

THE CORROSIVE EFFECTS OF ALKALINE NICKEL-PHOSPHORUS PLATING ON CRYSTALLINE SILICON

Erkan Emre, Stefan Braun, Giso Hahn

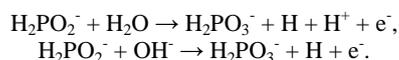
University of Konstanz, Department of Physics, P.O. Box X916, 78457 Konstanz, Germany
Tel.: +49 7531 883174, Fax: +49 7531 883895, Email: erkan.emre@uni-konstanz.de

ABSTRACT: In the process of finding alternatives to conventional silver thick-film metallization for silicon solar cells the interest in chemical deposition of nickel layers is rising. Electroless plating of nickel/phosphorus layers is a common surface coating method to protect metallic surfaces from corrosion and is currently examined as an option for solar cell metallization. However, some chemical compositions for this process contain alkaline substances (e.g. sodium hydroxide or ammonium), which are known to chemically react with silicon. This work examines the effect of Ni/P plating on crystalline silicon substrates with varying n-type emitters (20 Ω /sq, 50 Ω /sq, 80 Ω /sq and 120 Ω /sq). Two different chemical bath compositions, both with an alkaline electrolyte, are tested at different temperatures and varying plating durations. By comparing the mass of Cz-Si wafers in different stages of the Ni/P plating process (before plating, after plating with the Ni/P layer intact, after plating with the Ni/P layer removed) one can detect an average silicon etching depth between 40 nm and 80 nm \pm 13 nm. ECV measurements suggest an even higher damage to the emitter of >250 nm up to a complete consumption of a shallow emitter. SEM imaging reveals a morphological change of the wafer surface.

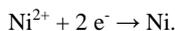
Keywords: c-Si, metallization, nickel plating, etching

1 INTRODUCTION

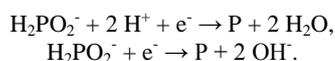
Most electroless Ni/P plating baths are based on two essential agents, i.e. nickel sulfate (NiSO_4) or nickel chloride (NiCl_2) and sodium hypophosphite (NaH_2PO_2), both of which are present in an aqueous solution. Through the reduction of the hypophosphite ion (H_2PO_2^-) on the catalytic substrate unbound electrons are deposited onto the substrate surface



These electrons attract nickel ions (Ni^{2+}) to the substrate and reduce them into a neutral state

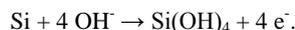


Simultaneously, hypophosphite ions react with the hydrogen ions and leave phosphorus behind, which is built into the depositing nickel layer



In practical application two chemical compounds are mixed together. One of them contains both the nickel salt and the sodium hypophosphite amongst other reaction influencing substances, e.g. complexing and stabilizing agents. The other component acts as a pH regulating electrolyte. Common substances in commercial use include e.g. sodium hydroxide or ammonia for alkaline and sulfuric or hydrochloric acid for acidic plating baths [1].

Alkaline solutions, however, are especially known to react with silicon and create silicic acids [2], e.g.



This kind of reaction, which can find its use in KOH/IPA or NaOH/IPA texturing for example, is highly undesirable in the metallization process of Ni/P plating on shallowly doped emitters of silicon substrates. Despite this fact, a large number of commercial Ni/P plating baths work in an alkaline range.

This work recognizes the chemical theory on which Ni/P plating is based and strives to examine and

understand the corrosive effects of alkaline electroless Ni/P plating on n-type doped silicon emitters.

2 SAMPLE PREPARATION

The sample preparation sequence is depicted in Figure 1. The experiment was based on pyramid-textured $156 \times 156 \text{ mm}^2$ p-type Cz-Si wafers, which were divided into four sets each with a POCl_3 emitter of 20 Ω /sq, 50 Ω /sq, 80 Ω /sq and 120 Ω /sq respectively. The phosphorus-silica glass was removed in lowly concentrated HF. To conclude the sample preparation, every wafer was divided into nine $50 \times 50 \text{ mm}^2$ samples by laser cutting.

