SOLAR SILICON FROM DIRECTIONAL SOLIDIFICATION OF MG SILICON PRODUCED VIA THE SILICON CARBIDE ROUTE (*)

M. RUSTIONI†(o), D. MARGADONNA†, R. PIRAZZI++, S. PIZZINI

+ PRAGMA S.p.A. - Via M. Ghetaldi, 64 - Roma - Italy
++SAMIN ABRASIVI S.p.A. - Via Piave, 76 Domodossola - Italy

DEPARTMENT OF PHYSICAL CHEMISTRY AND ELECTROCHEMISTRY - UNIVERSITY OF MILANO, Via Golgi, 19 - Milano - Italy.

ABSTRACT

A novel process of MG silicon production is presented which appears particularly suitable for PV applications.

The MG Silicon is prepared in a 240 KVA, three electrodes submerged arc furnace, starting from high grade quartz and high purity silicon carbide (patent pending). This last has been obtained by reacting in a Acheson type of furnace, high grade sand and carbon black.

The silicon smelted from the arc furnace under very smooth furnace operations has been shown to be sufficiently pure to be directionally solidified to 10-15 Kg, 23cm x 23cm square bricks, after grinding to than > 5 mm grain size and acid leaching, with a material yield larger than 90%.

With a MG-silicon feedstock containing about 3 ppmw B, 490 ppmw Fe, 190 ppmw Ti and 170 ppmw Al, blended with 50% of off grade EG silicon to reconduct the boron content to a concentration acceptable for solar cells fabrication, the 99% of deep level impurities concentrate in the last 5% of the ingot, which appears structurally perfect in the rest, after the first crystallization, while deep level impurities are close to the detection limits by ICP-ES technique after a second crystallization.

(o) Presente Address: ENICHIMICA, piazza Boldrini 1 - San Donato Milanese - Italy
(*) Work partially supported by E.N.E.A.
10cm\times10cm wafer, sliced from twice crystallized silicon ingots, after sizing showed resistivity in excess of 0.1 ohm cm, diffusion lengths in excess of 40 \mu m and PV conversion efficiencies in excess of 6\%, when processed like polycrystalline silicon wafers of EG quality.

Quite remarkable of this material is the fact that the OCV values range higher than 540 mV and that no appreciable shorts due to SiC particles could be observed, neither on the top or bottom slices.

It is felt that still considerable improvements of this process could be achieved, such to allow the direct use of MG silicon for solar cells fabrication, when considering that the use of the same raw materials in a direct reduction process got to a MG silicon containing only 2.5 ppmw boron and that still B concentration could be reduced by a suitable control of the residual pollution sources.

1. INTRODUCTION

"Solar grade" silicon is the ultimate product of a process which starts from suitable raw materials and yields wafers which could be directly used for manufacturing > 10\% efficient solar cells (1), satisfying at the same time the economic constraints which indicate as the target for a "solar grade" feedstock(*) a figure around or less than 10$/Kg.

This paper reports comprehensively the results of a research carried out by a team of Italian companies which succeeded in approaching very closely the efficiency and economics targets by a process which will be indicated as the HPS process from the names of the companies involved (Heliosil, Pragma and Samim Abrasivi).

This process, which will be discussed in details in the next sections, consist essentially of the following steps:

- The synthesis of high purity SiC from low boron (<0.5 ppmw) silica sands and carbon black (2).

- The reduction of quartz lumps in an arc furnace using SiC as

(*) We mean as "feedstock" a material which could be directly crystallized to obtain wafers usable for manufacturing PV cells, with a yield larger than 90\%.
the reductant (2).

- The purification of the MG silicon obtained in such a manner using a directional solidification technique.

Although the work is still in progress, nevertheless the results appear so encouraging that we strongly believe that the industrial feasibility of MG silicon route has been demostrated.

2. GENERAL REMARKS ON HPS PROCESS

Metallurgical silicon is currently manufactured by direct reduction of quartzites with carbon in a submerged electrodes arc-furnaces (DAR process).

