ADVANCED FRONT SIDE METALLIZATION FOR CRYSTALLINE SILICON SOLAR CELLS BASED ON A FULLY PLATED CONTACT

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ABSTRACT: Nickel-Silicon contact systems have been studied intensively on shallow industrial emitters, with special focus on the contact formation step. Two different means of antireflexion-coating (ARC) ablation, dry laser ablation and inkjet-masking and etching have been used. Nickel layers have been applied by electroless and light-induced plating (LIP) processes, and have been reinforced with LIP silver or copper. The plating process and the thermal silicide formation step have been varied for the electroless deposition process, making a statistical evaluation of the results. The nickel layer deposited by LIP has been found to form a good contact to silicon easier than the electroless nickel. This is contrary to earlier findings, and attributed to the use of a new electrolyte. Longer nickel plating durations have led to better results for subsequent silver plating. The best solar cells (Cz, 5x5 cm²) created reach efficiencies above 17%. The adhesion has generally been found to be higher for laser-ablated cells. The impact of the nickel contact formation on the junction has been studied by measuring the pseudo fill-factor (pFF). For relatively mild thermal steps, moderate losses in pFF have been found, yielding the best results.
Keywords: Metallization, Contact, Electrodeposition, Nickel.

1 INTRODUCTION

In order to reach grid parity for photovoltaic solar energy conversion, combined efforts are made to reduce the manufacturing costs for crystalline silicon solar cells while at the same time increasing their efficiency. In this context, increasing the typical cell size has led to a demand for an advanced front side metallization, in order to keep series resistance losses at a low level. A two-step concept, similar to the front side metallization of high-efficiency laboratory solar cells has been shown to exhibit various advantages [1]. Process schemes with fine line printed seed layers and light-induced plating of silver are already close to industrial introduction [2].

These process schemes are a mixture of established (printing and firing) and novel (wet-chemical) metallization techniques. Many efforts have been made to fully replace the standard techniques by an approach fully based on wet chemical processes, with nickel as seed layer. Several advantages are expected from such a metal system. First of all, the contact barrier height between nickel and silicon is lower compared to silver contacts on n-type emiters. Furthermore, a full area contact between the two materials can be made at a low temperature (<400°C), while the classical fired contacts need temperatures of 700°C or above and form only local contacts (i.e. crystallites). This has the potential to improve the contact resistivity and allows the application of superior passivation layers that are sensitive to thermal stress (e.g. a-Si) and the use of emitters with a reduced surface doping concentration. Additionally, wet-chemical metallization techniques induce very low mechanical stress to the thinner wafers that will be entering the production lines. This enables higher yields while at the same time lowering metallization costs. This is the case especially if copper is used as conductive material, which is possible with a suitable nickel layer as seed layer, because nickel will prevent copper from diffusing into the solar cell. On a high-efficiency substrate, the potential of this front side metallization technique has been demonstrated with a cell efficiency of 20.7% in our labs [3].

To allow an industrial application of any metallization technique, several requirements must be met. For the front side metallization, there are optical, mechanical, electrical and economical factors to be considered. An overview is given in Table 1. While for some of these properties novel metallization techniques based on nickel-silicon contacts are superior to the established screen printing, others are not yet in a stage to enable industrial introduction. However, further process development increases the chances to achieve this goal in the near future.

Table I: Desired properties in metallization systems for silicon solar cells and corresponding situation for screen-printed contacts and contact systems based

Electrical properties	**Screen Print**	**Ni-based LIP-Contact**
Low contact resistance (also on $R_{Sh}\uparrow$ emitter)	**o**	+
Low specific line resistance	**o**	+
No electrical cell damage	+	*Process depending*
Optical properties		
High aspect ratio, low shading	-	+
Mechanical properties		
Good adherence Si – Metal	+	*Process depending*
Good adherence between different metal layers	**( )**	*Process depending*
Economical properties		
Process time and efforts	+	-
Yield and Materials	-	**(+)**
Cell efficiency	**o**	+

2 EXPERIMENTAL

For the plating experiments, commercially available industrial substrates with a size of 156x156 mm², a shallow 65Ω/sq emitter, a SiN_x-ARC and a screen printed and fired aluminum rear side were used. These were cut into 5x5 cm² test cells. Two different techniques were examined for selective ARC-opening: the mask & etch method [4] and laser ablation. In the first technique a hydrofluoric acid resistant ink is applied to the ARC by inkjet printing, leaving gaps in the regions the grid is to end up (fig. 1a). Since this is done free of mechanical contact, the risk of breakage is minimized. The unprotected area of the ARC is etched by hydrofluoric acid, exposing the emitter (fig. 1b). The mask can then be stripped by an organic solvent (fig. 1c).