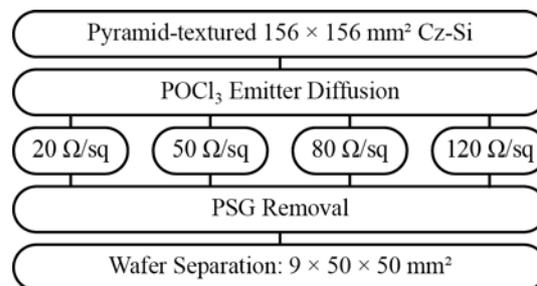


Figure 1: Sample preparation sequence used for the Ni/P plating surface effects experiment.

3 EXPERIMENT

An overview of the measurement and processing steps of the experiment can be found in Figure 2. The emitter profile of a control sample for each of the four emitters was recorded with electrochemical capacitance-voltage measurement (ECV). Native oxide on the silicon surface was removed with a short HF dip beforehand.

A set of wafers consisted of eight $50 \times 50 \text{ mm}^2$ samples. All wafers of a set were subsequently exposed to the Ni/P plating solution. The deposition process of the nickel-phosphorus layer was controlled by successively exposing single wafers to the plating bath with plating durations ranging from 30 s to 8 min.

Two commercially available Ni/P plating reagents were chosen to represent the temperature and pH range of

different products. A summary of their technical properties is given in Table I.

Table I: Properties of the utilized Ni/P plating reagents.

	Reagent A	Reagent B
Nickel source	NiSO ₄	NiCl ₂
Reducing agent	NaH ₂ PO ₂	NaH ₂ PO ₂
pH regulator	NaOH	NaOH
pH range	9.0–10.0	8.5–9.5
Temperature range	35–45°C	65–75°C

Sodium hydroxide is the main etching component of the plating bath. Its concentration was set to match the demanded pH range. A NaOH concentration of 0.3 mol/l was maintained in both plating reagents.

After having rinsed the wafers in deionized water, a second mass measurement recorded the mass of the newly Ni/P plated samples. The removal of the Ni/P layer occurred in aqueous nitro-hydrochloric acid. After the metal layer was removed, the samples were weighed for a third time. A final ECV measurement for selected samples provided a before-after comparison of the emitter structure.

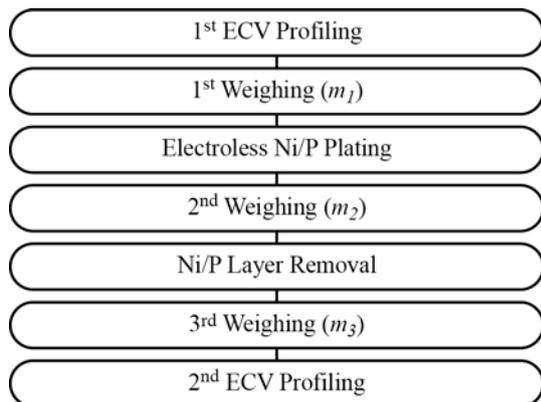


Figure 2: Overview of sample processing and measurements during different stages of the experiment.

4 ANALYSIS

Sample mass and emitter profile measurements at different stages of the experiment describe the change of morphology on the material surface.

Mass comparison of a wafer before Ni/P plating (m_1), after plating (m_2) and after plating with the Ni/P layer removed (m_3) provides general information about the influence of the plating bath on the silicon material.

ECV profiling allows a closer look at the emitter structure of a wafer. As Ni/P plating is a surface reaction on the silicon substrate, any damage to the material will also impact the emitter structure. By comparing the ECV profiles before and after plating one can find alterations on the surface structure of the wafer and conclusively on the emitter profile

SEM (Scanning Electron Microscopy) is used to examine the surface structure of the samples after the experimental sequence.

5 RESULTS

5.1 Comparison of masses: Ni/P layer thickness

By comparing the total mass of a sample after Ni/P layer deposition (m_2) with the mass after its removal (m_3), one can determine the mass of the deposited nickel layer and estimate the Ni/P layer thickness. Note that comparing the mass prior to the Ni/P deposition (m_1) with the one after deposition (m_2) does not take any silicon etching effects into account, which occur in the plating process. Figures 3 and 4 provide the results of the second and third mass measurements for the samples processed in plating agents A and B respectively. As different emitters behave almost identically in reagent A, their data has been omitted for the sake of clear arrangement.

