveal no difference between the HCl / HF and piranha cleaned samples, which was already mentioned in [4] but not further specified. Despite significantly different metal surface concentrations the average of the implied Voc at 1 sun intensity is 637 mV for both groups (Fig. 4). On average, 18 mV are lost without pre-diffusion cleaning. The values plotted against diffusion boat position are found in Fig. 4. The measurable etch-back effect of the piranha clean after PSG removal is about 5-8 mV.

![Fig. 4. Implied Voc values of the life-time samples of Experiment 1](image)

The lower recombination in the cleaned samples also affects the cells that were processed from the three groups. The efficiency drops by 0.6 %abs., independently of the cleaning after diffusion. However, the etch-back effect of the piranha clean is also visible on cell level. The difference between the samples that were etched and the ones that were not is 0.24 %abs., independent of the pre-diffusion clean. This gain is attributed to a gain in Jsc of 0.2 mA/cm² and a gain in Voc of 2 mV. Despite the etch-back the FF was not reduced.

From the fact that the gain from the etch-back is independent of the pre-diffusion clean we deduce that the reduced cell efficiency for the group without cleaning is not due to a higher surface recombination velocity. At least some of the initial surface contamination must have reached deeper regions and is still active after the etch-back.

![Fig. 5. Cell efficiency with HCl/HF clean (a) and with piranha clean (b) after diffusion](image)
3.3. Life-time results of Experiment 2

In the second experiment the differences in implied Voc of the life-time samples were not as easy to extract from the data as it was in the first experiment. First of all, this was due to the fact that the sheet resistances, and hence the life-time values, of different diffusions differed quite significantly. Not only in between diffusions but also between boat positions differences in sheet resistance were recorded. Secondly, due to the low number of samples averaging between groups did not lead to satisfying results. When plotting the implied Voc values of single emitter groups against the sheet resistance, we obtained curves like the one in Fig. 6. In three out of four times we could not detect a clear difference in implied Voc between the cleaned and the non-cleaned samples.

![Fig. 6. Implied Voc values of the 80 Ω/sq emitter group.](image)

We increased the number of data points by fitting over all four groups. Fig. 7 shows the fits of the implied Voc values plotted against the sheet resistance – now taking all of the data into account. The fits are of the cleaned and non-cleaned samples over all groups. While the result of the HCl / HF cleaned samples is not conclusive, the size of confidence intervals decrease after the piranha clean, and we can extract a difference of 5 – 8 mV. The gap between the fits widens slightly towards shallower diffusions. So in contrast to experiment 1 the difference between cleaned and non-cleaned samples is much smaller.

![Fig. 7. Implied Voc of all groups with HCl / HF cleaning (a) and piranha cleaning (b) after PSG removal](image)
4. Conclusion

Very high metal surface concentrations (especially Cu) were detected after alkaline texturing. In order to reduce these concentrations cleaning is necessary. Both of the investigated cleaning procedures – the HCl / HF procedure and the piranha clean procedure – are well suited as pre-diffusion clean to reach good results. However threshold values for a measurable effect on cells and life-time samples are much higher than expected, which indicates that the cleaning effort can be reduced to minimize cost of ownership. To demonstrate the robustness of phosphorus diffusion towards surface contamination fig. 8 plots implied Voc of symmetrical life-time samples against Cu surface concentrations that were measured in the two experiment plus some data points from previous experiment (note that no other elements are taken into account).

Fig. 8. Implied Voc of 65 Ω/sq diffusion, symmetrical life-time samples vs. Cu surface concentration so far. Only values with HCl / HF or no cleaning after PSG were used (that was not necessary when no “dirty” wafers were included). The extrapolated value is extracted from the linear fit in fig. 7 (a), extrapolated to 65 Ω/sq.

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