Progression of n-type base crystalline silicon solar cells

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ABSTRACT
This paper reviews the status of solar cell technology based on n-type crystalline silicon wafers. It aims to explain the reasons behind the strong and increasing attention for n-type cells, including the inherent advantages of n-type base doping for high diffusion length, and for the industrialization of designs with good rear-side electronic and optical properties. The focus will be on cells using diffused junctions.

Introduction

Most industrial crystalline silicon solar cells are based on p-type wafers. Applying a phosphorous-diffused emitter and a back-surface field created by aluminium-silicon alloying, results in the common multicrystalline or monocrystalline silicon solar cells used in the vast majority of PV modules. The exceptions to this rule have been (for many years) the cells and modules produced by Sanyo and Sunpower, who are using n-type wafers for their high-efficiency cells. Recently, Yingli Solar has also taken high-efficiency 'Panda' cells based on n-type wafers into production. In addition, practically all major research organizations and several companies, including Bosch and Suniva, have started to report activities in cell processing from n-type wafers. This paper aims to explain the reasons behind the strong and increasing attention for n-type cells, including the inherent advantages of n-type base doping for high diffusion length.

Heterojunction (HIT) solar cells will not be discussed in this article, as the principles of the low-temperature heterojunction cell processes are very different from diffused junctions. Of course, differences in p- and n-type wafer properties apply irrespective of whether or not the cell process is based on HIT or diffused junction technology although changes in wafer properties due to high temperature process steps will be absent in HIT processes.

Differences in properties of p-type and n-type wafers

One of the most important characteristics of wafers used for solar cells is the minority carrier diffusion length, which is directly dependent on the minority carrier recombination lifetime or 'lifetime.' A long diffusion length and high lifetime allow for higher efficiencies. A characteristic of n-type doped crystalline silicon is that it generally reaches (much) higher lifetimes than p-type silicon. This is one of the reasons for the interest in n-type wafers for solar cell production. In the following we briefly review why the lifetime in n-type wafers is generally higher, but also mention several nuances.

Boron-doped p-type Czochralski (Cz) wafers show lifetime degradation due to formation of a boron-oxygen related metastable defect, upon illumination or in general upon minority carrier injection. Since boron (dopant) and oxygen (growth process impurity) are abundant in typical p-type Cz wafers for solar cells, the effect is very important. The lifetime degradation has been parameterized [1]; 15 or 20ppma of oxygen (the range typical for Cz wafers) limit the lifetime in a 1Ωcm wafer to 20 or 12μs, respectively (diffusion length 250 or 190 micron), though 2 to 3× higher lifetimes are possible for optimized thermal processing. While these diffusion lengths are still longer than typical wafer thicknesses, they severely limit the potential cell efficiency in high-efficiency cell designs [2].

Absence of boron or oxygen in wafers will avoid this boron-oxygen related lifetime reduction [3]. Oxygen reduction can be realized by magnetic Cz (MCz), for example, or floatzone (FZ) ingot growth; however these techniques are not yet available for low cost production. Boron can be avoided altogether by switching to Ga doping (Al-doping results in defects [4]). Ga-doped Cz for example is applied by Suntech in its high-efficiency Pluto cells [5]. A technique to remove the boron-oxygen defect is so-called regeneration [6], which does not yet appear to be applied commercially. Obviously, switching to n-type wafers will entirely avoid the boron dopant and the associated lifetime reduction [7].

In the last decade, another reason for higher lifetime in n-type wafers has become clear: the reduced impact of typical transition metal impurities [8]. In particular, the impurities which have donor-type character (i.e., toggle between positive and neutral states when they cause recombination) will, due to their charged state, have an increased capture rate for minority carriers in p-type wafers (electrons), but not for minority carriers in n-type wafers (holes). Such impurities happen to be the faster diffusing impurities. This means that process-induced contamination such as Fe causes typically (much) more recombination in p-type wafers than in n-type wafers. Cr is a relevant exception it is an impurity which diffuses relatively fast, and can be a relevant process impurity, but causes quite similar recombination in p-type and n-type wafers [9]. Acceptor-type impurities will show the opposite behaviour: they cause recombination in n-type rather than p-type wafers;

