# **Crystalline silicon solar cells with selective emitter and the self-doping contact**

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Reviewed

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One of the key questions of our world is the energy-supply of the people while protecting the environment suitable for life. One solution for this problem is the use of renewable energy sources. In Hungary the share of this energy amounts to only a few percents of the total energy-supply. While the using of the biomass and the geothermal springs are only near-term solutions, for long-term the utilizing of solar and wind energy has to be considered.

# **1. Introduction**

The advantages of the solar energy are:

- In practice it is available without limits;
- Using this energy we can save fossile energy-sources for other needful applications;
- Environment-friendly,
- it does not contribute to global warming.

Photovoltaic systems convert directly the radiance of the Sun to electric power by solar cells, therefore they are very attractive energy sources, because they do not generate any pollution during operation. Their lifetime can be as long as 20-30 years and they need very little maintenance that consists of almost only keeping their surface clean.

For crystalline and multicrystalline silicon solar cells one research trend of the current is to prepare the front side contacts such way that optimizes the solar cell parameters. The main problem is the following. For the best solar cell parameters a low doped and shallow (so with high square resistivity) n-type silicon layer is necessary on the top of a p-type layer, altough on such layer we cannot prepare a good ohmic metal contact. For a good ohmic contact a highly doped and deeper (so with low sqare resistivity) n-type layer is required.

One solution for this problem is the use of selective emitter instead of homogeneous emitter. This metallization technology creates a highly doped layer under the contact, and a low-doped layer between the contacts, so both requirements are satisfied, and the efficiency of the solar cells increases as compared to the ones with homogeneous emitter.

Today for commercial crystalline and multicrystalline solar cells the manufacturers are using the screen printing technology for metallization, because it is simple and cheap. An important research trend is the improving and optimizing of this or other inexpensive technologies to make the production of solar cells more and more cheap. Hence it is worthwile to use this technology also for solar cell prototypes for research aimed as increasing the efficiency so that both research trends could achieve the aims after a successful cell improvement.

In this article after a short explaining of the basic terms in this section, we look on the theory of selective emitter and its realized technologies in the 2nd section, and in the 3rd section we examine the theory and realization of the self-doping metallization technology.

# Basics [2,3]

Before the detailed exposition of the technologies of selective emitter we review the basic terms used in connection with solar cells (parameters, coatings, crystalline structure).

# Parameters:

AMO, AM1 and AM1.5: the intensity of solar radiation in free space (Air Mass 0, AM0) is 1353 W/m<sup>2</sup> on the average with a special irradiance spectrum. Assuming one air mass at perpendicular incidence (AM1) a weaker irradiance power density reaches the surface of the Earth (925 W/m<sup>2</sup>), because the molecules of the air filter the spectrum of the solar radiation. In case of a not perpendicular incidence, the air mass is bigger for the radiation, so the power density is less, e. g. at 45 degree incidence (AM1.5) it is about 844 W/m<sup>2</sup>. However there is also an indirect (diffuse) radiation on the Earth because of the photons scattered by the molecules of the air. This increases the AM1.5 intensity to about 970 W/m<sup>2</sup>, which is a good approximation for the usual terrestrial applications. For characterizations of solar cells the AM1.5 irradiance spectrum normalized to 1 kW/m<sup>2</sup> is used.

Short-circuit current density  $(J_{sc})$ : the short-circuit current of the illuminated solar cell (it belongs to V=0 V voltage) gives the maximum current in the device, because in practice it is equal to the current generated by the light ( $I_{sc}$ = - $I_L$ , where  $I_L$  is the light generated current). Because the current depends on the surface

area, the current density is used instead of it  $(J_{sc}=I_{sc}/A)$ , where A is the surface area). In addition it depends on the solar spectrum, the intensity of the light (the number of the incident photons), the efficiency of the current collection, and the optical parameters. In silicon solar cells the maximum available short circuit current density at AM1.5 spectrum is 46 mA/cm<sup>2</sup>.

Open circuit voltage ( $V_{oc}$ ): it is the maximum available voltage in the solar cells (it belongs to I=0 A current). Its value is:

$$V_{oc} = V_T \ln(1 + \frac{I_L}{I_0}) \cong V_T \ln \frac{I_L}{I_0}$$

where  $V_{\rm T}$  is the thermal voltage that is constant for a given temperature,  $I_0$  is the saturation current. The open circuit voltage depends mainly on the saturation current of the device, because it can vary within several orders, and to a smaller degree it depends also on the light generated current ( $I_{\rm L}$ ). Hence  $I_0$  depends on the recombination mechanism, we can say  $V_{\rm oc}$  characterizes the recombination. The highest value that has ever been measured on silicon solar cells is 720 mV at one sun intensity, AM1.5 spectrum and room temperature.

Fill factor (FF): this is the ratio of the maximum delivered power ( $P_m = V_m I_m$ ) and the product of the open circuit voltage and the short circuit current (the maximum available values) at a given illumination, so it characterizes the maximum power we can extract from a solar cell:

$$FF = \frac{V_m I_m}{V_{oc} I_{sc}}$$

It can be calculated theoretically, but in fact it used to be a smaller number because of the parasitic resistances, so usually it is measured for a real solar cell. Its value depends mainly on the operating point, the open circuit voltage, and the recombination rate of the cell, so it depends on the the structural quality of the device. The greater the recombination rate, the less the FF and the V<sub>oc</sub>. Because the V<sub>oc</sub> does not change much in a material system it affects the FF to a small degree. The theoretical value of FF that belongs to the highest V<sub>oc</sub> ever reached in a Si solar cell is about 0.85.

