ABSTRACT: A method for transition metal sampling on the surface of as-cut and isotextured multicrystalline silicon wafers that allows quick and easy sampling without clean room environment is presented. The obtained samples were analysed via ICP-MS. The samples were tested for the presumably most harmful species identified from literature: Ag, Al, Cr, Cu, Fe, Mn, Mo, Ni, and Ti. The method was applied to the isotexture process. The cleaning cascade after the etching was investigated and it was found that initial as-cut wafers surface contamination is reduced significantly. As-cut wafers were identified as main source of contamination of the isotexture etch bath. With the help of the measured concentrations the enrichment of transition metals in the etch bath was simulated. Due to bleed/feed processing the equilibrium of metal intake to the etch bath is reached after 6,000 – 10,000 wafers. Additionally, the cleaning efficiency of standard cleaning procedures was studied. The influence of surface contamination on the oxidation step for a SiO2/SiNx passivation stack was investigated and it was shown that surface contamination can vastly decrease the lifetime of a wafer during a high temperature process.

Keywords: transition metal impurities, process analytics, ICP-MS

1 INTRODUCTION

Transition metal contamination during processing plays an important role concerning the quality of a semiconductor product [1]. In contrast to the IC industry, hardly any publications on surface contamination during solar cell processing exist. Standard IC methods for sampling of surface contaminations are hardly applicable for solar wafers as they require polished surfaces or advanced and expensive sampling equipment [2]. Furthermore, sampling either requires expensive automated (clean room) equipment close to the production line, or the whole wafer has to be sent for analysis, by which it is prone to the uncontrollable risk of contamination during transportation. Therefore a method was developed that allows the sampling on rough, e.g. isotextured, surfaces, close to the machine, and the contamination-free transport of the sample to an analytic laboratory.

This method was used to study the saw-damage removal and isotexture etch process. Additionally, several cleaning procedures were studied and lifetime samples were prepared to gain understanding of the impact of surface metal contamination during a high temperature process step.

2 EXPERIMENTAL

The first goal of the project was to develop a tailored sampling method to extract surface contamination. For this purpose the Sandwich Etch sampling method was developed: The average surface concentration of two wafers is determined by pipetting 1 mL of sampling solution onto one wafer. Another wafer is placed on top, hence a sandwich is formed. The wafers are rubbed against each other to ensure that the surfaces are wetted. The adhesion forces are strong enough so that the sandwich can be handled safely. The total amount of liquid in-between the wafers can be determined by placing the sandwich on a balance. The sampling solution is made up from diluted HF and H2O2. Ultrapure chemicals and water are used due to expected concentration of around 1 – 10 ppbw. After 10 min of reaction time the wafers are separated and the solution is collected using a microliter pipette and transferred to a clean PFA vessel.

Figure 1: The Sandwich Etch sampling procedure.

In the following experiments the samples were then sent to the BASF analytical laboratory where they were measured using an Agilent 7500cs ICP-MS.

The average surface concentration of both wafers is calculated from the total amount of solution on the wafers and the measured concentration. The detection limit of this method is in the range of $1 \times 10^{10}$ atoms/cm$^2$ and below, depending on the element. Blank values were obtained by transferring sampling solution directly into PFA vessels. Clean room environment for the sampling is not necessary. The crucial steps are quick and easy so that the risk of contamination during sampling, for example through dust, is small.
3 RESULTS AND DISCUSSION

3.1 Investigation of the isotexture process

The developed sampling method was applied to the acidic saw-damage removal and isotexture process. Wafers are etched in an etch bath made up from HNO$_3$ and HF using a RENA inline wetbench. The etching of the wafers is followed by a cleaning cascade of which the cleaning efficiency is studied. First, the wafers are rinsed in DI water (sampling point (1) in Fig. 2). The second step is an alkaline rinse of diluted KOH solution which is necessary to remove porous silicon from the etching. This step is followed by another aqueous rinse (2). Last, the wafers are rinsed in diluted HF/HCl to remove silicon oxide and metal contamination from the surface and rinsed in DI water (3). Two samples were taken at each sampling point (1 – 3). While at (1) it was possible to take the wafers directly from the machine the sampling after the alkaline rinsing step (2) was not feasible. Therefore, the wafers were taken at the end of the machine while the acidic rinse was switched off.