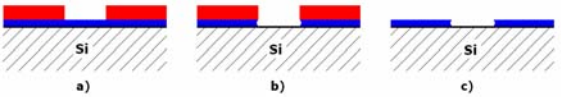

Figure 1: Schematic image of the mask & etch sequence

The laser-ARC-ablation is done by scanning the wafer with a pulsed laser beam in the desired grid pattern. Since the geometry of the random pyramids focuses the light on their edges [5], the emitter is primarily exposed in these areas. This leads to a smaller opened area than with the use of masking and etching, but it is well sufficient for electrical contact. Laser ablation allows the application of extremely thin fingers for minimal shading loss.

These methods have the distinction of a low cost opening with a minimized risk of breakage, since they are performed free of mechanical contact.

The used electrolytes were commercially available silver, copper and electroless nickel plating solutions, and a simple Watts type nickel electrolyte for light-induced plating (LIP) set up in our labs. Temperature and electrolyte properties were kept constant between all experiments and according to the manufacturer's specifications. Potentials and currents were applied and measured by either using a versatile multichannel potentiostat (VMP, Bio-Logic) for the silver deposition experiments, or a programmable source measure unit (Keithley) with a coupled power amplifier. A schematic image of the plating bath's setup can be seen in fig. 2.

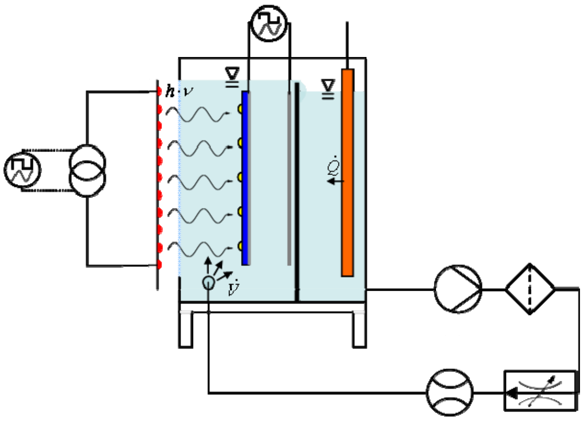

Figure 2: Schematic image of the used plating bath setup

In case of the electroless nickel plating no rear side voltage is necessary. Deposition only takes place on catalytically active surfaces, meaning the exposed areas of the emitter and not the ARC. Light is used for adjustment of the electrochemical potential of front and rear side (see fig. 3).

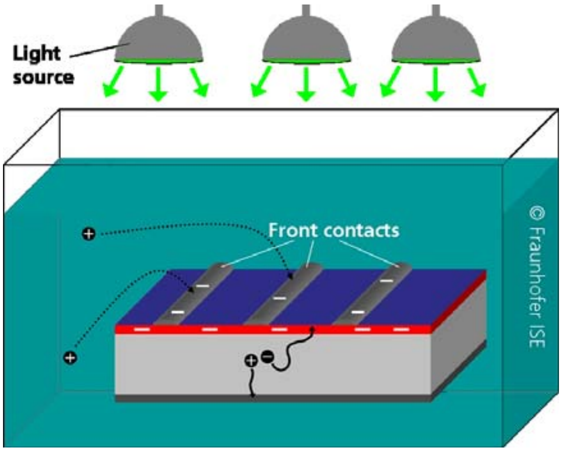

Figure 3: Schematic image of the light assisted electroless plating

In case of the light induced plating, the power produced by the illuminated cell is used for plating. A voltage is applied between the rear side of the cell and the nickel, silver or copper source (see fig. 4). Deposition only takes place on conductive surfaces, meaning the opened areas, not covered by the ARC.