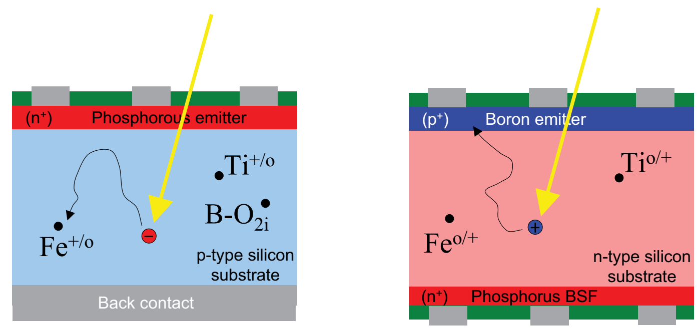

Figure 1. Schematic representation of the differences in recombination at impurities for p-type versus n-type solar cells. Typical transition metal impurities are donor-type, resulting in a large capture cross-section for electrons, but a much smaller one for holes. Therefore they are effective minority carrier recombination centres in p-type cells, but not in n-type cells. In addition, in p-type Cz, boron-oxygen-related defects are present, which are important recombination centres.

They also typically diffuse very slowly. Such impurities which are harmful in n-type rather than p-type wafers are, for example, Au and Zn.

In practice, lifetimes of many milliseconds are readily obtained in n-type Cz. Even in n-type mc-Si, very high lifetimes have been measured [10]. However, the crystal defects in mc-Si appear to reduce the carrier lifetime more or less equally for n-type and for p-type [11]. It is not currently clear whether there is a significant diffusion length advantage of n-type mc-Si over p-type mc-Si (however, other advantages of n-type cell architecture, which will be discussed below, remain applicable).

> "The crystal defects in mc-Si appear to reduce the carrier lifetime more or less equally for n-type and for p-type."

For n-type Cz reduction of the diffusion length due to oxygen-induced crystal defects has been reported [12,13], but it also that this can be minimized by suitable design of the cell thermal processing [12].

In conclusion, for very high-efficiency cell concepts (requiring very long diffusion lengths, such as back-junction back-contact, or having exceptional surface passivation, such as HIT), n-type silicon as a base material has clear benefits. Nevertheless, it is possible that for particular cell designs (e.g., a diffused emitter on the front and dielectric passivation on the rear) and with particular care to avoid process-induced contamination, similar efficiencies can be reached in Ga-doped or MCz p-type, as in n-type silicon. After all, UNSW still holds the cell efficiency record with a cell based on a p-type FZ base [14].

Differences between n-type and p-type cell processing

The reasons for the current industrial emphasis on p-type cells are manifold. Martin Green gives an historic perspective [15], mentioning aspects such as the convenience of phosphorous gettering, and aluminium-silicon alloying to create a back-surface field (BSF), which applies to p-type substrates, and the complications of boron diffusion as a technology to form an emitter on an n-type substrate.

Until recently the passivation of a boron emitter was also considered a bottleneck, with only thermal oxidation available as a high quality passivating step, with some doubts about its long-term stability [16]. Silicon nitride typically does not provide practical passivation for boron emitters [17]. Also, the complexity and therefore cost of creating and isolating two separate diffusions (emitter and BSF) on either face of the cell may have been considered to be a bottleneck. In this respect the standard p-type cell process is very simple with only eight or nine process steps, and every additional process step means a cost increase that has to be paid for by increased cell efficiency.

However, for all these bottlenecks there has been much progress in recent years, and therefore interest and activities in n-type cells have increased dramatically. For passivation of the boron emitter there are now at least five methods that seem to work well, with coating by Al_2O_3 via atomic layer deposition (ALD) – probably the best documented [18]. Several companies are actively developing equipment for the PV industry to deposit Al_2O_3. Industrial boron emitters have now been reported with emitter recombination currents (J_{oe}) below 30fA/cm^2 [19,20] based on a variety of passivation layers, which compares favourably with industrial phosphorous emitters for which typical numbers appear to be somewhat higher [21]. Incidentally, this low J_{oe} shows that the boron emitter of n-type cells does not need to be influenced much by recombination due to impurities (e.g. Fe or boron-oxygen defect), or crystal defects induced by boron diffusion [22]. It may be fortunate in this respect that the gettering of Fe by a boron emitter is not very good [23]. We refer to an earlier article from this journal for more details on (boron) emitter diffusion [24]. Notably, since that publication more results have been published for implanted boron emitters [25].