*Efficiency*: the ratio of the maximum delivered power and the power carried by the incoming photons:  $\eta = P_m/P_{be}$ . For a given material system, its value depends on the temperature of the solar cell, the solar spectrum and intensity of the incident light, and the technological and material properties of the solar cell structure. Hence for the measurement of the efficiency a standardized light source is used (with one sun intensity and normalized AM1.5 spectrum), and a constant room temperature (25°C) is ensured.

Sheet resistivity: for the top emitter layer of the solar cells, the resistivity as well as the thickness of the layer is often unknown or hard to be measured. However, a value known as the "sheet resistivity", which depends on both the resistivity and the thickness, can be easily measured using a "four point probe" for the top surface n-type layer. For a uniformly doped layer, the sheet resistivity is defined as:  $\rho_{\Box} = \rho/t$ , where r is the resistivity of the layer, and t is the thickness of the layer. The sheet resistivity is increasing by the increasing of the resistance of the layer (so by the decreasing of the doping), and by the decreasing of the thickness of the layer.



Internal quantum efficiency (IQE): The quantum efficiency (Q.E.) is the ratio of the number of carriers generated by the solar cell to the number of photons of a given energy incident on the solar cell, as a function of wavelength or as energy. Internal quantum efficiency refers to the efficiency with which photons that are not reflected or transmitted out of the cell can generate collectable carriers. The QE curve caracterizes well the material parameters of the solar cells (surface recombination, bulk diffusion length, etc.)

#### **Coatings:**

Surface passivating layer: It is a transparent dielectric layer grown on the top surface of silicon, which has an appropriate material stucture for reducing the number of dangling silicon bonds and defects at the top surface, so the surface recombination velocity of the carriers decreases. The passivation effect can be increased further by bulk passivation using hydrogenation in the Si bulk to reduce bulk defects by hydrogen.

Anti-reflection coating (ARC): It is a transparent insulator layer with an appropriate thickness that increases the efficiency of the solar cell by reducing the photon reflection of the surface, optimized for a wavelength of 0.6  $\mu$ m since it is close to the peak power density of the solar spectrum. Using a special material for it (e.g. SiO<sub>2</sub>, SiN<sub>x</sub>) this layer can also function as a passivating layer. The efficiency can be increased further by surface texturing that causes a mat surface. The increased area and the structured surface results in increased photon absorption and decreased reflection.

#### Crystalline structure:

Single crystalline Si (Cz-Si, FZ-Si): Solar cells need good quality and cheap bulk material with few crystalline defects so the minority carrier lifetime (and the diffusion length) can be fairly long to have a high probability for the generated carriers to reach the contacts. Such quality single crystalline solar cell with silicon bulk material can reach an efficiency greater than 20%. In this case the whole Si wafer is a single crystal with the same crystalline orientation and overall structure. The manufacture of the silicon wafer needs high temperature, long time and good care, so its price is accordingly high. Cz-Si stands for Czochralski manufacturing process, and FZ for floating zone process. Cz-Si bulk material contains relatively high oxygen and carbon contamination levels that can decrease the bulk minority carrier lifetime, moreover the oxygen activates at high temperatures so this wafer is more sensitive to high temperature processing. The FZ-Si contains much less oxygen and carbon contamination levels so the minority carrier lifetime is of the order of millisecs. However this better quality bulk material is more expensive than Cz-Si.

Multicrystalline Si (mc-Si): The high cost of good quality single crystalline silicon materials were strong motivation to the utilizing of multicrystalline semiconductor bulk materials. In multicrystalline bulk material each crystalline grain has a crystalline structure, but each of their orientation is different. Other handicap of the multicrystalline material is the high defect density at the grain boundaries that decreases the minority carrier lifetime by increasing the local recombination rate, leading to a lower efficiency. On the other hand it is easier and cheaper to manufacture it. The handicaps decrease if the grain sizes are bigger than the diffusion length, so minimum a few millimeter. It is important that no grain boundary is allowable in parallel with the surface so the current does not have to flow through it. We can satisfy this requirement if the usual grain size is bigger than the thickness of the wafer.

# 2. Technology of the selective emitter

#### Theory [1,4,5,6,7]

The optimal emitter of the silicon solar cells with homogeneous emitter is a result of a compromise of the requirements of low dark current and low contact resistance. For passivated surface emitter the surface dopant concentration must be below 10<sup>20</sup> cm<sup>-3</sup> and the emitter must be shallow to keep the dark current (emitter saturation current density,  $J_0$  low. However for a sufficient contact (where the surface thus has no passivation), especially for a screen-printed contact the surface dopant concentration must be higher than 1019-10<sup>20</sup> cm<sup>-3</sup> for n-type silicon and 10<sup>17</sup> cm<sup>-3</sup> for p-type silicon, and the emitter must be relatively thick (>0.3  $\mu$ m). Therefore the homogeneous emitter needs such high suface dopant concentration and emitter thickness (so 0.3-0.4 µm), but this makes the surface passivation almost impossible.

We must also note that for increasing dopant concentration the surface state (interface trap) density,  $N_{it}$  increases, so the recombination increases, too.