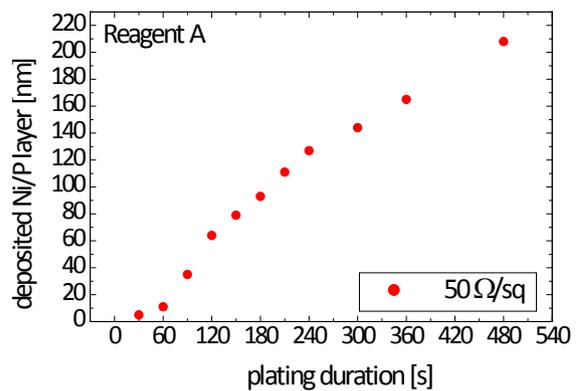


Figure 3: Ni/P layer thickness for plating reagent A in dependency of the plating duration. The error in measurement of layer thickness is ± 10 nm (not depicted). A continuous growth of layer thickness is visible.

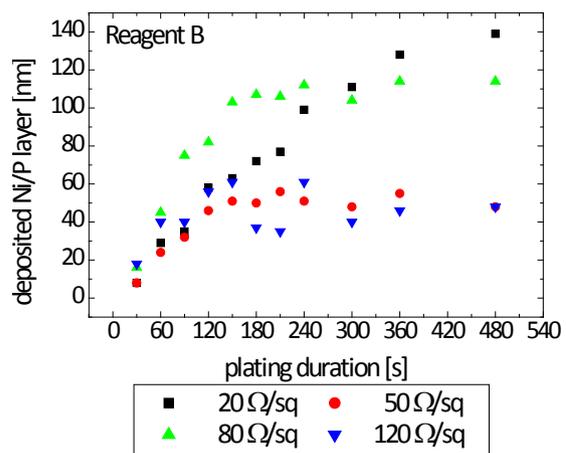


Figure 4: Ni/P layer thickness for plating reagent B in dependency of the plating duration. The error in measurement of layer thickness is ± 10 nm (not depicted). Layer growth is not as uniform as the smooth growth visible for reagent A. However, the layer thickness seems to reach an upper limit over time.

For both reagents longer plating durations result in an increased amount of deposited nickel and an increased layer thickness. Reagent A gives a relatively high thickness and steady growth of the Ni/P layer (Figure 3). Layer growth of samples processed with reagent B is not steady over time and more fluctuating (Figure 4). However, a saturation level of Ni/P layer thickness can be assumed for the given process duration. Doping concentration of the sample does not imply a uniform

influence on the deposition process. Samples with the shallowest emitter matching $120 \Omega/\text{sq}$ reveal the highest deviation in their data.

5.2 Comparison of masses: Si etching depth

By comparing wafer mass before Ni/P plating (m_1) and after its removal (m_2) one can find the amount of silicon material which was dissolved during the plating process. By assuming a uniform loss over the whole wafer surface the depth of the material etching can be estimated. The results for both reagents are provided in Figures 5 and 6.

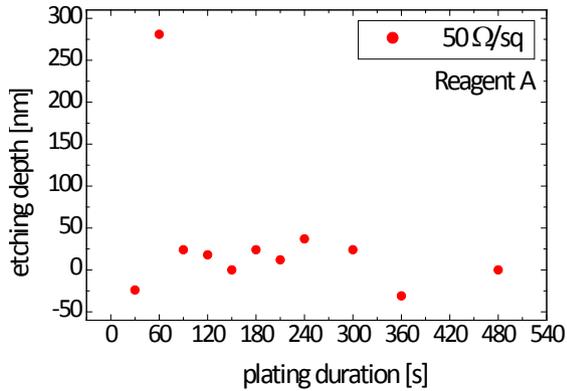


Figure 5: Si etching depth for plating reagent A in dependency of the plating duration. The error in measurement of depth is ± 13 nm (not depicted). The value of approx. 300 nm at 60 s is to be disregarded as a random error. Results of negative and scattered data around the zero axis provide insignificant information to safely assume silicon etching.

