NICKEL PLATING ON P+ SILICON –
A CHARACTERIZATION OF CONTACT RESISTIVITY AND LINE RESISTANCE

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ABSTRACT: Nickel plating on p^+ Si is a promising approach for the metallization of n-type Si solar cells. Ni acts as diffusion barrier for copper, which is used for thickening of the Ni contacts. In this work the adhesion and the contact resistivities of Ni plated lines on different boron emitters as well as the line resistances are evaluated. For that purpose, boron emitters with different sheet resistances on Czochralski n-type Si wafers are used. The dielectric passivation layer (SiN_x) on top of the emitter is locally opened by photolithography or by laser ablation to perform a line structure, which is afterwards electroless Ni plated. During a sintering step, nickel silicide is formed to achieve the required adherence and contact resistivity to the Si. To improve the adherence of the Ni plated layer and therefore to decrease the contact resistivity, a plating process with two separated Ni plating steps, named "two-step Ni plating", is introduced. With this process narrow and sharp lines (15-80 µm) with contact resistivities of about 0.6 mΩcm² are demonstrated. Using electrodeposition of Cu, line resistances of 0.45 Ω/cm are measured with line widths below 50 µm. This work demonstrates that the introduced plating technique is well suited for high efficient solar cell.

Keywords: Metallization, plating, characterization

1 INTRODUCTION

There are several publications concerning electroless nickel plating on highly n-doped silicon. In 2002 Lee demonstrated conclusive results on solar cell level using electroless nickel plating and electrochemical copper plating [1]. In contrast there are only few publications concerning nickel plating on highly p-doped silicon [2].

Ni plating has numerous advantages compared to other metallization techniques (e.g. screen printing):

- The metallization is inexpensive because there is only the need of a special Ni solution, which is commercially available.
- The front and rear side metallization can be realized simultaneously.
- Fast metallization is possible due to the opportunity of simultaneous batch type plating.
- Thickening with copper is possible; in this case Ni works as a diffusion barrier to avoid copper impurities (defect levels) in the silicon.
- No firing step is necessary, that means that the passivation quality of a temperature sensitive dielectric passivation layer (e.g. Al_2O_3) is not affected.

2 EXPERIMENTAL

The sample preparation is shown in Figure 1. Cleaned n-type Czochralski silicon wafers with a resistivity of 1 Ωcm are subjected to three different BBr_3 diffusions, aiming at three different sheet resistance ranges. Therefore the diffusion time, the diffusion temperature and the drive-in time are adjusted to achieve a homogenous sheet resistance distribution on each wafer, which can be measured with a four point probe measurement system. Afterwards a silicon nitride layer is deposited using a PECVD (plasma enhanced chemical vapor deposition) system. The SiN_x layer is opened locally using either a standard photolithography based process if samples are utilized for contact resistivity measurements or a ps-laser ($\lambda = 532$ nm) if samples are utilized for line resistance measurements. The standard photolithography based process deemed as a reference process, because of sharp line structures and no damaging of the boron emitter.
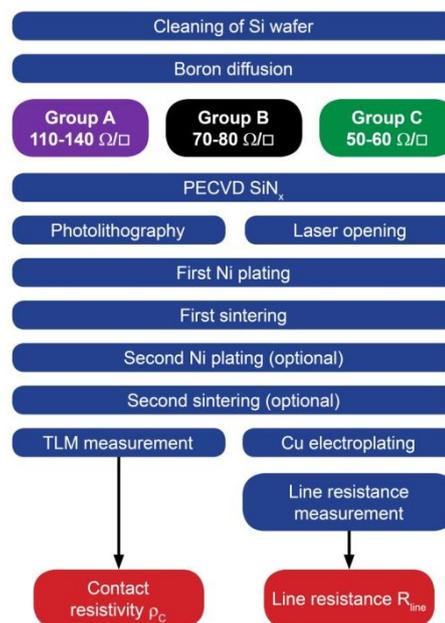

Figure 1: Sample preparation procedure for contact resistivity and line resistance measurement.