The overall reduction reaction could be described, formally with the following equation:

\[ \text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO} \]  \hspace{1cm} (1)

According to the scheme shown in fig. 1, the process actually occurs in a multi-step pattern, with a series of reactions taking place simultaneously at different heights of the furnace, depending on the temperature which rises from the top to the bottom. With reference to fig. 1, one can observe that on the cooler portion of the furnace, where the temperature is lower than \(1500^\circ\text{C}\), the thermodynamically most probable reaction is the following one:

\[ \text{SiO}_2 + \text{C} \rightarrow \text{SiO} + \text{CO} \]  \hspace{1cm} (2)

while only in the inner and hotter portion of the furnace, thermodynamics favours the reactions:

\[ \text{SiO} + 2\text{C} \rightarrow \text{SiC} + \text{C} \]  \hspace{1cm} (3)

and:

\[ \text{SiC} + \text{SiO} \rightarrow 2\text{Si} + \text{CO} \]  \hspace{1cm} (4)

The last one provides silicon from SiC and SiO. It appears that SiC is an intermediate by-product in the direct reduction process of silica and therefore SiC must be considered a primary and unavoidable pollutant of MG silicon, unless being able to control the rate of reactions (3) and (4), which is never the case when operating industrial arc furnaces.

On the other hand, SiC may be directly and efficiently ma-
ufactured using resistance furnaces of the Acheson type (this is in fact the way by which silicon carbide is produced world-wide for the abrasive industry) according to the following equation:

\[ \text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO} \]  \hspace{1cm} (5)

Therefore synthetic SiC is very attractive as the reductant (instead of carbon) of SiO2 in an arc furnace. In this case the overall reduction equation occurs according to:

\[ 2\text{SiC} + \text{SiO}_2 \rightarrow 3\text{Si} + 2\text{CO} \]  \hspace{1cm} (6)

which involves, apparently the evolution of only 2/3 of moles of CO every mole of silicon produced, which is just 1/3 of the amount of CO evolved in the direct arc furnace reduction process as appears in reaction (1).

The lower amount of gases evolved (which causes the lower amount of heat lost and smoother furnace operation) is not the only advantage of the HPS process in respect to the DAR process. Meanwhile, infact, also the theoretical electrical energy demand (per mole of SiO2) is one third, and this should improve the overall electric yield of the HPS process, since the production of SiC in Acheson furnace occurs quite effectively. Actually, in spite of the excess heat needed in the HPS process for bringing the intermediate SiC to the reaction temperature in the arc furnace, after being produced in the Acheson furnace, still the overall electrical yield of the HPS process is comparable with the DAR process, as it appears in Table I and Table II, which will be further commented in the next section. A further advantage of the HPS process arises from the physical requirements of the raw materials used in Acheson furnaces which do not need to be compacted or extruded before feeding them into the arc furnace, as required in DAR process in order to allow a smooth furnace operation.

Finally, the fact that the graphite electrode consumption is reduced by a factor of three in the arc furnace step of the HPS process and that no electrode consumption is involved in the Acheson process, makes contamination of the produced silicon lower.

It must also be considered that high operation temperature (> 2200degreeC) are reached in the inner part of the Acheson furnace. The high temperature gradient makes possible the transfer of impurities from the inner part to the cooler outer zone via gas phase as well solid phase. Therefore, during the synthesis of SiC in the Acheson furnace a significant purification of the reactants and product takes place that results
in well crystallized, transparent SiC platelets in the inner part of the furnace. The purification may also be enhanced carrying out the synthesis of SiC in the presence of NaCl or chlorine gas which allows the formation of volatile halides.

Besides residual metallic impurities (whose amount depends on the reduction yield of the parent oxides present in quartzites), the MG silicon smelted from the arc furnace always contains carbon in excess over saturation conditions which precipitates as silicon carbide.

Being firmly established in the literature and confirmed by previous experiments that bulk SiC and impurities (except boron and phosphorous) could be removed by crystallization procedures (3-6) quite better than using intermediate slagging or leaching steps, the HPS process is completed by a twice crystallization in a Bridgman furnace, conducted according to a proprietary knowledge (7).