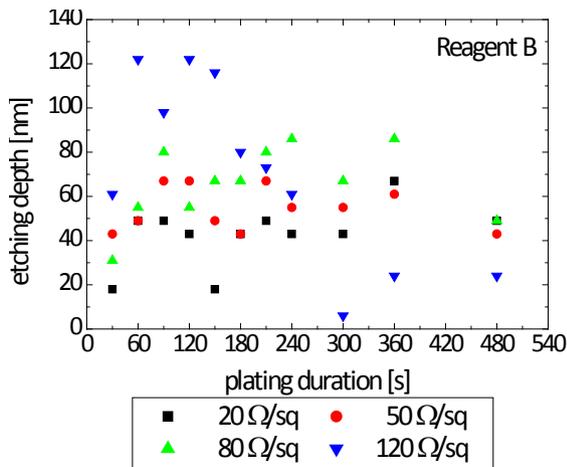


Figure 6: Si etching depth for plating reagent B in dependency of the plating duration. The error in measurement of depth is ± 13 nm (not depicted). Silicon etching reaches a depth of over 80 nm. Data for $120 \Omega/\text{sq}$ renders conflicting information (compare Figure 4).

Results of reagent A do not safely show a uniform etching effect (Figure 5). The value of approx. 300 nm at 60 s is to be disregarded as a random error. The data of etching depth is scattered around the zero axis and does not range up to significant values.

Results of reagent B however clearly indicate a material loss (Figure 6), although no uniform increase can be seen in the given time range. With a high variation of sample data an average etching depth between 40–

80 nm for longer plating bath exposure times is found instead. Results for samples with $120 \Omega/\text{sq}$ emitters are conflicting, as longer plating durations seem to indicate a lower etching depth.

Unlike the plated Ni/P layer thickness the data suggests that the etching process is also dependant on sheet resistance of the samples. Data from Figure 6 is rearranged over sheet resistances in Figure 7. Samples with higher sheet resistance indicate a higher material loss than samples with a lower sheet resistance at the overall duration.

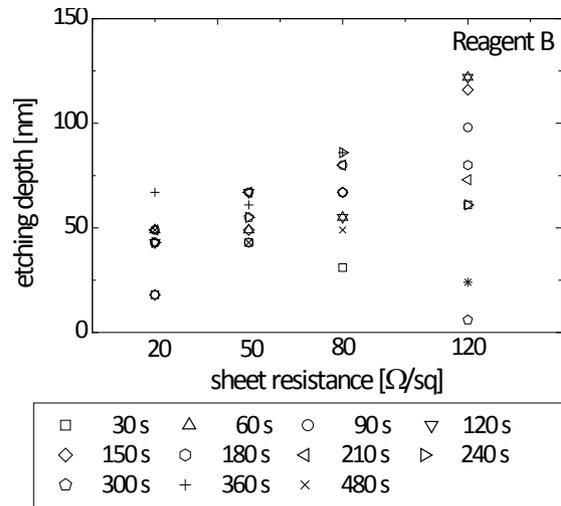


Figure 7: Si etching depth for plating reagent B in dependency of the sheet resistance. The error in measurement of depth is ± 13 nm (not depicted). All plating durations are combined in each column. Samples with higher sheet resistance suggest a higher loss of silicon.

5.3 ECV Profiling: emitter damage

Figures 8 to 11 show ECV measurements of the samples processed in reagent B for 4 min. The graphs depict the emitter profiles before and after Ni/P plating and the removal of the metal layer. The data which is taken after the Ni/P removal is shifted to an approximate doping concentration before etching.

It can be assumed that variances in dopant concentrations between the two profiles originate from differences in surface morphology of the unprocessed and processed sample. As the surface morphology changes and a spatially inhomogeneous removal of the highly doped area can be assumed, the ECV profiling differs in terms of sample area and homogeneity.

