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# Insights into the reliability of Ni/Cu plated p-PERC silicon solar cells

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## Abstract

Selective laser ablation of dielectric layers in combination with plated Ni/Cu/Ag contacts have been investigated by many photovoltaic researchers. Despite that there has been quite some practical progress on improved processing, the reliability of plated Ni/Cu/Ag cells still needs further insight and understanding. In this paper, the impact of laser induced defects that result from a ps-laser (wavelength 355nm) ablation on the performance of p-type PERC cells has been studied. A thermal stress experiment at 235°C is applied. It is shown that the defects formed during the laser ablation process do indeed decrease the cell performance. A higher laser fluence results in lower fill factor and therefore lower efficiency. Moreover, the cells with higher laser fluence ablation degrade faster compared to the cells which had lower laser fluence to open the dielectric layer. The second part of the paper focuses on characterization of the p-n junction of the laser ablated cells by Deep Level Transient Spectroscopy (DLTS) before and after thermal ageing. A hole trap around 80K was found for all samples, which is related to point defects induced during the cell processing. A broad peak around 200K observed for the ablated cells with high laser fluence could correspond to dislocations induced by the laser ablation. This peak is shifted to higher energy (closer to the silicon mid-gap) after annealing, which may be due to impurity decoration during the annealing.

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**Keywords:** Laser ablation; Plated Ni/Cu; solar cells; Reliability; DLTS

## 1. Introduction

Developing an improved method for the metallization of silicon solar cells has been extensively studied recently. The contact formation using Ag screen printing is still the dominant technology in the commercial solar cell market

as it is simple and suitable for mass production. However, electrodes formed by screen-printing with metal pastes are not compact and have pores between the wafer and electrode which results in a relatively high contact resistance that restricts solar cell efficiency [1-3]. Besides that, there is a general consensus that Ag pastes are limited to surface concentration levels around  $1 \times 10^{20} \text{ cm}^{-3}$  which is not ideal in terms of recombination [4]. Moreover, Ag is an expensive and noble material and hence is subjected to a high price volatility. The mounting cost of Ag pastes and decreasing silicon wafer thickness encourage silicon solar cells manufacturers to develop alternative metallization techniques.

Among the promising front metallization techniques, the plated Ni/Cu has been considered as one of the most viable candidates for future use as contact technology for silicon solar cells. The conductivity of copper is compatible with silver while its raw materials cost is nearly a hundred time smaller. The plated Ni layer acts as an Cu diffusion barrier and Ni silicide is formed by annealing to enhance the adhesion and lower the contact resistance between metal stack and silicon. Moreover, using Ni/Cu plating technique is a good solution to improve the cell efficiency because of reduced shading loss. By using laser ablation to open the passivation layer before the plating step, it is possible to achieve a narrow contact opening width of less than  $15 \mu\text{m}$ . However, despite these advantages, a final acceptance by the c-Si PV community for introducing Cu in solar cell processing can only take place after profound reliability results and an estimation for the module's lifetime. There are some factors which could influence long-term reliability of plated Ni/Cu cells such as: laser damage, Ni/Cu diffusion, Ni silicide quality... Despite that there has been quite some practical progress on improved processing, the reliability of plated Ni/Cu cells still needs further insight and understanding.

In this paper, thermal ageing testing for p-type PERC cells with shallow emitter and front Ni/Cu metallization are discussed as a function of laser damage. The second part of the paper takes a closer look at the electrical characteristics of the cells before and after thermal ageing using Deep Level Transient Spectroscopy (DLTS).

## 2. Experiment details

In this work, large area ( $156 \times 156 \text{ mm}^2$ ) p-type, 1-3  $\Omega\text{cm}$ , magnetically grown CZ-Si wafers, with starting thickness of  $180 \mu\text{m}$ , are used. After random pyramid texturing both sides by KOH texture and inline rear polishing of the rear surface using a  $\text{HF}/\text{HNO}_3$  solution, the wafers were processed according to the process sequence given in Figure 2.