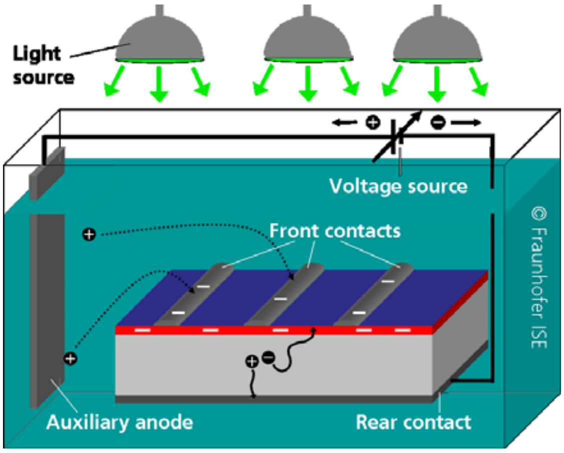

Figure 4: Schematic image of light induced plating

The properties of the resulting nickel layers vary in their advantageous fields of application. The Ni-LIP method is rather simple and has a high plating rate, while requiring only minor process maintenance, though obtaining good homogeneity of the plated layer is challenging. It is well suited for seed layer deposition and barrier layer deposition - also on a printed and fired seed. The light assisted electroless plating is an extremely simple process with a very good control of layer homogeneity. Electrolyte maintenance is more demanding, since chemicals are used up, constantly changing concentration proportions. It is suitable for seed layer deposition, while barrier layer deposition is limited due to relatively low deposition speed (even if accelerated by light).

Temperature stress experiments for simulated ageing and long term stability estimation were carried out using an ordinary hotplate with a programmable control unit. Pseudo fill-factor (pFF) measurements were made with the Suns-V_{OC} technique as described by Sinton and Cuevas [6], using the generalized analysis type, with temperature correction to 25°C.

The statistical evaluation of the results has been done with STATISTICA®, Version 9.0. The 3D-plots shown in the paper represent a fit to a model of the experimental system created by the software. The black dots in the diagrams represent the measured values.

3 RESULTS & DISCUSSION

As can be seen in table I, development for a metallization based on nickel-silicon contacts is necessary mostly regarding electrical cell damage and adhesion.

Cell damage may be induced during thermal contact formation, analogous to screen printing. In the classical understanding, a cell is “overfired” if metal penetrates into the space charge region, leading to increased recombination and shunting. For screen printing, processes and pastes have been optimized to suit even the currently used shallow industrial emitters. The contact formation between nickel and silicon is very challenging on shallow emitters, as nickel diffuses quickly in silicon at moderate temperatures.

The adhesion is linked with the contact formation as both are influenced by the formation of silicides. However, the most important factor for good adhesion seems to be the surface roughness of the silicon on which the nickel is being plated. Rough surfaces have been found to be favorable to very smooth ones [7], which is in good agreement with our results.

3.1 Investigation of contact formation and cell damage

In order to optimize the contact formation step, a variation of plating and sintering conditions was made. The used cells were ablated by laser and mask & etch, the nickel seed layer was applied with light supported electroless nickel plating. Contact formation was carried out in a tube furnace under forming gas atmosphere, the temperature was varied between 300°C and 500°C, the duration between 30 seconds and 900 seconds. The initial nickel layer thickness was varied by adjusting the plating duration between 10 seconds and 120 seconds. The idea is that by having a very limited initial layer thickness, the formed silicide will not penetrate far into the wafer. As mentioned above, the damaging mechanism of nickel in solar cells is related with the metal reaching the space charge region (fig. 5). Theoretically, the thickness of the silicide should be limited to twice the initial metal layer thickness in the considered temperature regime (Ni_2Si and NiSi-formation, [8]).

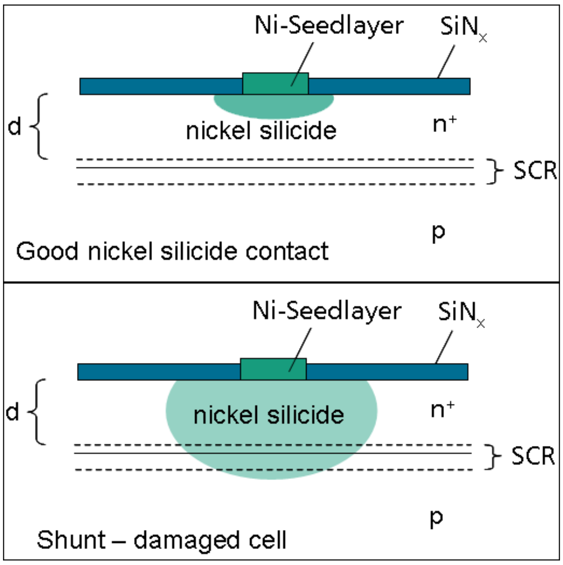

Figure 5: Damaging mechanism of nickel in silicon solar cells

The pseudo fill factor is a very good means to evaluate the junction quality and thus the state of junction impurification. We measured the pFF for all cells used before and after the thermal treatment.