The overall series resistivity of the cell, including the effects of the interfaces and the electrode materials, has to be lower than 1  $\Omega$ cm<sup>2</sup>, and the maximum of the contact resistance is 10m $\Omega$ cm<sup>2</sup> in it by practice. On the basis of modelling and experiments for a non-screen-printed contact the optimal homogeneous emitter has a sheet resistivity of 60  $\Omega/\Box$ , a doping of 2x10<sup>19</sup> cm<sup>-3</sup>, and a depth of 1,4 mm. For a screen-printed Ag contact the sheet resistivity of the emitter has to be lower than 45  $\Omega/\Box$  for an acceptable contact resistivity and a FF of not less than 70%. However such a highly doped homogeneous emitter decreases the response to short wavelength photons because of the high doping effects and the high recombination velocity that cannot be decreased sufficiently even by surface passivation.

The selective emitter, which has a high doping just under the metallization, can afford sheet resistivities even 70-200  $\Omega/\Box$  between the contacts. Therefore the high doping effect in the emitter decreases, and good ohmic contact and high FF can be realized with low dark current and good carrier collection yield. In this case the surface of the solar cell can be well passivated between the metal contacts, and the emitter under the metallization is less critical for firing through by the contact. Note that for the same emitter sheet resistivity the deeper and less doped emitter causes less loss in the photogenerated current density than the shallower and higher doped emitter.

On the basis of a theoretical model [6] the emitter surface doping concentration under the contacts (where the surface recombination was considered as infinite) is optimally  $10^{20}$  cm<sup>-3</sup>, and its depth is 3-10 µm, and the doping profile has to be decreased persistently inside the substrate. However for the illuminated areas the surface doping concentration is ideally  $10^{18}$ - $10^{19}$  cm<sup>-3</sup> constantly until a depth of 0,2-0,4 µm, where it has to be decreased abruptly.

The metallization of the silicon solar cells is a critical factor for the set of the overall electric and physical properties. The metallization can be a thin layer film (e.g. sputtering, vaporization) or thick layer (e.g. screen printing, stencil printing). The thick layer metallization technology is cheaper so it is often used for commercial and research manufacturing.

The thick layer metallization for the crystalline solar cells is used for realize the electric contacts and to assist the photocurrent collection. Advantages are the high photocurrent density, the low contact resistivity, relatively low line resistance, relatively good line resolution (50-100µm linewidth can be achieved), good solderability, adhesion and chemical strength, as well as the high productivity through the simple, quick and cheap technology. However the disadvantages compared to other techniques are the higher line resistance of the contacts caused by lower aspect ratio and higher resistance. The contact pattern is printed in one sweep of the squeegee, no vacuum or photolithography required for the metallization. The source of the problems is

the paste firing as its temperature is usualy in the range of 400-1000°C, and it is important that the contact metal must not penetrate the diffused layer too deeply. We can ensure this by firing the paste with the lowest possible temperature and duration. Hence nowadays the rapid thermal processing (RTP) technology is often used.

The *interdigitated back contact (IBC) cell structure* is simple and cheap, however it gives high effeciency.

Both of its positive and negative electrodes are on the back side of the cell, so on the illuminated side the contact metal does not overshadow the cell. On the front side only a very shallow and low doped homogeneous diffusion (for n-type substrate the optimal surface phosphorous doping is 10<sup>18</sup> cm<sup>-3</sup>) ensures the better surface properties. However on the back side there are also the n-type and p-type contacts, so in this case the local doping and hence the selective emitter is inevitable.

#### Realizations

Today in the industrial manufacturing of crystalline solar cells with homogeneous emitter conveyor belt systems are often used for the emitter diffusion (cleaning, screen printing, drying, annealing furnace etc.) [8]. In this process flow the diffusion source on the textured side of the p-type Si substrate is typically a sprayed or spinned on liquid containing phosphorous, or a screenprinted phosphorous paste. In the following drying step all solvents and organic components are evaporated or burned out of the doping source material. The wafers are further transported on the belt into a multizone furnace, where the appropriate emitter is made in temperatures typically above 900°C. Here the phosphorous diffuse into the substrate from the doping source. After that a passivating and antireflection layer is deposited on the surface followed by the screen printing of the metal contacts, and a subsequent drying and firing process (in 900°C). Lately instead of furnaces a conveyor belt system rapid thermal annealer is used, where the diffusion can be decreased to seconds.

The selective emitter structure was created in many ways. These technologies basically have two types: technologies that need scheme aligning, and self-aligning technologies. The scheme aligning process is more difficult, so it is more expensive. In case of aligning metallization to the underlying diffusion the misaligning is critical because if the metallization overlies from the highly doped area to the weakly doped area, the dark current of the device will increase and the contact resistance will be worse. It can also happen in this case that the metal get into until the p-n junction so it can shortcircuit the whole cell. To avoid this the scheme of the highly doped diffusion has to be larger with the scale of misaligning error (for screen printing it is 1-2 µm, for photolitography it is much less). However in this case the dark current increases, and a dead layer formes where the highly doped area overlies the metallization. Furthermore in case of the laser overdoping technology (see IV.) the manufacturing cost is increased by the longer use of laser. In case of the etch-back technology (see II.) a dead layer also formes when the etch protective layer must be screen-printed aligned to the metallization. However in this item the most significant processes are grouped by the manufacturing techniques. Table shows us the published properties of the mentioned selective emitter solar cells.