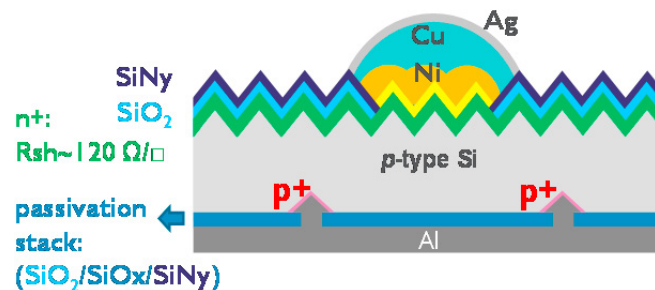


Fig.1. P-type PERC cell structure

Prior to  $\text{POCl}_3$  diffusion, the silicon wafers were subjected to a surface clean in order to remove organic and metallic contamination before the fabrication process. A  $\text{HF}$  2% solution was applied to remove phosphorus silicate glass, which formed during the  $\text{POCl}_3$  diffusion step. After an SPM(Sulphuris-Peroxide-Mixture)/ $\text{HF}$  clean, a dry thermal oxidation was employed to passivate the emitter and in order to drive-in phosphorus atoms in the Si bulk, forming thus an  $0.5 \mu\text{m}$  deep homogeneous n+ emitter with a sheet resistance of  $120 \Omega/\text{sq}$ . and low surface concentration ( $N_s < 10^{20} \text{ cm}^{-3}$ ). Subsequently, the  $\text{POCl}_3$  diffused emitter was further passivated with a PECVD  $\text{SiN}_x:\text{H}$  layer, and at the rear a PECVD  $\text{SiN}_x:\text{H}$  was applied on top of the PECVD  $\text{SiO}_2$  layer. The contact openings for the rear dielectric stack were formed on all cells by UV ( $355 \text{ nm}$ ) nanosecond laser ablation. The opened diameter is

approximately 30 $\mu$ m. Subsequently, 2 $\mu$ m of aluminium was deposited by Physical Vapor Deposition (PVD) onto the rear surface, followed by a firing step in an inline belt furnace resulting in a local BSF (Back Surface Field) formation. The dielectric layer on the front was opened by an UV-ps laser ablation. The laser speed was kept the same for all the samples, only the laser fluence was changed: 0.63J/cm<sup>2</sup> (soft laser) and 0.96 J/cm<sup>2</sup> (hard laser). A reference cell group, in which the front dielectric layer was opened by wet etching, was also made. Prior to plating, a short HF dip was performed to remove any native oxide in the contact opening areas. Approximately 1 $\mu$ m of Nickel was deposited by Light Induced Plating (LIP) followed by 8 $\mu$ m to 10 $\mu$ m of electroplated copper. Then the samples were immersed in the silver bath to form a thin capping layer. Finally nickel silicide was formed by annealing in a nitrogen ambient.

In this work, thermal ageing, which is considered to be the most detrimental for Cu-based metallization, is discussed. Ageing experiments are performed in vacuum ambient for temperatures up to 235°C. Samples are immediately removed from the oven and measured electrically at various times. Samples are considered to have failed if the electrical properties reduce to 95% of the original value. The cells were characterized based on light I-V and SunsVoc measurements.