![Sampling points of the RENA inline wetbench](image)

**Figure 2:** Sampling points of the RENA inline wetbench.

The elements found above the detection limit in all experiments were Fe, Al, Cu, and Ti, less regularly also Ni and Cr. Typical results of an experiment are shown in Fig. 3.

**Fig. 3** shows that Al and Fe are only introduced to the wafer surface in the alkaline rinse which can be explained by the high pH [3] and higher specification of KOH for these two elements. Whereas Cu and Ti contamination on the surface has its main source in the etch bath. The acidic cleaning step reduces all elements (except for copper where the findings are inconclusive).

Also, etch bath concentrations were measured. No relation between etch bath concentration and surface concentration sampling point (1) could be found. However, this may be well explained by taking the findings of surface concentrations of as-cut wafers into account (Tab. I). These differ widely among wafers and are several magnitudes (up to five) higher than the surface concentrations after the etching process. Hence, a more critical factor for the metal surface concentration of the wafers after etching appears to be the initial surface concentrations of the as-cut wafers than the etch bath concentration.

![Surface concentration of Al, Fe, Cu, and Ti](image)

**Figure 3:** Surface concentration $c_{SP}$ of Al, Fe, Cu, and Ti at the different sampling points (compare Fig. 2). Error bars is the measurement uncertainty. Right y-axis: measured concentration, left y-axis: concentrations corrected for mean blank values.

| Surface concentration ($c_{SP}$) [10$^{10}$ Atome/cm$^2$] |
|-----------------|--------|--------|--------|--------|--------|--------|--------|
| Ag   | Al    | Cr    | Cu    | Fe    | Mn    | Mo    | Ni    |
| Different    | < 4   | 608   | 12    | 2383  | 4293  | 60    | < 1   | 214   | 61    |
| manu- facturers | < 3   | 2332  | 29    | < 2   | 676   | 7     | < 1   | 15    | 210   |
| blanks       | < 4   | 42    | < 2   | 4     | 23    | < 2   | < 1   | < 2   | 5     |
|            | < 3   | 73    | < 2   | 37    | < 2   | < 1   | < 2   | 2     |

**Table I:** Results of as-cut wafer concentrations on three wafer pairs from different manufacturers.
3.2 Simulation of the enrichment of metals

Taking the large differences of surface concentrations before and after etching into account transition metals are expected to be enriching in the etch bath. However, since the isotexture process is operated in discontinuous bleed/feed mode saturation is likely. To investigate the enrichment of metals in the etch bath, concentrations before and after a certain amount of processed wafers were measured. Also, the dependence on the quality of the chemicals was under investigation. For this reason two etch baths were made up from chemicals of two different grades of purity.

The etch bath concentration of metals was measured by ICP-MS after a throughput of 0 and 2600 wafers for each etch bath. The machine was operated under bleed/feed conditions which means that every 300 wafers 20 L of 140 L were replaced by fresh chemicals (of which the concentrations were also measured).

An Excel-based simulation was created taking this information into account. The introduction of metals from the wafer surface $c_{SF}$ was varied to match the measured etch bath concentration. The calculated introduction to the etch bath of metals per wafer came close in terms of magnitude to the measured values (see Tab. II).

![Figure 4: Simulation of the enrichment of transition metals in the isotexture etch bath. Higher purity chemicals used in left hand side bath.](image)

The simulation suggests that values for Cu, Ti and Al values are even higher than the measured ones. This may be due to the fact that the recovery rate has not yet been optimized for concentrations that high. The largest discrepancy between measured and simulated concentration is for Al which goes in line with the observation that measured Al values for different samples of the same kind often vary strongly (compare Fig. 6).

Comparing the initial etch bath concentrations with the equilibrium concentration, it becomes obvious that at equilibrium state the etch bath concentrations are much higher. Depending on the quality of the chemicals the equilibrium concentration is by a factor of 4 to 200 times higher than the initial concentration.