A practical aspect of concern for n-type cell processing might be the resistivity variation through an n-type ingot, which will be larger than for a p-type ingot due to the different segregation coefficients of the dopants phosphorous (k≈0.3) and boron (k≈0.7). However, for high-efficiency cell designs, the typical resistivity variation in a phosphorous-doped ingot is acceptable.

Opportunity for bifacial n-type cells and modules

N-type cells, when using a full area-diffused BSF, offer the possibility of a bifacial layout – where light is collected from the rear as well as the front. This is a distinct difference with conventional p-type cells. Bifaciality results can be excellent (e.g. 90% in [20]). A recent review of bifacial technology lists results of a *30% and higher gain* in power yield for bifacial modules with suitable installation of modules ('suitable' meaning for example painting the base surface below the modules white)[26]. The paper also mentions the advantage of a reduced operating temperature. However, not all cell architectures are suitable for bifacial application. The use of a locally diffused BSF on the rear probably requires a fine pitch of contact points which will allow little bifaciality, and also IBC cells are only moderately suitable for bifacial application [27].

Basic n-type cells

In this section we describe the most basic n-type cells, with full-area emitter on front or rear, and contact grid on the front. They are:

1. The cell with emitter on front and BSF on rear (BSF cell, or p$^+$nn$^+$ cell). It normally has a boron-diffused emitter and a phosphorous-diffused BSF.

2. The Al rear-emitter cell with a front-surface field (FSF cell, or n$^+$np$^+$ cell). It normally has a phosphorous-diffused FSF, and is also known as PhosTop cell.

Both cell types have a variant with local junction formation on the rear, either local BSF or local emitter.

BSF n-type cell

Many variations of this cell have been published, including the following types:

- bifacial BSF type cell (Fig. 2): full area emitter on front and full area BSF on rear, which are contacted by contact grids. Front and rear-passivating dielectric coatings.

- PERT: passivated emitter rear totally-diffused. Can be identical to the above, but

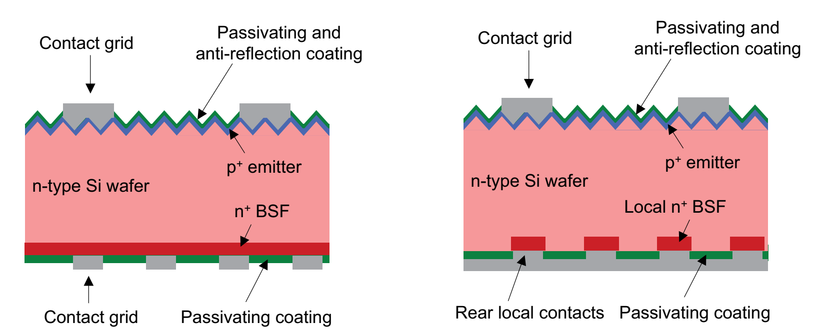

Figure 2. Left: p$^+$nn$^+$ bifacial BSF type cell. Right: Local BSF (PERL) cell structure. Variations such as selective diffusion and mixtures of the two cell types are possible.

typically has rear point contacts with local heavier BSF diffusion, and a full-area metal layer to interconnect the point contacts.

- PERL (Fig. 2): passivated emitter rear locally-diffused; most of the rear area is undiffused. Local BSF diffusion under the rear contacts. Typically a full area metal layer to interconnect the point contacts.
- PERC: passivated emitter rear contact. Rear undiffused. Typically high density of rear point contacts, and a full area metal layer to interconnect the point contacts. This will not yield a high efficiency unless the rear point contacts are passivated (for p-type this can be done by using aluminium point contact metallization where a local BSF is created by alloying).