For experiments with mask & etch opened contact areas, we found the drop in pseudo fill factor indeed to be relatively low, even at high sintering temperature and duration (fig. 6). However, this is also true for the longest chosen plating durations. An SEM investigation of the resulting contacts showed that the thickness of the nickel layer was still limited to several hundred nanometers. It is likely that the nickel source was too thin to allow a penetration into the silicon as far as the space charge region. The effects observed are only very minor.

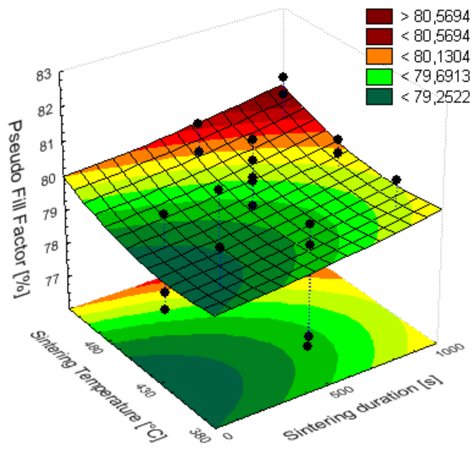

Figure 6: Pseudo fill factor after sintering for mask & etch-ablated solar cells for different sintering temperatures and durations.

A high pseudo fill factor is one major requirement to get a high FF and thus highly efficient solar cells. However, as we attempted to plate a silver grid on top of the created Ni-Si-contacts, the resulting structure was incomplete (less than 50% of the intended grid was formed, fig. 7). We believe that this is due to the almost complete consumption of the nickel seed as silicide, and an insufficient capability of silver to plate, or at least to adhere directly on nickel silicides. An influence of the ablation step cannot fully be excluded, but optical examinations have shown good contact openings. Using lower sintering temperatures and durations, very good grid formation by silver plating was achieved, with good reproducibility (fig. 8). These cells also showed only moderately lowered pseudo fill factors (graph not shown). In order to observe the effect of pFF-drop at high temperatures, we are currently running further experiments with thicker initial nickel layers.

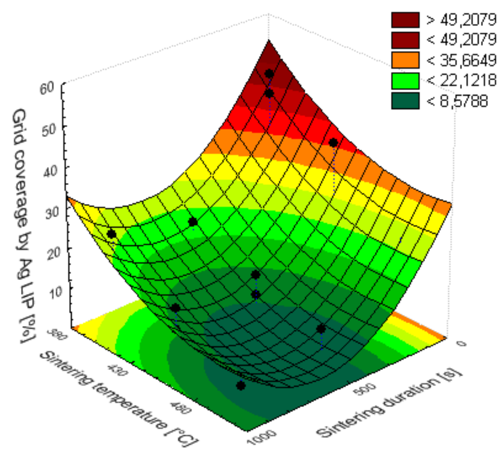

Figure 7: Resulting percentage of the grid covered with silver after the subsequent reinforcing step for mask & etch-ablated solar cells for different sintering temperatures and durations.

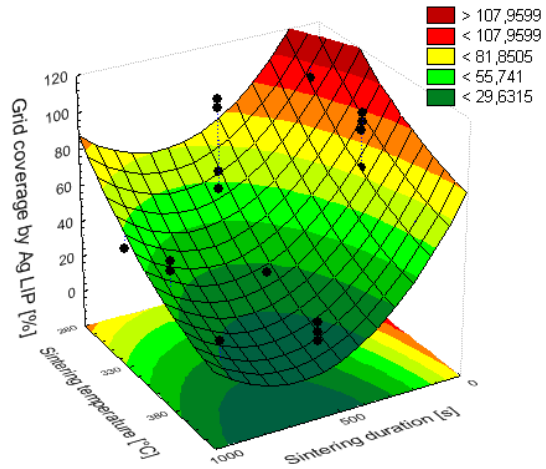

Figure 8: Resulting percentage of the grid covered with silver after the subsequent reinforcing step for mask & etch- ablated solar cells sintered at lower temperatures. Values above 100% are artefacts of the statistical model.