**I.)** The double diffusion technique with *photolitography* is used for high efficiency cells, because you can reach the finest scheme resolutions with it, however it is the most expensive solution. The other techniqes (II.-V.) try to make this original technique cheaper, simpler and however able to produce still good quality selective emitter solar cells.

a) In the original technique an oxide mask layer is applied on the surface. This oxide is removed by photolitography where the contact areas are designed (applying the emulsion layer, drying, exposing through a photolitography mask, developing, firing, oxide etching on the opened areas, etching the emulsion from the remained oxide) followed by the forming of the highly

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|----|-----|---------------------|-------|-------|---------------------|---------------------|-----------|-------------|-----------------|--------------------|
| #  | Cr. | Aera                | Text. | HZ    | passiv.             | ARC                 | Bulk res. | N. T. emit. | Contact         | Efficiency         |
| 1  | FZ  | 4 cm <sup>2</sup>   | yes   | no    | SiO <sub>2</sub>    | SiO <sub>2</sub>    | n/a       | n/a         | sput. or evap.  | 22,8 %             |
| 2  | FZ  | 4 cm <sup>2</sup>   | yes   | no    | SiO <sub>2</sub>    | SiO <sub>2</sub>    | n/a       | n/a         | sput. or evap.  | 24,4 %             |
| 3  | mc  | 1 cm <sup>2</sup>   | yes   | n. a. | SiO <sub>2</sub>    | SiO <sub>2</sub>    | n/a       | n/a         | sput. or evap.  | 19,8 %             |
| 4  | с   | n. a.               | no    | no    | SiN <sub>2</sub>    | SiN <sub>x</sub>    | n/a       | n/a         | screen-printed  | 13,2 %             |
| 5  | Cz  | 100 cm <sup>2</sup> | yes   | no    | yes                 | nincs               | 1 Wcm     | 70 Ω/□      | sp. or e.buried | 12,8 %             |
| 6  | FZ  | n. a.               | no    | no    | SiO <sub>2</sub>    | SiN <sub>x</sub>    | 1 Wcm     | 80 Ω/□      | sp. or e.buried | 14,26 %            |
| 7  | mc  | n. a.               | n/a   | n/a   | yes                 | TiO <sub>2</sub>    | n/a       | 60 Ω/□      | screen-printed  | 12,8 %             |
| 8  | mc  | 25 cm <sup>2</sup>  | no    | yes   | no                  | porSi               | n/a       | 100 Ω/□     | sputtered       | 14,1 %             |
| 9  | mc  | 130 cm <sup>2</sup> | no    | yes   | yes                 | yes                 | n/a       | 100 Ω/□     | screen-printed  | 13,1 %             |
| 10 | Cz  | 100 cm <sup>2</sup> | yes   | no    | SiN <sub>x</sub> :H | SiN <sub>x</sub> :H | n/a       | n/a         | screen-printed  | 17,3 %             |
| 11 | mc  | 100 cm <sup>2</sup> | n/a   | no    | SiN <sub>x</sub> :H | SiN <sub>x</sub> :H | n/a       | n/a         | screen-printed  | 15,3 %             |
| 12 | Cz  | 25 cm <sup>2</sup>  | yes   | no    | no                  | no                  | n/a       | 130 Ω/□     | screen-printed  | 13,05 %            |
| 13 | Cz  | 90 cm <sup>2</sup>  | yes   | yes   | yes                 | yes                 | 10 Wcm    | n/a         | screen-printed  | 18%                |
| 14 | mc  | 100 cm <sup>2</sup> | yes   | yes   | yes                 | kétrétegű           | 1 Wcm     | n/a         | screen-printed  | 16,9 %             |

#### Table

Reading of abbreviations: Cr.: crystalline type of

- substrate
- FZ Floating Zone,
- Cz Czochralski, c – single crystalline,
- unknown type,
- mc multicrystalline,

Text.: textured, H2: hydrogenated, passiv.: passivated, ARC: antireflection coating, Bulk res.: bulk resistivity, N.c. emit.: sheet resistivity of not contacted

emitter

doped areas by a conventional diffusion step. Then subsequent openings etched in the oxide by a photolitography step again, where the weakly doped areas are formed by diffusion, followed by etching the whole oxide layer. Then the passivation and antireflection oxide layer is formed, which is etched on the contact areas by a subsequent photolitography process. Here the metal contact layer is deposited followed by the forming of the contact scheme (perhaps by photolitography again). This technology was used for creating the selective emitter for the known highest efficiency crystalline Si solar cells (PERC - Table, line 1 [9], and PERL cells - lines 2-3 [10]). Note that each oxide deposition needs temperatures about 1000°C that increases the production cost. Another disadvantage is that two separate diffusion step needed that complicates the process. The long and high temperature annealing needed for highly doping can degrade the quality of the substrate. Further disadvantages come from multiple scheme aligning.



The structure of the PERL cell

b) PIII-diffusion with photolitography [11]. First the starting deep and highly doped homogeneous emitter is etched entirely in the uncontacted areas by photolitography process. Then a shallow emitter formed by PIII (plasma immersion ion implantation) diffusion on the entire front surface followed by the aligned screen printing and firing (950°C, 1 minute) of the contact paste, so it also activates the implantation (Table, line 4). This technige is simpler, needs only one photolitography mask to form the selective emitter, so it is quicker, while even fine scheme resolution can be achieved. Furthermore the metallization is located higher than the illuminated surface, thus in case of good aligning the overlapping of the metallization to the illuminated weakly doped emitter has less probability. However this technology is even relatively complicated, the metallisation is aligned, and there is a possibility that the emitter under the contacts does not join the illuminated emitter that can block current collecting.

c) A simpler double diffusion technique: after the mask deposition the highly doped emitter formed in the area of the contacts, and after the mask etching a weak doping is made on the whole surface (Table, line 5 [12]). Its advantage compared to the previous process is the eliminating of the emitter etch step.