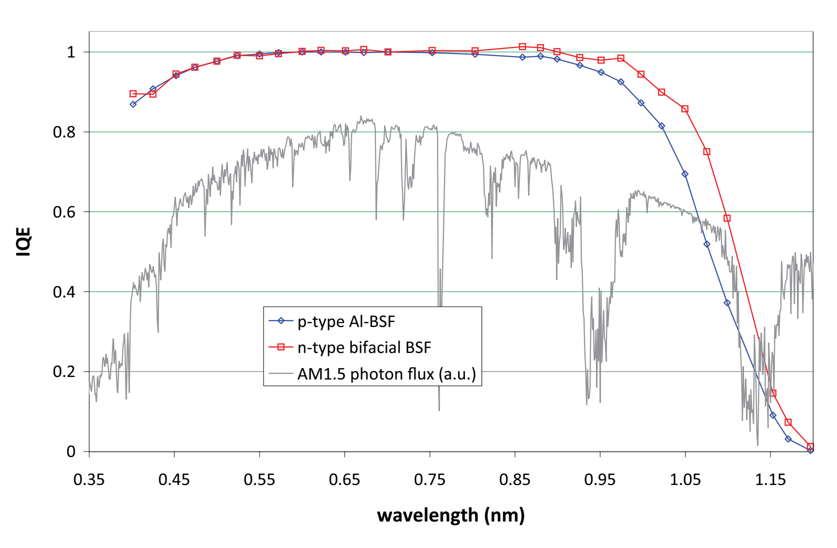

Figure 3. example of internal quantum efficiencies (normalized at 700nm) of industrial-type p⁺nn⁺ bifacial BSF type cell (red) and conventional Al-BSF p-type cell (blue). The gain in the infrared is due to improved diffusion length, improved internal rear reflection, and improved rear surface passivation. Photon flux versus wavelength in AM1.5 (grey) shows the importance of the IR wavelength region.

In 1978, Sandia labs published excellent results for p^+nn^+ cells (probably not bifacial; the BSF appears to have been fully covered by metal contact) [28]. The Sandia paper explains the advantages of the structure: a transparent emitter; gettering as well as passivation by the BSF; and a long hole diffusion length in the base.

In recent years the development of p^+nn^+ bifacial cells using simple industrial techniques such as screen-printing was pursued by many institutes [2,19,20,29-31]. Yingli Solar has adopted and piloted the technology in a joint project with ECN and Amtech [32] and subsequently commercialized the concept, so far reporting a best cell efficiency in trial production of 19.5% (independently confirmed) [33] and in production of 19.9% [34]. Other companies like Bosch and Suniva have made public that they work on production technology of p^+nn^+ type cells. Suniva reported 19.1% (independently confirmed) using implantation in cooperation with Varian [35].

In addition to the cells with nearly 20% efficiency made by industrial techniques, there have also been efforts on laboratory cells, demonstrating new processes, materials and the potential of particular cell designs. In particular ISE has reached very high cell efficiencies upto 23.9% for a cell structure with full-area BSF, using emitter passivation by Al_2O_3 (pioneered in collaboration with University of Eindhoven) [36]. Comparisons of different emitter profiles were reported. PERL [37] as well as PERT [16] laboratory cells have been reported. The rear-side recombination seems to be only marginally different between these two cell types, as their V_{oc}s are very similar.

Compared to conventional p-type Al-alloyed BSF cells, the high efficiencies obtained with p^+nn^+ cells are due to several factors. Ranked by approximate importance they are:

1. Improved light trapping due to much better internal rear reflection than an Al-BSF provides.
2. Improved diffusion length in the base.
3. Improved rear-passivation due to BSF with passivating dielectric coating.
4. Low emitter recombination current, probably somewhat better than for comparable phosphorous emitters on p-type wafers.

Fig. 3 illustrates the impact of improved bulk recombination, rear-surface recombination, and improved rear-side optical performance for measured internal quantum efficiencies (IQEs) of industrial-type n-type and p-type cells made at ECN. The difference in IQE accounts for a difference in I_{sc} of close to 4%.