ECV measurements of samples after Ni/P plating showed difficulties in detecting a phosphorus doping concentration close to the surface. Often, only after initial penetration of the wafer surface reasonable data could be obtained.

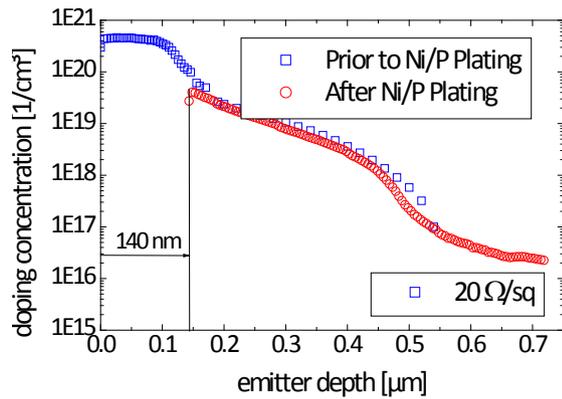


Figure 8: Emitter doping concentration before and after plating for a sample with a starting sheet resistivity of $20 \Omega/\text{sq}$. The dead layer as well as the initial part of the kink of the emitter structure is missing after plating.

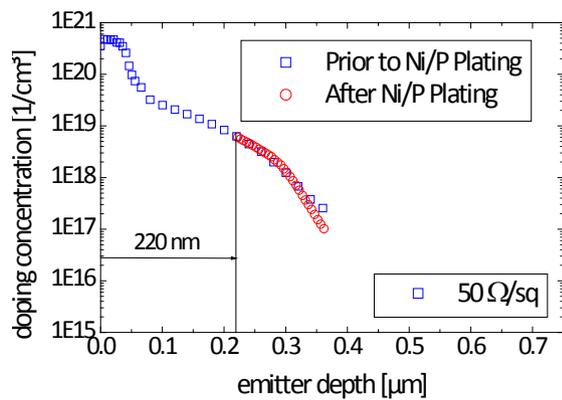


Figure 9: Emitter doping concentration before and after plating for a sample with a starting sheet resistivity of $50 \Omega/\text{sq}$. The dead layer, kink and the part of the tail of the emitter structure is missing after plating.

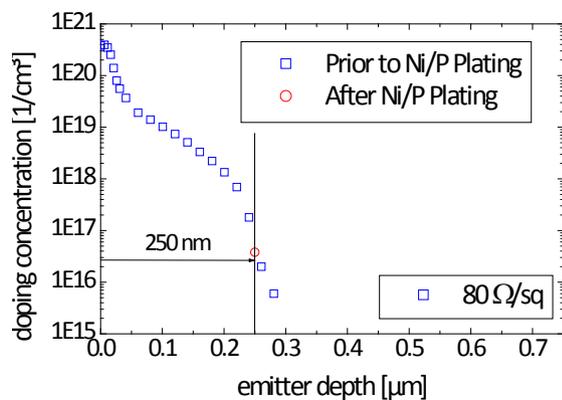


Figure 10: Emitter doping concentration before and after plating for a sample with a starting sheet resistivity of $80 \Omega/\text{sq}$. ECV measurement after the Ni/P plating process reveals merely a very low surface concentration of phosphorus. Almost the complete emitter structure is missing.

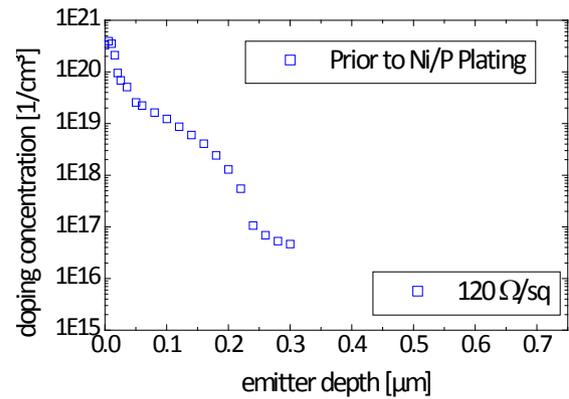


Figure 11: Emitter doping concentration before plating for a sample with a starting sheet resistivity of $120 \Omega/\text{sq}$. No discernible phosphorus concentration was measurable after Ni/P plating. Apparently, the complete emitter structure has been removed or damaged.