listarting weakly doped homogeneous emitter is masked, then the highly doped emitter formed on the contact scheme area by this mask (Table, line 6 [13]). Its advantage compared to the previous technique is that the mask layer does not need to be etched if it has further functions (e.g. using  $SiN_x$  it can also serve as passivating layer and ARC). Fine resolution can be also achieved. Disadvantages are the need for metallization align, the relatively complicated technology (double diffusion), thus it is not suitable for mass production. **II.)** *Etch-back techniques* are based on the selective

d) A more simpler technique is the following. The

etching of the homogeneous emitter using the metallization scheme to form a selective emitter. The top layer of the emitter with high surface doping density is etched between the contacts, so the emitter becomes thinner and the surface doping density becomes lower a little, so the sheet resistivity of the emitter becomes higher. Furthermore the metallization rises from the level of the illuminated surface so the overlap of the contacts to the etched emitter, and so the increasing of the contact resistivity and the dark current can be avoided easier. The etch-back process is usually time consuming and it is hard to control it, because the thickness of the highly doped layer is usually about 0,3 µm, and if the n+ layer remains due to the imperfect etching, then the power decreases.

a) A simple etch-back technology described as follows [14]. An n++-type front side homogeneous emitter (16-20  $\Omega/\Box$ ) formed in a p-type Si from a screen-printed diffusion source followed by screen printing and firing (720°C) the back side metallization (Ag-Al) and screen printing and firing (645°C) the front side silver paste. After that a polymer protective layer screen-printed and dried (150°C) that protects the contacts against the influence of the etching liquid. Between the protected metal contacts the emitter etched-back by the HF/HNO<sub>3</sub> liquid until it reaches the appropriate sheet resistivity. With such a solar cell (Table, line 7) 0,5-1% absolute efficiency improvement can be showed compared to the conventional homogeneous emitter cell with 40  $\Omega/\Box$ sheet resistivity. This technology is relatively simple, a little quicker than the previous ones and needs low temperatures. However the protective layer of the contacts has to be aligned to the metallization, but we can optimize the size of it if we know the width of the underetching. Another drawback is that the etching of the liquid is hard to set accurately so the reproducibility is lower.

b) The *porous Si* etch-back techniqe uses that during the porous Si formation the emitter is etched-back, and as the porous Si also acts as an ARC and passivating layer, no further layers needed. With appropriate etching liquid the texturing also creatable in the meanwhile (line 8 [15,16]). This is a very simple technique for making a solar cell, it is quick and cheap, and needs



Process of etchback selective emitter formed by porous Si

minimum of annealings and materials. It can be a disadvantage that the porous Si scatters the light inside the cell, so an amount of the photons gets in the highly doped emitter under the metallization, where the recombination probability is higher. In case of screenprinted contacts a further drawback is the weak etching of the metallization and the underlying Si surface due to the HF contained electrochemical etching, so the contacts become more fragile and their contact resistivity increases, thus the FF decreases. In case of sputtered metal contacts

the etching does not degrade the quality of the contact and the FF, and so it becomes a self aligned process, however it is a more expensive and slower technique.

c) Another possibility is the *self-aligned plasma etchback* technique, where the screen-printed metallization is the mask layer. The highly doped homogeneous emitter between the contacts is thinned by plasma etching (RIE, using SF<sub>6</sub>) [17]. A 0,35% avarage absolute efficiency improvement was reached with such a solar cell made by conveyor belt technique (Table, line 9) compared to cells with homogeneous emitter. The highest power can be achieved by etching about 90 nm Si layer (in case of p-type Cz-Si substrate) [18]. Its advance is the self-aligning, furthermore the series resistance and the bulk recombination decreases, thus the FF increases due to the plasma process.

**III.)** With the following methods we can *form the differently doped areas in one high temperature annealing step* thus the manufacturing time and cost decreases.

a) Using a *diffusion barrier* for the diffusion  $(100-1000 \text{ nm thick } SiO_2)$  much phosphorous gets into the silicon through the opened windows of the oxide, and few phosphorous gets through the oxide barrier forming weakly doped and shallow emitter there [19]. Varying the properties of the diffusion barrier (thickness,

permeability, doping) the doping rate of the underlying Si can be controlled, however it is relatively hard to set it accurately. Using SiO<sub>2</sub> paste for creating the barrier the concentration of the SiO<sub>2</sub> also influences the emitter doping.



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Silicon wafer

barrier

b) By doping the oxide layer, the technique becomes the following: a highly phosphorous doped  $SiO_2$ (PSG) deposited on the whole surface is etched between the contact areas with the help of a screen-printed mask layer followed by the etching of the mask layer and a subsequent deposition of a weakly phosphorous doped PSG on the whole surface. Then a rapid thermal heating (1000°C, 45 s) realizes the phosphorous diffusion. After that the metal paste screen-printed with aligning and fired (Table, lines 10-11 [20]). The properties of the emitters can be easily set by the amount of phosphorous in the PSG. These PSG lavers are thin and transparent so it can used even to light-assisted diffusion. Disadvantages are the aligned metallization and the etching of the PSG that complicates the technology.

c) A simpler and cheaper similar technology is the following: a phosphorous *doping source paste* screenprinted on the areas of the metallization followed by the applying of a weakly doped spin-on material on the whole surface, and the diffusion annealing (950°C, 80 s). Then the formed glass etched and the metal contacted with aligning (Table, line 12 [21]). With such a cell 1% absolute efficiency improvement reached compared to the homogeneous emitter cells. Note that two screen printing step and aligning are needed.