![Figure 5: Cleaning procedures before high temperature process at ISC, conducted in a hand wet bench.](image)

Cu concentrations are often claimed to be crucial. The simulation shows that even for the high purity chemicals with very small initial concentrations equilibrium concentrations are determined by the introduction of as-cut wafers. They reach more than 300 ppbw which almost reaches the dimension of the less pure etch bath where the concentration accumulates to 400 ppbw.

Equilibrium – after which no further enrichment is expected – is reached early in a bath life-time, after a throughput of 6.000 to 10.000 wafers, which is not much compared to an average bath lifetime of several hundred thousands of wafers.

3.3 Impact of surface contamination

For the investigation of the impact of metal surface contamination the cleaning efficiency of different additional cleaning processes were compared. For the cleaning a hand wetbench was used. “Old” and “new” cleaning baths were compared. Old cleaning baths had been in use for a throughput of approximately 1.000 wafers.

Surface concentrations were determined using the Sandwich Etch sampling method. Three samples were prepared directly after the isotexture process, after a standard HCl / HF clean (3 % / 2 %), and after an additional Piranha $\text{H}_2\text{SO}_4 / \text{H}_2\text{O}_2$ clean (conc. / 10 %) (Comp. Fig. 5). All percentages are weight/weight.

![Figure 6: Surface concentrations after cleaning (a) to (c).](image)

The influence of the cleaning procedures on a thermal SiO$_2$-SiN$_x$ stack on p-type multi-crystalline wafers was determined by preparing two-sided lifetime samples. The minority carrier lifetime was measured with µW-PCD (not calibrated to injection level). All percentage values are weight/weight percentages.

The resulting surface concentrations for Fe and Al are displayed in Fig. 6. The high concentrations after the isotexture process (including the cleaning cascade) are due to the fact that the solutions of the HCl/HF rinse of the inline wet bench (see Fig. 2) had not been replaced by fresh solution for an indeterminate amount of time.
Cleaning efficiency increases from cleaning procedure (b) to (c) and (d) to (e). The “new” baths (d and e), however, appear to have a lower cleaning efficiency than the “old” baths. For (e) this is affirmed by the lifetime map in Fig. 7 and can be explained by the problems encountered during makeup of the new piranha solution. The target concentrations where not quite reached due to strong heat generation. For the new standard cleaning baths (d) no straightforward explanation can be presented. The measured lifetime is much higher than expected from the surface concentration.

![Figure 7: Lifetime maps using the same scale (5 – 50 µs; black – red).](image)

Plotting lifetime versus average surface contamination (Fig. 8) no significant correlation for Al can be observed while Fe seems to be correlating. The fact that no correlation for Al was found goes in line with the general assumption that Al only produces shallow trap levels that do not lead to recombination of photogenerated carrier pairs. In contrast to this Fe contamination on the surfaces influences the lifetime of the samples but probably Fe alone cannot be held responsible for the decrease of lifetime. Interesting in this case would be the Cu concentration, however, the measured results were, yet again, inconclusive – a fact that was taken into consideration and works on better recovery rates for Cu are in progress.

4 CONCLUSION

It was shown that surface contamination can have a strong influence on solar cell processes. Especially for high temperature steps, such as a thermal oxidation, lifetimes can be significantly reduced which can have negative effects on the ready-made cell performance. Therefore, exact knowledge about surface concentration of transition metals during processing is crucial. The developed tailored sampling method together with ICP-MS elemental analysis has proven to be a well-suited tool for this purpose. Applying the method to the isotexture process deeper knowledge on the behavior of metal surface concentration during processing was gained.

However, much more work is necessary to get the full picture and optimize a whole cell production process. With the help of the Sandwich Etch method cleaning necessity and efficiency can be determined and monitored, and tailored cleaning procedures can be developed for each step. Another application of this method is the clean room monitoring by placing “realistic” sample wafers in crucial parts in a production line and analyzing the so the collected airborne contamination.

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6 REFERENCES