Before the plating step, a pretreatment of the wafer surface is necessary in order to assure good adhesion of the deposited metal. Samples are first treated with diluted HF in order to remove any native oxide on the wafer surface. Afterwards samples are rinsed in de-ionized water. Subsequently, Ni is electroless plated using an alkaline Ni salt solution. The solution consists mainly of Ni chloride that works as Ni source and a reducing agent to get the reaction started. To control the pH value, sodium hydroxide is added to the solution. The

deposition of the metal is the result of a redox-reaction at the silicon surface. The Ni solution is heated in a beaker and temperature and pH value are controlled during the heating and plating process. The beaker is covered to avoid the evaporation of NaOH, which is attended by a decrease of the pH value. Afterwards a rinse in de-ionized water is followed. To achieve the contact between silicon and nickel a sintering step is carried out immediately, and in this connection, nickel silicide is formed.

Contact resistivities of the samples fabricated either with the one-step Ni plating or with the two-step Ni plating process are measured by TLM (transfer length method) [3].

The samples for the line resistance measurement undergo the two-step Ni plating followed by electrochemical copper plating; afterwards the line resistance measurements are performed.

3   RESULTS

3.1 Boron emitter characterization

The boron concentration profiles of the emitters are measured with a commercial ECV (electrochemical capacitance voltage) setup. The results are shown in Figure 2.

The sheet resistance R_{Sheet} of the emitter layers can be calculated with equation (1). The $x_{n,m}$ are the measurement points at different depths with the corresponding resistances ρ_n.

$$R_{Sheet} = 1 \Big/ \sum_{\substack{n=1\\m=0\\n>m}}^{N} \frac{x_n - x_m}{\rho_n} \qquad (1)$$
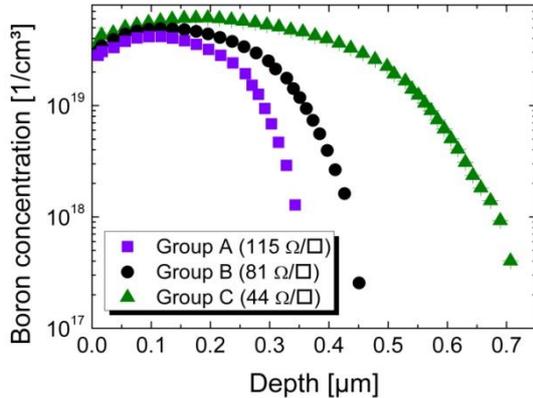
Figure 2: Boron concentration profiles of one emitter of each diffusion group (see Figure 1), measured with an ECV measurement system.

3.2 Contact Resistivity Measurement

For first investigations, the one-step Ni plating process is used, which means that only one nickel plating and a following sintering step is used. The samples are prepared as shown in Figure 1. The surface boron concentrations for group A, B and C are in the range of $2\text{-}4 \times 10^{19}$ cm^{-3}, measured with ECV, as shown in Figure 2. From the concentration profiles R_{Sheet} is calculated, additionally R_{Sheet} is measured with four point probe technique.

Figure 3 illustrates the contact resistivities of samples which underwent a one-step Ni plating and sintering step,

as well as the calculated sheet resistances and contact resistivities from the TLM measurements.

It is evident that the measurements data are not in accordance with the linear fit. Therefore the calculated sheet resistances do not agree with the measured sheet resistances based on four point probe or ECV (see Figure 1). This is on the one hand side due to a non satisfying adherence of the plated Ni layer and on the other side due to a less dense nickel layer, which is illustrated in Figure 4.
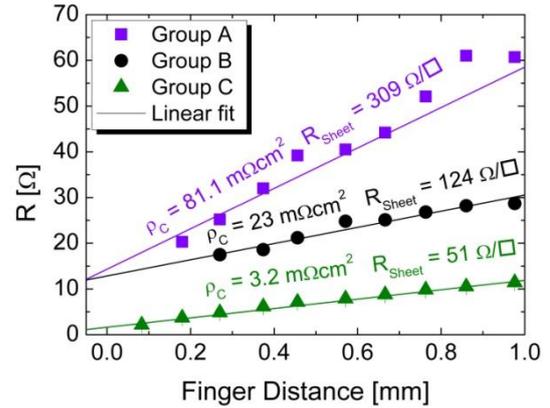
Figure 3: Results from the TLM measurement on samples which underwent the one-step Ni plating.