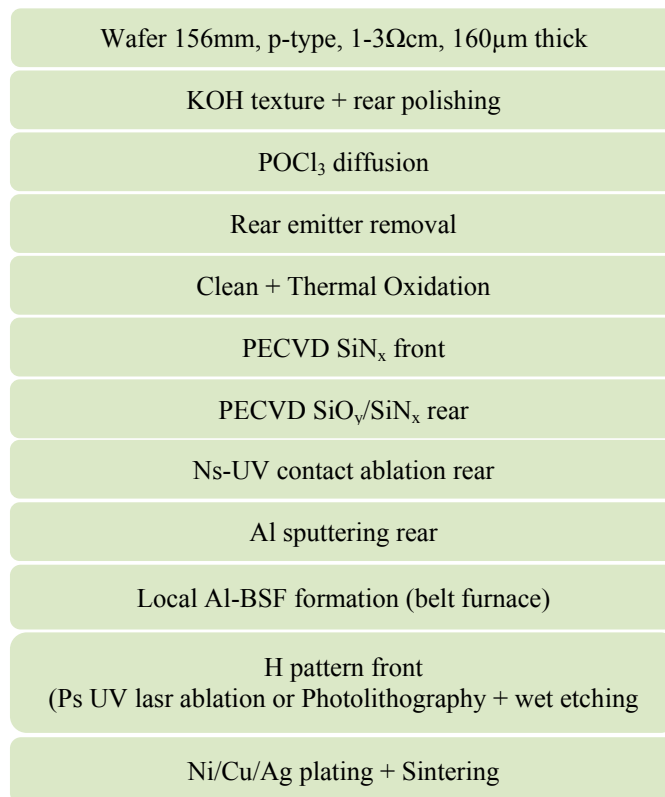


Fig. 2. Process sequence for p-PERC cells

A Fourier-transform Deep Level Transient Spectroscopy (DLTS) [5] was carried out for cells before and after thermal stress testing to assess the deep level defects present in the p-type silicon substrate. The cells were diced to small 5 mm by 5 mm samples by a ns laser. The dicing was done from the rear side of the cells in order to avoid damage induced by this laser to the front pn junction. The DLTS has been performed using a Fourier Transform (FT-)-based digital system, which a Boonton capacitance bridge operated at a fixed frequency of 1MHz. A bias pulse from depletion to forward bias was applied to the front contact, with the silicon substrate grounded in order to fill the traps in the depletion region. A sufficiently long pulse of typically 1 ms was employed which saturates the DLTS peak height. The emission transient in the capacitance following the filling pulse was used to derive the

spectrum by a combination of FT coefficients. Samples were mounted in a liquid nitrogen flow cryostat, enabling temperature scan DLTS from 75K to around RT (320K).

### 3. Results and discussion

#### 3.1. Thermal ageing reliability

Ageing experiments are performed in vacuum ambient at a temperature of 235°C. This temperature was chosen because it is close to the nickel silicide sinter temperature. It is known that if any Ni/Cu would diffuse during the ageing process, it would first degrade the pseudo Fill Factor (pFF). The results of pFF versus time are shown in Figure 3a.

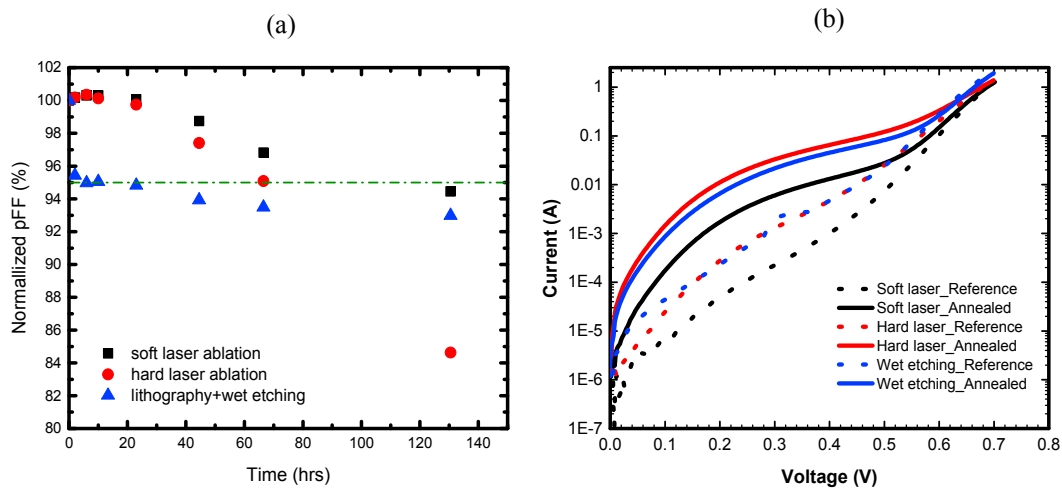


Fig.3. (a) Monitoring of normalized pFF after sintering at 235°C for different times, (b) dark IV curve of different cells before and after thermal ageing

A clear degradation of the cell performance as function of the annealing time is observed. The cells which have contact opened by hard laser ablation fail faster than the ones using the soft process. The pFF of the lithography followed by a wet etching (reference cells) drops even after a few hours annealing. Quite similar behaviour for the reference cell was reported by Labie *et al* [6]. The dark I-V curves of the different types of cell before and after failure are shown in Figure 3b. A striking feature is the hump appearing slightly below 0.6V (so around Maximum Power Point) for all type of cells, which correlates with the FF drop after failure by thermal annealing. These humps are the result of the saturation of Shockley-Read-Hall recombination via the defect levels, which dominates behaviour at low forward bias [7]. There might be different fail mechanisms between laser ablated cells and wet etched cells, because (i) we noticed a problem with adhesion for the wet etched cells, which would lead to higher contact resistance compared to laser ablated cells and (ii) higher sinter temperature was required for the wet etched samples compared to laser ablated samples in order to have adhesion.