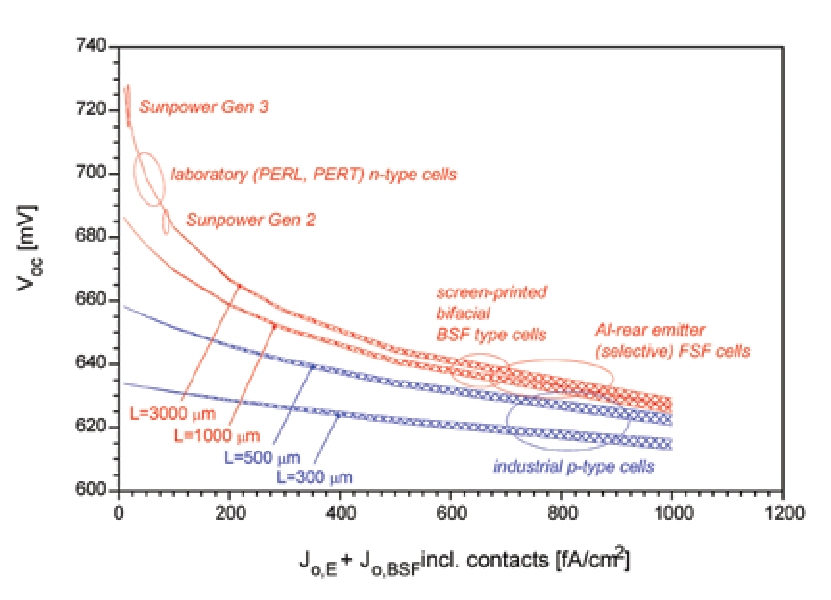

Figure 4. Model calculations of the dependence of V_{oc} on recombination current *Jo* in emitter and BSF (including contact recombination) and on minority carrier diffusion length L in the base. Typical ranges for L in n-type wafers (red, lifetime approx. 1–10ms) and p-type (blue, lifetime approx. 30–100µs) have been taken. The hatched areas cover a variation of the ratio $J_{o,E}/J_{o,BSF}$ between 1/3 and 3. Ellipses roughly indicate the estimated present parameter ranges for the various cell types (Sunpower data from [12]). Reducing the emitter and BSF recombination and, in particular, the contact recombination will move the bifacial BSF type cell performance towards the lab cell performance.

Fig. 4 illustrates by model calculations how V_{oc} depends on recombination current at the front and rear of the cell, and the bulk diffusion length, according to the following equations [38]:

$$V_{oc} = \frac{kT}{q} \ln\left(\frac{J_{sc}}{J_0} + 1\right) \quad (1)$$

with, assuming low level injection (LLI) in the base,

$$J_0 = J_{oe} + \frac{J_{o,BSF} \cosh(W/L) + \frac{qDn_i^2}{LN_d} \sinh(W/L)}{\cosh(W/L) + \frac{J_{0,BSF}\, LN_d}{qDn_i^2} \sinh(W/L)} \quad (2)$$

which for the BSF uses the relation between J_o and S_{eff} valid for LLI:

$$S_{eff} = \frac{J_0\, N_d}{qn_i^2} \quad (3)$$

N_d, D, L are dopant density, diffusion constant, and diffusion length in the base, respectively. J_{oe} and $J_{o,BSF}$ are the emitter and BSF recombination current densities, respectively, which are a function of recombination current densities at the various diffused and passivated surfaces and at the contacts. FF will typically slowly increase with increasing V_{oc} [38]. The resistivity used in the calculations for Fig. 4 is 2Ωcm.

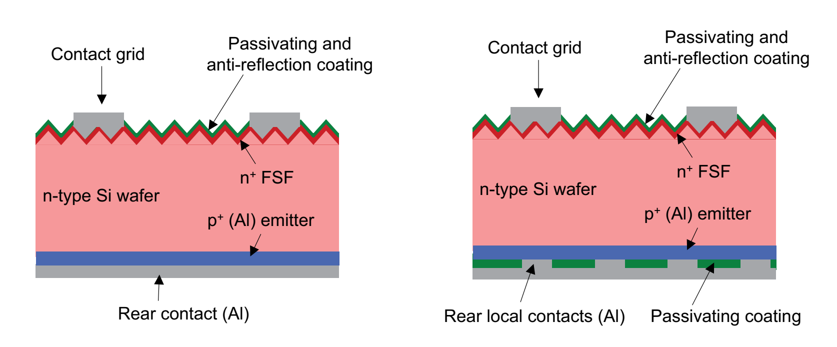

Figure 5. n+np+ FSF Al back-junction cell. Right: variations with selective diffusion, local emitter regions, etc., are possible.