5.4 SEM imaging: surface morphology change

SEM analyses of the processed sample surfaces reveal a change of the surface morphology. Inhomogeneous etching is clearly visible on samples at previously high sheet resistances. Pictured in Figures 13 to 16 are the surfaces of samples processed in reagent B for 3 min 30 s. Figure 12 shows an unprocessed wafer surface for comparison.

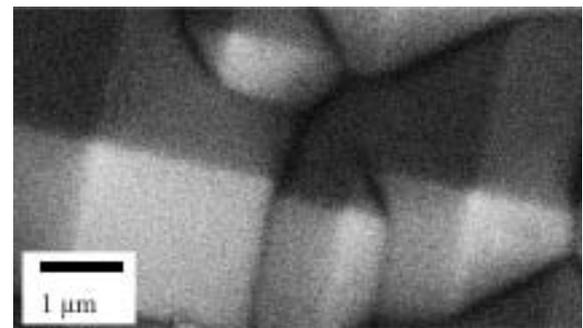


Figure 12: SEM surface analysis of an unprocessed sample for comparison.

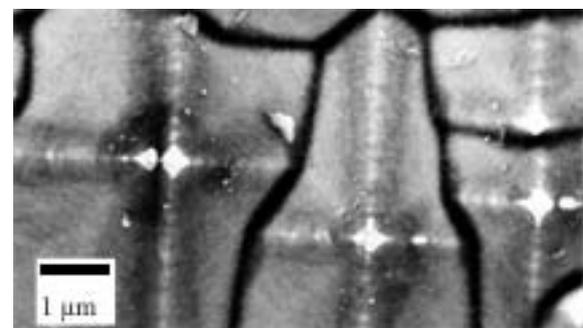


Figure 13: SEM surface analysis of a sample with a starting sheet resistivity of $20 \Omega/\text{sq}$. Residues of nickel grains are discernible on the pyramid faces.



Figure 14: SEM surface analysis of a sample with a starting sheet resistivity of 50 Ω/sq. A structural change of the pyramid surface becomes visible.

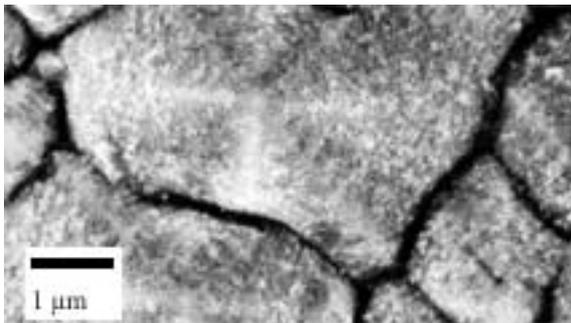


Figure 15: SEM surface analysis of a sample with a starting sheet resistivity of 80 Ω/sq. Structural damage of the pyramid surface is even more distinctive.



Figure 16: SEM surface analysis of a sample with a starting sheet resistivity of 120 Ω/sq. A high morphological change of the surface can be observed.

6 DISCUSSION

By comparing the mass of the sample before and after Ni/P plating and removal one could reveal that silicon from the substrate was removed during the plating process.

Evidence was found that alkaline Ni/P plating on crystalline silicon can have a disruptive effect to the substrate and is highly dependent on the plating process parameters. Plating at 35–45°C could be performed without evident silicon material damage. Processing at higher temperatures of 65–75°C resulted in significant silicon material etching of up to >80 nm.

As the silicon etching behavior of NaOH is known to be similar to KOH, one can calculate the estimated etch rate of the used solutions [2]. Please note that these estimates do not take the following into account:

- Highly phosphorus doped crystalline silicon is used instead of undoped crystalline silicon.
- The chemical agent contains more ingredients than just H₂O and NaOH.
- Hydroxide ion concentration is highly variable due to its involvement in the Ni/P plating process.

However, this approach can still help in understanding the experimental results. The calculated values are given in Table II.