Selective emitter created by auto-doping technique

d) The *auto-doping* technique: a phosphorous paste screen-printed in the metallization areas onto a p-type Si substrate followed by a diffusion step (960°C, 5 min), so a highly doped and deep n-layer formed under the paste, and a lower doped and shallower n-layer formed between the paste stripes in an indirect way (due to the evaporated P-gas). After the etching of the paste the Ag paste screen-printed with aligning (lines 13-14 [8, 22]). Note that less P source needed thus the cost is also lower. However aligning is needed, and the variance of the values increased due to the indirect diffusion.

e) With one screen printing step of *self-aligned doped (self-doping) metal pastes* onto a weakly doped homogeneous emitter (see next unit) the process becomes very simple and rapid. There is no need for aligning, the material input is economic and it needs minimal annealing. However the composition of the paste is hard to be set properly.



Selective emitter and metallization created by self-doping metal paste

**IV.)** Another method for making a selective emitter is the *laser overdoping* technique [23].

a) A spin-on diffusion source is used to form the homogeneous, weakly doped emitter followed by a local heating by a laser with appropriate energy in areas where the highly doping needed. It can reach linewidths in the range of 10-25  $\mu$ m. However the metallization must be aligned, the process needs long time and it is complicated due to the using of laser.

b) However we can use also a *self-aligning contacting* that can be realized by electroless plating. This time the laser must burn through the whole thickness of the phosphorous doping source meanwhile the overdoping. Then the surface can be plated directly through the openings by an electroless plating solution. An appropriate doping source (e.g. doped SiO<sub>2</sub> or SiN<sub>x</sub>) can be used as metal mask, passivating layer and ARC as well making the manufacturing simpler.

V.) A *buried contact* structure can be formed by any of the above technologies, thus the resistivity and the ratio of the metallized surface, so also the shadowing decreases.

This technique needs only a trench forming and a clean etching before the highly doping diffusion, then the contact metal can be filled in it. The mask of the trench forming can be equal to the mask of the undercontact diffusion and of the metallization, so it can integrated easily into the previous technologies. However it is more complicated, more expensive, and the metal/ Si interface is increased, thus the V<sub>oc</sub> decreases. On the basis of modelling the buried contact selective emitter cells has a 0,5-0,6% absolute efficiency enhancing compared to the non-buried screen-printed contact selective emitter cells [7]. Several technology integrated the buried contact forming, such as the double diffusion technique (mechanical grooving [24], laser drilling [25], chemical etching [12]) and auto-doping technique [12].

# 3. Doped metal pastes and the utilizing

# Theory [4,26,27,28]

#### The metal paste

In case of screen printing or other thick layer applying technique the forming of a thick layer is made by special pastes. A paste is a dispersion of solids (conductor and inorganic phases) in an organic vehicle. A contact paste for a solar cell is hard to produce due to the many requirements:

- 1. Low contact resistivity to the silicon
- 2. Low line resistance (high electrical conductivity)
- Negligible effect to the Si substrate (does not degrade the electrical quality of the silicon by creating recombination centers)
- 4. Little linewidth, good resolution
- 5. Good solderability
- 6. Good adhesion

(makes a mechanically strong bond to the silicon)

- 7. Low cost
- 8. Applyable by an economical process (e.g. by screen printing)

The backside contact material is also expected to create a BSF (Back Surface Field). In the absence of other inorganic species the silver in paste often used for contacting the front side does not interact with the silicon or forms interfacial species until 830°C where a eutectic is formed [26]. The silver does not react with the anti-reflection coatings as well. Thus the inorganic components are essential because they make possible the physical contacting between the silver and the silicon due to the ARC cutting through. The so called glass frit is good for that, however it dissolves the silicon as well.

#### The self-doping metal paste

The screen printing technology creates a bad ohmic contact on the high sheet resistivity emitter, however the alloyed self-doping paste (SDP) can help that. For a self-doping contact material a plus requirement is the ability to allocate an amount of doping material into the underlying silicon. These requirements are sufficed by a known contact material, the aluminium in case of contacting a p-type silicon. The aluminium dopes the silicon by an alloying process that needs temperatures above the Al-Si eutectic point (577°C). The alloy contains 12,5% of Si and 87,5% of Al by weight. This eutectic electrode has a proper electric conductivity for the currents of the solar cell, and an excellent ohmic contact and interface to the silicon. In addition the aluminium is available in a form of screenprintable paste for a reachable price.

However there is no similar material for contacting the n-type silicon, but there is a possibility for making a selective emitter by using silver pastes alloyed with phosphorous or antimony doping material, which increases the doping under the contacts meanwhile the contacts formed. In this case there is no need for any more aligned screen printing, so the yield is higher and the cost is lower due to the simpler technology. This self-doping, self-aligned contacting technology can make contacts even onto emitters with sheet resistivity of 100-200  $\Omega/\Box$ .

# Solving the short-circuit problem

The molten metal can consume some of the underlying silicon (about 0,3  $\mu m)$  so the level of the regrown

Si can be lower than the level of the surrounding Si, thus the metal can easily short-circuit the p-n junction. Mixing Si in the self-doping metal alloy paste, the level of the metal-Si interface becomes higher than the level of the Si wafer. Using sputtered Ag/Si/B alloy a good quality p-n junction was succesfully created.