#### 3.2. DLTS observation

Previous work has shown the laser ablation induced dislocations do indeed increase the recombination current in the ablated area [8]. The dislocations further extend to the silicon bulk especially when a high laser fluence is applied, which could be detected by DLTS. More detail on DLTS properties and principle could be found from [9]. Some of the temperature (T-) scan DLTS-spectra of Figure 4 have been observed while warming up from 75K to room temperature and applying bias pulses. Typically, in p-type silicon, positive peaks correspond to hole traps, negative peaks to electron traps. As can be seen in the Figure 4, three hole traps are found for the soft laser ablated

samples (fig.4a) and two hole traps found for the hard laser ablated samples (fig.4b).

The shallow peak H1, which is revealed at 80K for all samples, suggest this deep level trap induced during the cell processing, could act as a donor level. According to the [10, 11], this deep level could belong to either substitutional Cu at 100K or substitutional Nickel at 80K. In order to understand this peak, activation energy need to be calculated. The activation energy of this peak could be extracted from an Arrhenius plot as following

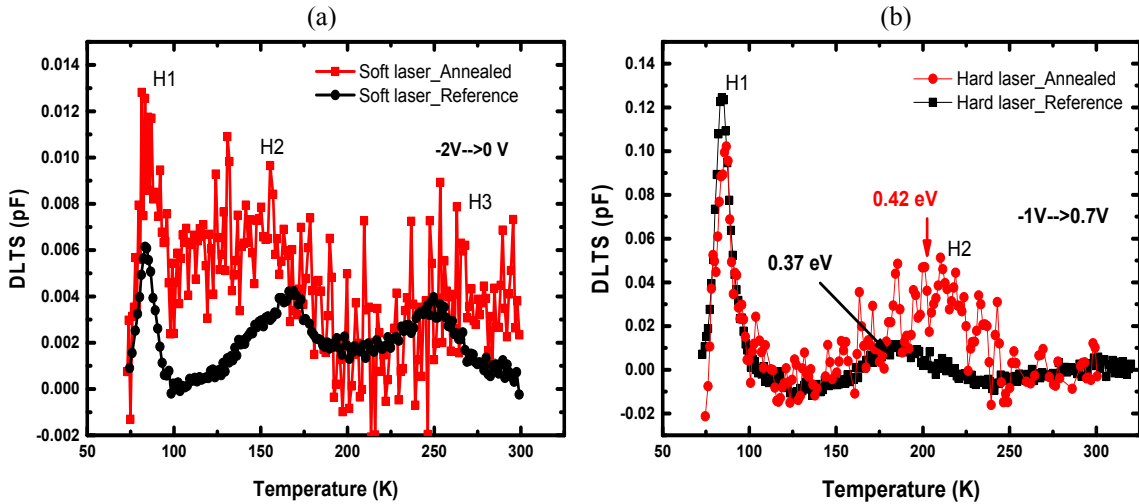


Fig.4. DLTS-spectra before and after annealing of samples following a (a) soft laser ablation or (b) a hard laser ablation process

The emission rate for hole in p-type Silicon  $e_h$  is defined as

$$e_h = \frac{1}{\tau} = \sigma_p \beta T^2 \exp\left\{-\frac{(E_T - E_V)}{kT}\right\} \quad (1)$$

Where  $\tau$ : emission time constant (s)

$\sigma_p$ : capture cross section of hole ( $\text{cm}^2$ )

$\beta$ : pre factor ( $\text{s}^{-1}\text{cm}^{-1}\text{K}^{-2}$ )

$(E_T - E_V)$ : activation energy

$$\text{therefore} \quad \ln(\tau T^2) = -\ln(\beta \sigma_p) + \frac{E_T - E_V}{kT} \quad (2)$$