Together, these two figures illustrate the difference in IV parameters between n-type and p-type cells.

> "When applying a boron-diffused BSF, maintaining a high diffusion length in a p-type wafer might be challenging."

For this cell structure, with two differing diffused layers on both faces of the wafer, the diffusion process is more complex than for p-type cells. For example, the use of both BBr_3 and $POCl_3$ tube furnace diffusions has been described [20], use of BCl_3 instead of BBr_3 and use of PECVD SiO_x diffusion barrier [31], etc. Also, diffusion sources such as spin-on or printed layers [29] have been used.

A valid question is whether or not with comparably more complex processing than the standard p-type cell process, it is also possible to create a p-type bifacial BSF cell (n^+pp^+ cell) with comparable advantages. One of the challenges in that case would be to obtain wafers with high diffusion length (e.g. Ga-doped or magnetic Cz), and maintain this high diffusion length during processing. Especially when applying a boron-diffused BSF, maintaining a high diffusion length in a p-type wafer might be challenging. The high temperature for boron diffusion easily contaminates a

Type	Area (cm^2)	Metallization	V_{oc} (mV)	Efficiency (%)	References
bifacial BSF	239	screen printed	641/-	19.49/19.89	[33]/[34]
PERL, laboratory	4	evaporated front grid, rear full area evaporated	705	23.9	[2]
PERT, laboratory	4	evaporated front grid + plating, rear full area evaporated	695	21.9	[16]
Al-rear emitter, selective FSF	6" Cz	screen printed	639/641	18.5/18.5	*[45,46]/[49]
Al-rear emitter, Al_2O_3 passivated, laboratory	4	evaporated	649	19.8	**[43]

Obtained 18.6% on a 5" FZ wafer.
*** An efficiency of 20.0% was actually obtained with a-Si rear side passivation, but judging from the V_{oc} the potential of Al_2O_3 passivation seems to be better.*

Table 1. Results of the various n-type cell concepts (non-back contact).

wafer with Fe, which is a severe lifetime killer for p-type wafers but not for n-type wafers. Siemens worked on p-type cells with boron BSF until several years ago [39]. For p-type high-efficiency designs, it is more common to omit the full-area BSF and apply a PERC or PERL cell design, but this requires a finely spaced rear-contact grid for low series resistance losses, and therefore requires low recombination (high quality local BSF) under these contacts.

Aluminium rear-emitter cell

An alternative process to create n-type cells by a relatively simple process is by applying phosphorous front diffusion and Al-alloying on the rear, i.e., very close to the current industrial p-type cell process [40–46] (see Fig. 5).

In its basic form this process has the disadvantage that it lacks the efficiency improving factors one, three and four of the bifacial BSF cell of the previous section. Without removal of the Al and Al-Si alloy layers on the rear, the V_{oc} of such cells is limited by the emitter recombination to about 640mV [41]. In addition, conventional cell interconnection is impossible since the complete rear surface area should be Al-doped, as the commonly used Ag interconnection pads would be large areas with high recombination loss ('electrical shading' areas). Alternative interconnection might resolve this problem [44, 47].

Despite the limited rear surface passivation, an efficiency of up to 19.3% was recently obtained on FZ material by using a plated front grid and SiO_x/SiN_x front-surface passivation, and with full rear-area Al coverage (i.e., cutting off the cell edges on which emitter is absent) [46].

To improve the rear recombination and enable conventional interconnection, cell processes have been developed where, after Al-Si-alloying to create the emitter, the remaining Al layer and the Al-Si alloy are removed by wet chemistry, and the rear surface is coated with a passivating layer such as a-Si, Al_2O_3, or SiO_x [43, 46]. This can improve the cell efficiency to a level more comparable to the bifacial BSF type cell, as reported efficiencies well over 19% demonstrate. However, for lab cells the V_{oc}s are still significantly lower than for a B-emitter; this shows that the emitter recombination current is significantly higher (J_{oe}=160–180fA/cm^2 is reported in [48]) than for a well-passivated B-emitter. A quick estimate shows that free carrier absorption in the Al-emitter is probably roughly the same as in the B-emitter.