The scanning electron microscope (SEM) image (Figure 4) shows round Ni pellets, with a diameter of about $100 - 200$ nm. But in addition there are black spots visible, which indicate, that no Ni is deposited. Therefore a following electrodeposition with copper leads to lifetime limiting defect levels in the silicon.
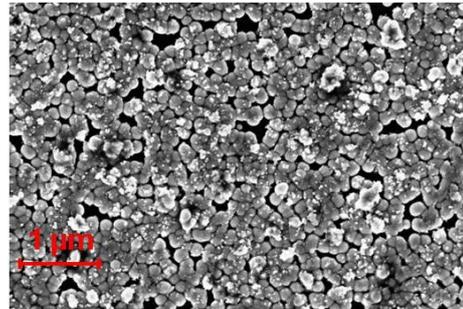
Figure 4: SEM image of a one-step Ni plated layer. The black spots indicate the open Ni layer and show the underlying Si.

For that reason, one-step Ni plating cannot be used as a seed layer for electrodeposition of Cu. Thus two-step-Ni plating is introduced. The first Ni deposition and sintering step forms a thin Ni seed layer, which has a good adhesion to the silicon but not the desired density. Consequently, a second Ni and sintering step is employed to realize a dense Ni layer. The results of the TLM measurement are shown in Figure 5.
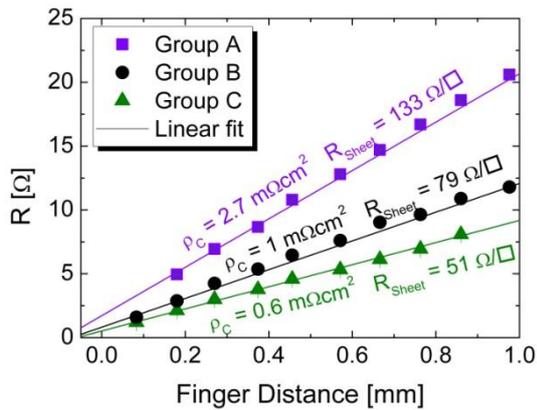
Figure 5: Results from the TLM measurement on samples which underwent the two-step Ni plating.

The calculated sheet resistances for the two-step Ni plating process are in good agreement with the ECV and four point probe measurements. The calculation of the contact resistivity results in values below 3 mΩcm² for all used sheet resistances up to nearly 140 Ω/□. For decreasing sheet resistances the contact resistivity is decreasing, too. For a sheet resistance of about 50 Ω/□, even a contact resistivity of 0.6 mΩcm² is achieved, thus the two-step Ni plating process is well suited for high efficiency solar cells.

Figure 6 shows a scanning electron microscope image of a layer plated with the two-step Ni plating technique. No silicon is visible, the Ni layer covers completely the silicon. With this plating technique thickening of the finger of solar cells with Cu can be realized without generating defect levels, which lower the efficiency of the solar cells.
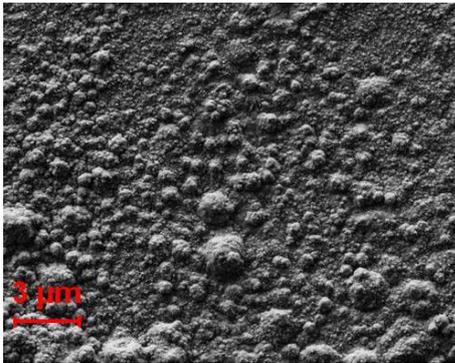

Figure 6: SEM image of a two-step Ni plated layer completely covers the silicon.