#### An alternative self-doping technology

A self-doping negative electrode can be made by starting with the applying of an unalloyed Ag layer onto the Si surface. Then the Ag and the substrate must be heated above the Ag-Si eutectic temperature (but below the melting point of the Si, e.g. 900-950°C for 2 minutes) in an ambient gas contained phosphorous. The Ag and Si begin to melt, meanwhile the P atoms of the ambient gas absorb into this Ag-Si liquid mixture in a larger amount than into a solid Si suface. Then with the decreasing temperature the melted Si reformes containing the P doping atoms in it, and below the Ag-Si eutectic temperature the Si formes a solid phase alloy with the Ag embedded in the substrate. This Ag-Si alloy is the final contact material. Due to the eutectic weight ratio much more amount of Ag will be in this material than Si, so good electric conductivity ensured. Note that the solid Si also receives the gas phase P atoms but in a much less amount than the melted metal.

The silver can be replaced by another metals (e.g. tin). For making a negative electrode the P can be replaced by other member of Group V of the Periodic Table, and for making a positive electrode it can be replaced by a member of Group III as a dopant vapor.

#### **Unsolved problems**

It is not clear yet that the growing conditions at the eutectic temperature how influence the quality of the grown Si, and how can it grow epitaxial as the part of the Si-metal alloy. It is possible that a spontaneous nucleation occures in the melted material. Therefore the cooling must be slowly at the eutectic temperature. The material quality of the Si growed by the self-doping metal system is an important subject of research.

# Realizations

#### The firing of the metal paste and the contact resistivity

The screenprintable paste can be qualified by measuring the contact resistivity, because it governs the electric behaviour [26]. The contact resistivity depends on the sheet resistivity of the emitter that can be changed by the reaction of the metal and the silicon. Thus the interaction model of the emitter and the metal can be observed when the contact resistivity changes during the high temperature processes.

In case of n-type emitter the surface goes through four states during the firing of the metallization (*figure*):

- I. The antireflection coating (ARC) is unbreaked, high contact resistivity.
- II. The ARC is breaked through in part (the TiO<sub>x</sub> is dissolved but not the SiO<sub>2</sub> layer), high contact resistivity.



States during the forming of the Ag contact

III. The ARC is breaked through entirely, a good contact formed with the emitter, low contact resistivity.

IV. The emitter layer also etched, so the sheet resistivity of the emitter slowly increases, then the p-n junction damages due to the diffusion of the metal oxide.

To minimize the Si etching after the contacting a rapid thermal annealing must be used. Observing the effects of the annealing we can see that the contact resistivity decreases dramatically between 700 and 800°C, and the minimum can be reached at about 800°C. For higher belt speeds beyond 800°C the contact resistivity increases again, probably due to the interface processes of the quick metal firing.

So applying the Ag-Si eutectic point (830°C) or higher temperatures by rapid thermal annealing the formed contact is not the optimal, so several problem can occured (e.g. thermal expansion differences, Si etching).



Firing temperature and belt speed effection to the contact resistivity

# Using the self-doping paste and the significance of the glass frit

The creating technology of a selective emitter solar cell by self-aligned self-doping P doped Ag paste was the following [29]. An n-type homogeneous diffusion layer with a sheet resistivity of 75  $\Omega/\Box$  and a depth of about 0,25 µm created in a p-type wafer followed by the deposition of a SiN<sub>x</sub> antireflection coating by PECVD. Then the back side Al layer screen-printed and annealed in a conveyor belt furnace (860°C, 2 min) followed by the screen printing of the self-doping Ag paste (DuPont PV168) on the top of the SiN<sub>x</sub> layer, then it was dried and alloyed (900°C, 2 min).

Good contact resistivity reached (2 m $\Omega$ cm<sup>2</sup>) by fritted paste, however it increased quickly by the decreasing of the base doping (below 10<sup>18</sup> cm<sup>-3</sup>), and at 10<sup>15</sup> cm<sup>-3</sup> base diffusion it became too high due to the high sheet resistivity of the formed emitter (700  $\Omega/\Box$ ).

If an n<sup>-</sup> homogeneous emitter layer also existed then the contact resistivity became acceptable (1-12 m $\Omega$ cm<sup>2</sup>) until n<sup>-</sup> layers with sheet resistivity of 100  $\Omega/\Box$ . The problem is that the frit of the paste etches a thin layer of the Si surface.

The selective emitter cells with 75  $\Omega/\Box$  n<sup>-</sup> layer had a little lower serial resistivity and higher FF compared to conventionally produced cells with 40-45  $\Omega/\Box$  homogeneous emitter. The serial resistivity was about 0,75  $\Omega$ cm<sup>2</sup>, the shunt resistivity was 2-25 k $\Omega$ cm<sup>2</sup>, the efficiency was increased by about 0,3%. These values can be made even better by better surface passivation. Based on modelling the front side recombination velocity must be below 10000 cm/s to make the selective emitter effective.

# The properties of the surface passivated self-doping selective emitter cell

A similar solar cell with 100  $\Omega/\square$  n<sup>-</sup> emitter made in another experiment, but under the SiN<sub>x</sub> layer a SiO<sub>2</sub> passivating layer applied, and both side contacts were cofired [30]. The optimal heating process was a rapid thermal annealing at 900°C.

The dark current (recombination current) in the emitter of the 45  $\Omega/\Box$  homogeneous emitter cells was  $J_{oe}$ = 337 fA/cm<sup>2</sup>, while for the selective emitter cells it was 185 fA/cm<sup>2</sup>.