The first crystallization step allows to segregate most impurities (SiC included) in the last 5% of the solidified ingot. This part can be easily separated by sawing and the resulting product is the "solar grade feedstock".

Then, the wafers sliced from ingots grown in Bridgman furnace using "solar grade feedstock" (second step of crystallization) are directly usable for solar cell fabrication.

A schematic flow-diagram of the HPS process is reported in Fig. 3.

3. EXPERIMENTAL

A) Synthesis of high purity SiC

SiC has been prepared starting from high purity silica sand and carbon black. The mechanical mixture of both components has been agglomerated by extrusion or briquetting using sucrose as the binder. By this way, 18000Kg of pellets have been prepared which were allowed to react in the Acheson furnace, whose schematic lay-out is reported in Fig.2. The average impurity content in the pellets is reported in Table I, as determined by ICP-ES techniques after dissolution. In the same table, the impurity content in SiC produced in the middle part of the furnace, is also reported together with the expected impurity contents calculated from the amount of impurities in the raw materials, assuming no impurity losses during the SiC production process. It appears that, with the exception of titanium, the impurity content is lower than that expected,
indicating a purification effect during reaction of the mixture due, as already discussed, to impurity migration towards the cooler part of the charge. These purification effects are particularly relevant in the case of boron and phosphorus: in both cases a purification factor of the order of ten is obtained.

The silicon carbide obtained by the Acheson process is very brittle and porous. Both factors are very beneficial for the use of SiC in the arc furnace, as brittleness limits intermediate manipulation steps before the final use to one single crushing step in order to reconduct the large SiC blocks to the right size (1-20 mm), and porosity enhances the permeation of the gases (CO and SiO) during the arc furnace operation and consequently enhances also the yield of reaction (4).

Crushing, however has been found to seriously affect the purity of SiC (see table I) and therefore the crushing step should be implemented by acid leaching.

B) Arc furnace experiments

Arc furnace experiments have been carried out in a 240 KVA three-phase submerged electrodes arc furnace. A picture of the furnace is shown in fig. 4, while fig. 5 reports a schematic lay-out and table III reports further technical details.

The furnace has been fed with SiC and 20-60 mm quartz "nuts" which have been obtained by grinding, HCl leaching and de-ionized water rinsing of large natural quartz blocks whose original impurity content is reported in table II.

High purity graphite tools or SiC tools have been used throughout during the furnace operation (smelting, breaking the crusts which form on the surface of the charge and limit the vertical electrode movements as well as the escape of the gases) in order to avoid the silicon pollution caused by the furnace handling.

Fig. 6 reports details of a typical run when the furnace is fed with SiO2 and SiC. It appears from the energy consumption curve that the furnace operates smoothly and that the specific energy consumption averages 13 Kwhr/Kg after the furnace start-up period, which takes about one day. Smelting operations were carried out every 8 hrs and silicon was poured in an high purity graphite mould.

Sampling of silicon for impurity content analysis was carried out at the beginning, in the middle and at the end of the
smelting operations directly on the molten silicon in order to avoid that segregation affects in the solid ingot during cooling could affect the reliability of the analysis.

Results referring to a typical run (# 10/2) are reported in Table III and compared with a typical DAR run (# 12/6) which was carried out in the same arc furnace few months ago (6,8), before having introduced the routine use of carbon black and SiC runs in furnace operations.

It is worth noting that, in spite of improved furnace operation, still a substantial pollution of the produced silicon is observed.

However, if one compares the deviation factors, calculated as the ratios between the actual and expected values, between the run HPS 10/2 and the run DAR 12/6, one observes that pollution has been definitively reduced for every impurity investigated, except for boron in the run HPS 10/2.

Furthermore, by remarking that grinding of SiC was another source of pollution, one could forecast that leaching of SiC could get a material, under the same furnace operating conditions of run HPS 10/2, containing 40 ppmw Al, 1.6 ppmw B, 340 ppmw Fe, 0.6 ppmw P and 350 ppmw Ti which is still the most harmful impurity present.

Within the possible pollution sources, the construction materials of the furnace and the surrounding atmosphere are the most critical, as they behave like "infinite size" pollution sources.