For the laser ablated solar cells, the influence of sintering temperature and duration on the pFF are more pronounced (fig. 9). The behaviour found for the grid coverage is the same as for the mask & etch ablated solar cells (fig. 10).

As mentioned the fraction of the opened ARC area is a lot smaller for the laser ablated solar cells. Already for rather low plating times, globular depositions of a certain size are observed in the SEM investigation in the ablated areas. This may be the reason for a greater impact on the pFF which was observed for the laser ablated solar cells. The similar behaviour for the coverage indicates that the nickel seed layer is probably still fully consumed for these conditions.

Longer plating durations led to a drop in pFF, but an important decrease was only observed if long plating durations and high sintering temperatures were combined. An SEM investigation showed that even at 120s of plating, the resulting layers are still in the range of several hundred nm thickness.

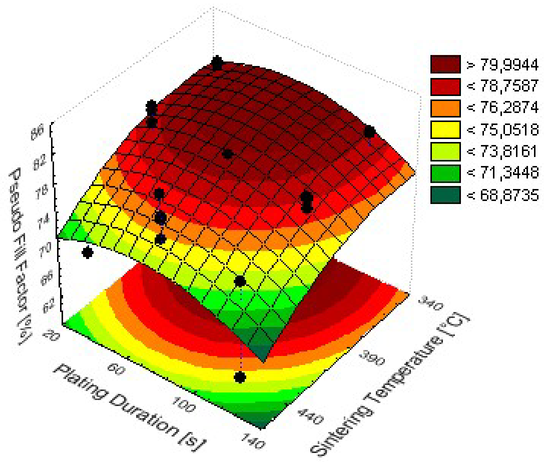

Figure 9: Pseudo fill factors of solar cells with laser ablated ARC sintered at different conditions.

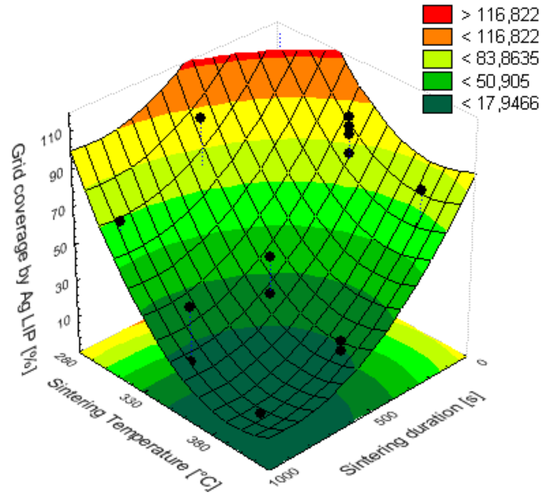

Figure 10: Resulting percentage of the grid covered with silver after the subsequent reinforcing step for laser ablated samples. Values above 100% are artefacts of the statistical model.

The system behaviour was found to be generally the same for both kinds of ablation, however, slightly higher temperatures were found to be favorable for the performance of laser ablated solar cells.

3.2 Solar cell results

For the solar cells with sufficient grid coverage, light- and dark IV-curves were taken. A reasonable measurement was only possible for some of the cells, so it was not possible to arrange the results in the same kind of diagram as shown before. The best solar cell results are shown in table II. As can be seen, the short circuit current is very high, especially for the laser ablated solar cells, which had initial opening widths of about 20µm. The relatively low fill factor is only partly caused by junction problems, as can be seen from the pFF and j_{02} values. The used grid design is optimized for use with screen printed metallization and needs to be adjusted for the Ni-Si approach. Although we already achieved quite high efficiencies, the technique has a higher potential if grid design, contact formation and emitter are optimized. Currently, the distance between two fingers is 2mm, following the design for a screen printed cell as reference. Simulations show that for the very narrow contact widths, especially for laser ablated cells (20µm openings) a distance of 1.5mm is suited better.