3.3 Line Resistance Using a Two-Step Ni Plating Process

For the line resistance measurements the samples are prepared as described in section 2. The width of the laser opened lines in the SiN$_x$ layer is in the range of 5-25 μm. Fig. 7 shows optical microscope images of a selected finger. The laser opening width of this line is about 22 μm which yields to a finger width after Ni plating of about 25 μm, but after copper plating the width is increased to 47 μm, and the line resistance is measured to 0.45 Ω/cm.
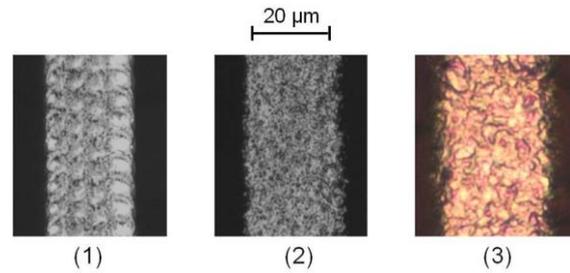

Figure 7: Optical microscope image of a two-step Ni plated layer. (1) after laser ablation, (2) after Ni plating, (3) after electrodeposition of Cu.

EDX (Energy-dispersive X-ray spectroscopy) measurements on this sample clearly indicate that the copper finger is very sharp and dense. With such a Ni seed layer with high Ni density, the electrodeposition with Cu is possible without causing lifetime limiting defect levels.
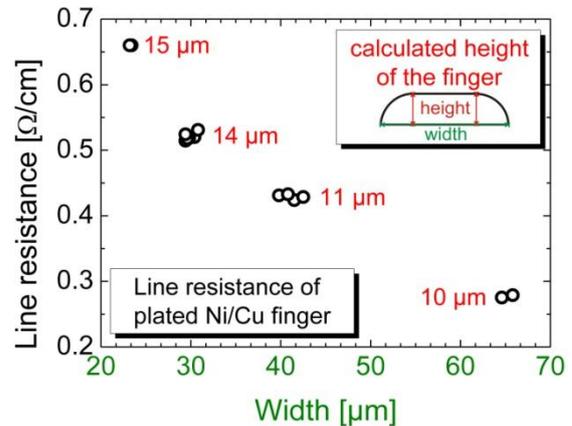

Figure 8: Line resistance measurements on different line widths, and corresponding calculated finger height.

Figure 8 shows the results of the line resistance measurements on different line widths. The figure shows the thinner the finger width, the higher the line resistance. However, low line resistances are achieved. Regarding the cross section of a plated finger (see Figure 9) using focused ion beam (FIB) technique, the shape of the finger is visible. The calculation of the finger height uses this shape. The aspect ratio is in the range of 0.45, which is very high for thin fingers.
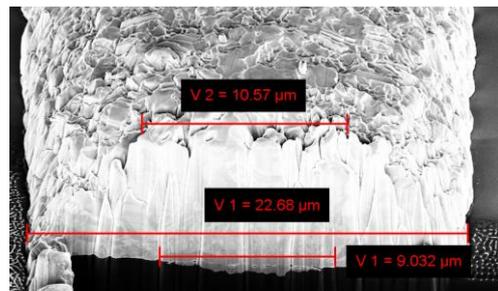

Figure 9: Cross section of a Ni plated finger, obtained using focused ion beam (FIB) technique.

4   SUMMARY

A two-step Ni plating process was developed for contacting highly boron doped Si layers. A contact resistivity of less than 3 mΩcm² on diffused boron emitters in the range of 50-140 Ω/□ for n-type silicon solar cells was achieved. By the additional application of electroplated copper, line resistance values of about 0.45 Ω/cm are reached with small finger widths below 50 µm. Consequently, the Ni plating process is well suited to manufacture n-type Si solar cells with high efficiencies.

5   ACKNOWLEDGEMENTS

6   REFERENCES

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