The FF of the selective emitter cells (0,768) was slightly lower than for the conventional cells (0,785), however the fill factors of the cells with 100  $\Omega/\Box$  emitter using conventional contact paste were much lower (0,479-0,709). The slight decreasing of the FF for the selective emitter cells was because the front side contact scheme was optimized to 45  $\Omega/\Box$  emitters (gridline spacing of 2,2 mm), so it can be restored.

The short circuit current of the selective emitter cells was increased by 0,8-1 mA/cm<sup>2</sup> to 33,4-33,6 mA/cm<sup>2</sup> compared to conventional cells, and the open circuit voltage was increased by 9 mV to 635 mV, therefore the efficiency increased by 0,4% to 16,4%. The measurements showed that the selective emitter cells without an oxide passivation layer cannot enhance the properties considerable compared to the conventional cells.

Comparing the IQE curves we can see that the short wavelength response is much better for the selective emitter cells, if the surface passivation is good, so the  $J_{sc}$  is better as well. For further wavelengthes these cells are also better than the conventional cells, and the long wavelength response is also slightly better due to the high temperature annealing making the BSF deeper and better.

#### Self-doping contact on dendritic web Si substrate

The advantageous properties of the dendritic web Si substrate are that it is thin (100  $\mu$ m), has a good electrical quality (the diffusion length of the minority carriers is multiple of the thickness), and it is cheap.

This substrate was used in an experiment with P contained fritless Ag paste (70 at% Ag, 0,07 at% P,

this is the maximum solubility of the P in the Ag at room temperature) [31]. The optimal annealing was at 1000 °C for 10 minutes. The contact resistivity was 0,013  $\Omega$ cm<sup>2</sup>, while for conventional Ag paste it was 1,9  $\Omega$ cm<sup>2</sup>.

It was showed that the P atoms got into the Si several micrometers in depth. At the Si surface the doping concentration was higher, so it formed a thinner Schottky-barrier at the metal-semiconductor interface, thus the contact current contained mainly tunnel current through the interface. Therefore the contact resistance is exponentially proportional to the Schottky barrier height and to the inverse of the square root of the doping concentration. This paste could make a pn junction as well.

#### IBC cell with self-doping contacts

An IBC cell can be formed by self-doping negative and positive electrodes on a Si substrate as follows [4]. First an n<sup>+</sup> layer diffused in the front side of the substrate against the surface recombinations, followed by the dissolving of the so created diffuse glass and the screen printing and drying of a Ag-Ga paste onto the back side. Then a Ag-Sb paste screen-printed onto the back side in an interdigitated scheme followed by the burning out of the organic particles of both pastes (400 °C). This followed by the cofiring of the self-doping positive (Ag-Ga) and negative (Ag-Sb) electrodes, forming the p-n junction as well (with the Ga for n-base or the Sb for p-base), meanwhile a thermic oxide growed passivating the free Si surfaces on both sides of the wafer. This can be achieved by an RTP annealing (900°C, 2 min) in an oxygen ambient. Then an ARC deposited on the uncontacted front side of the cell, so the electrodes can be directly soldered for interconnecting the cells into modules. The positive electrode can be made by pure AI as well, however it has a lower conductivity, its surface is oxidized thus it is unsolderable. The above process is suitable for mass production as well.

An other version of the process applies liquid or solid phosphorous source onto the front side of the cell that forms the front side  $n^+$  layer meanwhile the firing of the back side undoped negative Ag electrode, thus the evaporated P atoms get into the melted Ag-Si layer doping the underlying Si areas. Then the selfdoping Al or Ag-Ga positive electrode pastes applied and fired.

A self-doping IBC cell can be made using dedrit web Si subtstrate as well [32]. In this case the front side  $n^+$  doping can be formed during the crystal growing as well.

A commercial cell made using an n-type 20  $\Omega$ -cm dendritic web substrate, where the p-n junction formed by alloying a screen-printed AI, while a screen-printed self-doping Ag-P paste contacted the substrate. The Si<sub>3</sub>N<sub>4</sub> ARC applied by PECVD. The 5 cm<sup>2</sup> area cells have J<sub>sc</sub>=28 mA/cm<sup>2</sup>, V<sub>oc</sub>=0,55 V, FF=0,69 and the efficiency reaches 11%, and in the future it can reach even 15%.

# 4. Foresight

The aims of the developments are making cheaper solar cells and meanwhile keeping or improving the volume of the photoelectric efficiencies. This goes not only for chrystalline Si solar cells but for amorphous Si or for thin layer compound semiconductor solar cells (e.g. CIGS) as well.

Today it is not clear yet which way has the future. To decide it we must take into account the manufacturing cost, the usable photoelectric efficiency, the ability for mass production and the lifetime. For example now one of the cheapest solar cell type is the amorphous Si based structure, but its poor efficiency and its relatively short lifetime make it suitable using for only nearer terms. In special cases the area of the solar cell modules can also be an important requirement that can motivate the using of higher efficiency solar cells. Of course in parallel of the nanotechnology improvement the new type solar cell materials also appear (e.g. thin layer Si substrate, solar cell materials modified by guantum technology, photovoltaic carbon nanotube etc.), these will bring great enhancements in the world of photoelectric devices for the farer future.

However until that the actual technology must be improved, and one station for it is the more economic manufacturing of the selective emitter structure for the world's most applied crystalline Si solar cells, and therefore the using of self-doping screenprintable metal contact is an obvious solution.

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