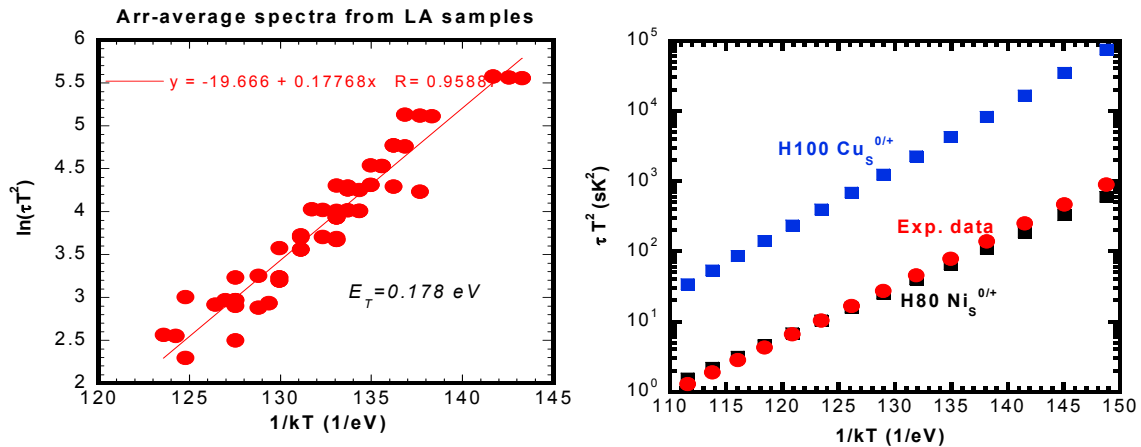


Fig.5. Arrhenius plot of the peak H80K

Figure 5a is an Arrhenius plot of the peak maxima obtained for the different spectra for all the laser ablated samples for the hole trap observed around 80 K. From the slope of the least-squares fit line, an average activation energy of 0.178 eV is derived, which indicates the deep level belong to the H(80K) locates around 0.178 eV from the valence band in p-type silicon. A comparison of this deep level with the known  $\text{Cu}_s$  and  $\text{Ni}_s$  levels is shown in the Figure 5b. It suggests the deep level H(80K) corresponds to the substitutional nickel donor level since there is a good overlap of both Arrhenius plots. This peak appears in all the samples, before and after thermal ageing, which means the nickel diffuses in already after the plating and sinter step. The concentration is estimated at the level of  $10^{12}$  atom/cm<sup>3</sup>, which is rather low. However, in perfect Si wafers, the Ni concentration is below what is found here, and, moreover, it is also considered as a lifetime killer or recombination center when it decorates extended defect like dislocations [12].

There is no copper detected in the silicon substrate, within the detection limit of  $10^{11}$  cm<sup>-3</sup>, as can be seen in the figure 5b as well.

Another two semi-shallow hole traps at 170K and 250K could correspond to interstitial carbon-interstitial oxygen ( $\text{C}_i\text{O}_i$ ) complexes from the substrates. Interestingly, there is a quite broad peak, which typically corresponds to dislocations in silicon, observed around 180K for the hard laser ablated samples. This peak shifts to a higher temperature (200K) and has a higher amplitude after thermal ageing. The energy of this peak is calculated to be around 0.42 eV at 200K after annealing, which is closer to the silicon mid-gap, meaning this deep level becomes more harmful for the solar cell. The shifting of this deep level could be due to more decoration by impurities in the dislocations [ ]. Finally, we recently observed a Boron doping profile change after thermal treatment for the laser ablated samples as well, further study of this behaviour is on-going.

#### 4. Conclusions and outlooks

The reliability of Ni/Cu plated p-type PERC cells is investigated by applying thermal stress tests and DLTS measurements.

Ageing experiments are performed at 235°C for different cell groups with either laser ablation (low or high laser fluence) or wet etching. A 5% Fill Factor degradation is taken as failure criterion. The cells groups failed after different annealing times due to the appearance of a hump in the dark IV-curve, resulting in a drop in FF. An optimized laser process prior to plating and sintering is therefore paramount to avoid this behavior.

The DLTS results show a hole trap at 80K observed for all the samples, which indicates this deep level (donor level) is induced during the cell processing. A broadened peak around 180K for the hard laser (high fluence) ablated cell could correspond to dislocations generated by laser. The shifting of this peak to a higher temperature and higher amplitude could be due to impurity decoration.

The next step of this work is to further analyze the DLTS results to point out any diffused Ni/Cu which could

interact with the dislocations. Afterwards, a correlation to electrical properties will be studied.

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