A variation of the Al rear-emitter cell that has been explored is based on the laser-fired contacts scheme [46]. Here a dielectric rear-side passivation is applied with only local Al-emitter areas, created by laser-firing of an Al layer through the dielectric. However, for this elegant process scheme so far the results are lagging behind the full-area rear Al-emitter cells, due to non-optimal junction quality.

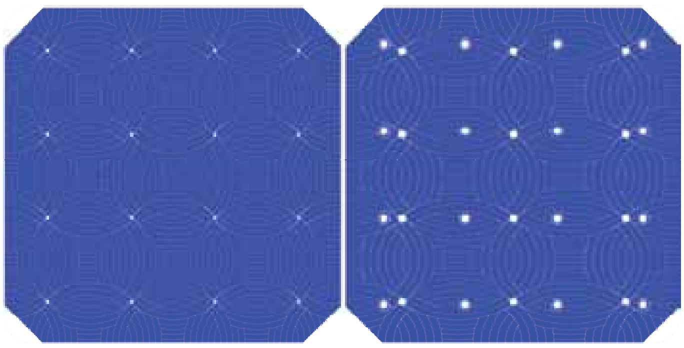

Figure 6. n-type bifacial MWT cell developed by ECN [55]. Left: front of cell; right: rear of cell.

Back-contact n-type cells

Back-contact n-type cells require more complex processing but offer the significant advantages of reduced shading losses (higher cell efficiency) and lower losses in module interconnection.

Back-contact cells have the major advantage that interconnection in a module will be on one side of the cells only. This will reduce the stress exerted by the interconnection on the cells. It allows the use of thinner cells, or cells larger than six inches. Back-side interconnection also has efficiency advantages. The interconnection conduits can be optimized for best series resistance losses without the constraints related to normal front-to-back tabbed interconnection: shadow loss (i.e. width of tab) and stress on cells (i.e. thickness of tab). The reduction of series resistance losses at the module level can result in a significant reduction of efficiency loss from cell to module, compared to standard interconnection; for example, the FF loss can be reduced to 2%, about 1.5% better than for traditional tabbed modules [52].

Only Sunpower is commercially producing back-contact n-type cells, of the back-junction back-contact type (also often referred to as interdigitated back-contact or IBC cells, although that term is rather ambiguous). Metal wrap-through (MWT) and emitter wrap-through (EWT) cells (cells where the back-contact is realized by connecting a front emitter to the back of the wafer through holes in the wafer) are in research phase.

N-type metal wrap-through and emitter wrap-through cells

MWT and EWT cells have been under development for p-type cells for more than 10 years [53]. Typically the cell process requires laser drilling of a small number (MWT) or a large number (EWT) of holes in the wafer. For MWT the front grid connects

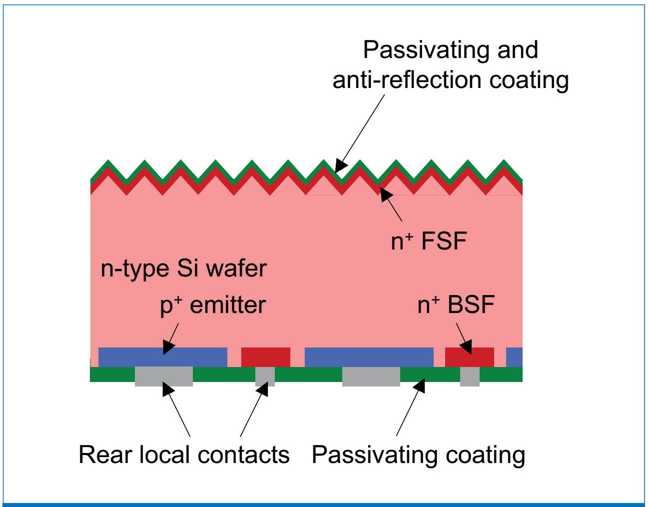

Figure 7. Schematic of an interdigitated back contact cell, such as is produced by Sunpower and is in development at many institutes and several companies. This cross-section of an n-type IBC cell made at ECN shows on the front side an n+ FSF which is coated with a passivating and anti-reflection coating. The p+ emitter and n+ BSF are located at the rear side and contacted using screen-printing. Contacts can of course be made with other methods, while also variations like point contacts or multiple emitter contacts are possible.

through these holes to contact pads on the rear, while for EWT there is no front grid, but the emitter is wrapped through these holes to contact pads on the rear. N-type EWT cells have to our knowledge not yet been reported. In principle, cell processing used for high efficiency p-type EWT cells such as RISE [52] might be applicable to n-type base material.