Table II: Solar cell results of the best cells created in the process described above (M&E: Mask & etch ablated solar cells).

	J_{SC} [mA/cm²]	V_{OC} [mV]	FF [%]	pFF [%]	R_S [Ωcm²]	η [%]
M&E	36.1	621	76.5	79.5	0.41	17.1
Laser	37.0	624	75.3	78.7	0.78	17.4

3.3 Investigation of adhesion

To investigate the adhesion, a simple TESA-tape test was performed. Due to the mentioned issues in plating the full grid, we only used cells with sufficient coverage of silver on top of nickel. Consequently, there was no possibility to correlate the result of the adhesion test with the sintering profile, as originally planned. However, it was possible to draw some conclusions from the tape test. From the seven mask & etch opened cells with full grid, only one passed the test without any grid removal, this was also the cell mentioned in table II. The remaining cells lost 5-50% of the grid where the tape was applied. From the group of laser ablated samples, 18 cells which had a full grid were tested. One third of these cells passed the test without damage, the others had moderate grid losses between 5-20%. In general, the dry laser ablation was found to give better adhesion, relatively irrespective of the applied temperature. This indicates that the surface structure plays a more important role than the silicide formation, although we admittedly only performed this test on cells which had been sintered at 300-400°C. It is worthy to mention that both champion cells passed the test without damage.

3.4 Use of copper as conducting layer

In a further experiment, the above presented findings were applied on solar cells which were intended to be finished by copper plating. In this case, we used the nickel LIP process instead of the electroless plating, as the layer thickness needs to be increased in order to effectively act as diffusion barrier layer to copper. The deposition speed is much higher for the LIP process than for the electroless plating. In this case, laser ablated solar cells were used.

With the sintering process found in the experiment before, a contact with similar properties was formed, although a much thicker nickel layer was deposited with different process (LIP) this time. The cell parameters for the best manufactured solar cell are given in table III.

Table III: Solar cell result for the best cell with NiCuSn-Metallization.

	V_{OC} [mV]	J_{SC} [mA/cm²]	FF [%]	pFF [%]	η [%]
Laser/Ni/Cu/Sn	623	37.1	73.9	79.9	17.1*

*: calibrated measurement: ISE-CalLab

In this experiment, there was a strong focus on the limitations of the solar cell long term stability due to copper diffusion. Our first results show that the used nickel-silicon contact system is very promising [9].

4 CONCLUSION

The investigated nickel-silicon contact system is very promising regarding several desired properties (low contact resistance, low shading, barrier against copper diffusion), if several issues are solved. The most important ones are a good contact formation without cell damage and a good adhesion. We found that by applying very thin nickel layers, the impact of the contact formation on the junction is minimized. However, probably due to full consumption of the plated nickel, the subsequent silver plating step failed in most cases, especially if high sintering temperatures were used. The ability of silver to plate and/or adhere on nickel-silicides is questionable. The experiment described in this work will be repeated with a thicker initial nickel layer. However, the best found solar cells yielded efficiencies of 17.1% (mask & etch ablation) and 17.4% (laser-ablation).

It is especially noteworthy that, even on the used shallow industrial emitter, pseudo fill factors of almost

80% were achieved, indicating that the found contact formation process induces only very little damage to the cell. An optimized grid design should be able to bring the FF closer to the pFF.

The adherence has been found to be an issue even for the qualitative tape test. Samples with laser ablated ARC show better adherence and pass the tape test for certain sintering conditions reproducibly. Solder- and peel tests are under preparation.

The best found contact formation process has been shown to be also effective for samples with thicker initial nickel layer as needs to be used for cells with copper as main conducting material.

As mentioned, working on shallow emitters is very challenging. Deep and selective emitters are generally beneficial for solar cells, and different process approaches in this direction are investigated intensively at the moment (e.g. laser-chemical processing, PSG laser-doping, printed dopants). Some techniques are already close to industrial introduction. The use of a selective emitter perfectly matches the requirements of a nickel-based metallization. The flexibility for the thermal contact formation step is increased, as the risk of SCR contamination is lowered. For the LCP-technique, the ablation can be done in the same step as the selective doping, additionally leaving behind a very rough surface which allows good adhesion. Further work will be done combining the nickel-based metallization approach with selective emitter processes.

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