By no means, therefore, is worthwhile to improve the quality of starting materials before having solved these problems to which we intend to observe the maximum of attention in the next period of time.

C) Purification of MG silicon by directional solidification.

As the material having the impurity content of HPS or DAR silicon reported in Table III could not be directly casted or CZ-pulled for getting ingots useful for solar cells fabrication, one intermediate purification step is needed and the directional solidification process was found to be very effective for this purpose.

The furnace and the crystallization procedures used have been already described (8-10): it operates in the Bri-
All purification experiments were carried out using quartz crucibles, coated on the inner walls by a thin layer of silicon nitride which avoids the direct contact of liquid silicon with the crucible walls and, therefore, avoids sticking effects with cause the breaking of both crucible and ingot.

In order to avoid spurious effects due to additional impurities introduced into the silicon charge during grinding procedures, which serve to obtain chunks of suitable size for casting, the charge was acid leached with an HF: HCl : H2O (1:1:4) solution at 60 degree C, for two hours, rinsed and dried.

The purification experiments reported in this paper have been carried out on material coming from the run HPS10/2, having the impurity content reported in Table III. After grinding, only the fraction having a grain size larger than 2 mm has been used, to facilitate the melting of the charge. The original charge was added of "off grade" EG silicon chunks to adjust the boron content to an equivalent resistivity value of 0.15 ohm cm or more.

From the ingot so obtained, a 1 cm thick slice was sectioned in the middle of the ingot, and then, by further slicing, 112 cubes of 1 cubic cm were obtained, each one was numbered and analysed for impurity content by the ICP-ES technique. Results for sample coming from a vertical row at the periphery of the ingot (nrs. 9, 11, 14, 15) and in the middle (nrs 50, 52, 54, 56,) are reported in table IV (see for reference fig. 7).

One remarks that the impurity content (except B and P) is strongly depressed in more than 90% ingot, while impurities segregate in the last 10% (see impurity content in cube nr. 56 and on the top samples) where also SiC segregates, leaving the remainder substantially free of SiC particles, as observed by visual inspection.

Segregation coefficients calculated from the original impurity content of the MG sample end of the first lowest cubes of each vertical row are also reported in table IV.

Although the segregation coefficients so derived are much higher than ones reported for from pulling, still the values obtained allow a high degree of purification from aluminum, iron and titanium which are the most abundant contaminants.

Obviously, no purification is observed for boron and pho-
sphorus. Unexpected large values are obtained for Ca and Mg: an accidental contamination during analysis procedures is suspected in these cases.

The "solar grade feedstock" was then obtained cutting away from the ingots grown, as above described, the top and the lateral sides. The material was then subjected to a second directional solidification with the same procedures of the first one. The resulting ingots was analysed in the same way as previously described. Results are shown in Table V.

Also in this case some degree of purification is obtained, although it occurs in lower extent than expected from data of Table IV. Since the resistivity measurements described in the next paragraph are in substantial agreement with analytical results, one has to conclude that some contamination occurred during the second solidification step.

D) Physical characterization and solar cells performance of HPS material.

10cm x 10cm x 0.04cm wafers cut from ingots prepared with "solar grade feedstock" as previously described, were subjected to physical and PV test (see Table VI for results). All slices examined resulted p-type, with an average resistivity of 0.13 ohm cm, which well compares with the expected one, obtained from the excess acceptor concentration (Na - Nd) = 2.4E17/cm³ calculated using the experimental values of B, P and Al concentration (see Table IV) and by taking the aluminum 30% ionized.

The diffusion lenght of the minority carriers, measured using the SPV technique resulted in average larger than 40μm with top values of 50μm which is definitely lower than the average Ld values (> 150μm) measured on "off grade" EG silicon wafers manufactured with the same casting process.

Solar cells, manufactured using the standard Pragma procedures, resulted in average 6.2% efficient while "off grade" E.G. silicon wafers processed in the same batch resulted 9.85% efficient.