The authors have reported bifacial n-type MWT cells [53] (see Fig. 6). Depending on the front grid design and the number of holes, a cell efficiency gain of several tenths of a percentage point can be obtained [61]. ECN have obtained up to 19.75% cell efficiency with low-cost industrial techniques on 156mm-size Cz wafers. This means that current technology allows low-cost back-contact cells of efficiency close to 20% or higher. Together with the possibility of using thinner wafers, and the benefit for module interconnection and efficiency, this is a promising route to low-cost high-efficiency modules. An advantage of MWT back-contact technology is that it should allow bifacial modules with quite good bifaciality, whereas IBC cells due to the requirement for finer grids on the back result in modules with rather low bifaciality [27].

Back-junction back-contact cells

IBC cells on n-type wafers have been around for more than 50 years. High efficiencies can be achieved on IBC cells because all current collecting contacts are located at the rear, eliminating all front shading losses (Fig. 7). At the same time, the rear structure can be optimized for maximum collection efficiency and minimal resistive losses. However, as the minority carriers need to travel to the emitter contacts on the rear of the cell, the cells are very sensitive to wafer quality. Furthermore, the device structure needs excellent surface passivation on both sides. Currently the most successful approach is that used by Sunpower with cell efficiencies of over 24% [12].

Recently, several institutes have published work on IBC cells [54–57] using low cost methods to fabricate the p^+nn^+ junctions and contacts at the rear surface. These methods range from screen-printing and laser processing [54] to the RISE concept which is based on laser ablation and self-aligned metallization by a single evaporation step [55]. Efficiencies up to 21.3% have been reached on n-Cz [54] and up to 22% on p-FZ [55]. The latter process can be applied to n-type without a change in design [55]. Most institutes so far demonstrated high efficiencies on relatively small areas ($4cm^2$). ECN has worked in collaboration with Siliken to achieve 19.1% efficiency on larger area IBC cells applying low-cost methods like wet chemistry and screen-printing

Type	Area	Metallization	V_{oc}	Efficiency	References
MWT	239	screen printed	644	19.65	[61]
IBC	155		721	24.2	[12]

Table 2. Best results for n-type back contact cell concepts.

[58]. Another lower cost cell approach that has been published is the use of a screen-printed Al-alloyed emitter which also reached 19.1% on n-Cz wafers [56,57].

On the front-side of IBC cells, the front surface field (FSF) serves not only to reduce recombination but the FSF (together with the bulk resistivity) also has to improve the lateral transport of majority carriers. The latter is important when the contact pitch on the rear becomes large [54], which can be the case if lower cost methods like screen printing are used to define the contact structure. Besides the FSF, the cell design requires the highest resolution patterning possible, within the patterning method used, to minimize lateral transport losses. On the rear side of IBC cells, the p^+nn^+ structure needs to be well passivated with appropriate dielectrics. Traditionally, high-quality silicon oxides have been used for this purpose which benefit from a low density of fixed charges and low interface state density. Lower cost methods like deposition of dielectric layers by for example PECVD are under investigation by several groups including ECN [58, 56].

Conclusions

This article has reviewed recent directions and results in solar cell technology based on n-type crystalline silicon wafers. Clearly, it is recognized in research and industry that n-type silicon offers advantages for creating very high efficiency cells, which is of high importance for reducing costs per Wp. Therefore, in addition to the very high-efficiency cells that Sunpower and Sanyo have been producing for a number of years, there are many new exciting developments and results of n-type cell technology, and it is very likely that n-type solar cells will rapidly gain a larger market share in the coming years.

Acknowledgements

The authors acknowledge the many colleagues and project partners inside and outside ECN with whom they have had the pleasure of collaborating on science and technology of this exciting field.

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