Table II: Estimated etch rates of the utilized Ni/P plating reagents at the given temperatures.

	Reagent A	Reagent B
Temperature range	35–45°C	65–75°C
Etch rate	1.8–3.8 nm/min	14.8–27.3 nm/min

A plating duration of at least 3 min is required to completely cover the silicon surface with the Ni/P layer [3]. However, after a minimum of 2 min Ni/P plating coverage of the largest part of the wafer is already achieved, save for the pyramid tips [4]. As the silicon surface becomes coated in Ni/P no more etching can occur. Considering that the wafer surface is shielded from the etching plating reagent after a 3 min plating duration, the results of Figure 6 have to be reconsidered. The silicon surface of samples with plating times larger than 3 min have not been exposed any longer to the etching plating reagent, as the Ni/P plating process shifts from the silicon surface to the already deposited Ni/P layer.

Taking the etch rates of Table II into account, the expected maximum etch depths should range between approximately 4–11 nm for reagent A and 30–82 nm for reagent B. These estimates show a positive agreement with the experimental data from the mass measurements.

However, simply comparing mass of the unprocessed and processed samples cannot indicate any morphological surface change of the wafer but merely material loss. ECV profiles reveal a greater amount of damage to the sample surface as emitter profiles become more difficult to measure. It is assumed that Ni/P plating not only removes silicon from the wafer but also damages its emitter and morphology close to the surface. This assumption is affirmed by SEM analysis.

As the results of Figure 6 suggest, a higher etching depth is associated with a low dopant concentration. The same has been observed in other work and could therefore be confirmed [5]. Similar behavior is found in the ECV profiles where lowly doped emitters were more deeply damaged.

7 CONCLUSION AND OUTLOOK

As high temperature electroless Ni/P plating with an alkaline agent is proven to be disruptive to the emitter of POCl₃ diffused silicon solar cells, it is crucial to reconsider different metallization approaches. The advantage of easy contactability of shallow emitters is rapidly diminished when said emitters are highly damaged or even entirely consumed in the metallization process.

To increase adhesion of nickel plated layers on silicon emitters sintering at temperatures above 200°C is common practice. Sintering, however, promotes atomic diffusion and can lead to early and increased shunting in

the case of already damaged emitters through Ni/P plating.

As some high temperature Ni/P plating reagents provide the ability to contact boron doped emitters on n-type silicon, they cannot easily be replaced by low temperature variants.

However, in an attempt to find alternatives to nickel metallization on phosphorus doped emitters an interesting approach is found in light-induced nickel plating.

8 ACKNOWLEDGEMENTS

The authors would like to thank A. Dastgheib-Shirazi, B. Raabe, S. Seren and J. Messmer for their support. The financial support from the BMU project FKZ 0325079 is gratefully acknowledged in particular for the processing equipment. The content of this publication is the responsibility of the authors.

9 REFERENCES

- [1] N. Kanani, Chemische Vernicklung: Nickel-Phosphor Schichten. Herstellung, Eigenschaften, Anwendungen. Eugen G. Leuze Verlag (2007)
- [2] H. Seidel, L. Csepregi, A. Heuberger, H. Baumgärtel, Anisotropic Etching of Crystalline Silicon in Alkaline Solutions: I Orientation Dependence and Behaviour of Passivation Layers, J. Electrochem. Soc. 137(11) (1990) 3612-
- [3] S. Braun, E. Emre, B. Raabe, G. Hahn, Electroless Nickel and Copper Metallization: Contact Formation on Crystalline Silicon and Background Plating Behavior on PECVD SiN_x:H Layers, Proc. 25th EUPVSEC (2010)
- [4] E. Emre, Untersuchung von Ni-basierten Kontakten für Si-Solarzellen, Bachelor Thesis, University of Konstanz (2010) 26.
- [5] H. Seidel, L. Csepregi, A. Heuberger, H. Baumgärtel, Anisotropic Etching of Crystalline Silicon in Alkaline Solutions: II Influence of Dopants, J. Electrochem. Soc. 137(11) (1990) 3626.