As it results from Table VI, not only the low values of short circuit current are responsible of the efficiency measured but also the OCV (540 mV) which is about 60 mV lower than the OCV which could be obtained with a FZ silicon having the same resistivity. The analysis of I-V curve for such solar cells shows that the shunt resistance is lower than one observed on cells manufactured starting from standard material, so
revealing a certain amount of shortage probably due to small particles of SiC which still remain after twice crystallization process.

4. CONCLUSIONS

From the results reported in the different sections of this paper it appears that a definitive progress towards the industrialization of a MG silicon process for solar uses has been obtained in the course of our research program. In our opinion it results that MG silicon is a possible low cost source of solar feedstock. It has been proven in fact, that:

-The use of SiC, which could be synthetized in an Acheson furnace at a reasonable grade of purity, improves definitely the arc furnace operations.

-The purity of HPS Si, before the first crystallization is significantly close to the expected one and impurity contamination sources were clearly indentified.

-Crystallization of HPS silicon, without any intermediate purification process yields a material capable of getting cell with efficiencies in excess of 8.5% if only the active area is considered.

Therefore, one can forecast that by improving the handling of SiC and by carrying the first crystallization step in the presence of Ca, followed by an acid leaching (according to a process suggested by Schei (11)), our material is already useful for >10% efficient solar cells.

ACKNOWLEDGEMENTS

Authors warmly acknowledge the Italian Comitato Nazionale per la Ricerca e lo Sviluppo dell'Energia Nucleare e delle Fonti Rinnovabili (E.N.E.A.) for the financial support given to the project on solar grade silicon. They are particularly indebted to G. Gazzola of E.N.E.A. for continuous encouragement. Authors are also indebted to P. Fabris and M. Tomassini for many helpful discussions and to M. Colombo, F. Rota and M.P. Bianchini for technical assistance.
LITERATURE

(1) S. Pizzini, Solar Energy materials, 6 (1982) 253

(2) P. Fabris, D. Margadonna, R. Pirazzi, R. Rustioni

(3) J.A. Amick, J.P. Dismukes, R.W. Francis, L.P. Hunt, P.S.
Ravishankar, M. Schneider, K. Mathei, R. Sylvain, K.
Larsen, A. Schei
Proc. Symp. Materials and new process Technology for
Photovoltaics.

(4) J.P. Dismukes, J.A. Amick, P.S. Ravishankar, E.E. Shipp,
L.B. Younghouse, J. Blake, R. Sylvain, G. Halvorsen,
technologies for Photovoltaic, Proc. Vol. 85 (The

(5) H.A. Aulich, L. Bernewitz, H.J. Fenzl, H. Pink, F.W.
Schulze, MRS-Europe, Poly-microcrystalline and amorphous

(6) S. Pizzini, M. Rustioni
Proc. sixth E.C. Photovoltaic Energy Conference

(7) M. Rustioni, R. Pirazzi, M. Tincani, D. Margadonna, S.
Pizzini
Proc. Symposium on Materials and new processing tech. for
press.

(8) S. Pizzini, C. Chemelli, M. Gasparini, M. Rustioni

(9) M. Beghi, C. Chemelli, S. Fossati, S. Pizzini, MRS Europe,
Poly-microcrystalline and amorphous semiconductors. Les

(10) C. Chemelli, M. Beghi, S. Fossati, F. Rota, L. Bigoni

(11) A. Schei. Private communication.
TABLE I - SYNTHESIS OF SiC IN ACHESON FURNACE: ANALYTICAL AND ELECTRICAL DATA
### Table II - Comparison Between the Arc Furnace Steps of the HPS and DAR Process

<table>
<thead>
<tr>
<th></th>
<th>HPS Process (SiO₂ + SiC) Run #5</th>
<th>DAR Process (SiO₂ + C) Run #12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy Consumption (Kwh/Kg)</td>
<td>11.9 (+11 required for SiC)</td>
<td>21</td>
</tr>
<tr>
<td>Electrodes (Kg/Kg)</td>
<td>0.06</td>
<td>0.11</td>
</tr>
<tr>
<td>Reaction Yield</td>
<td>95%</td>
<td>65%</td>
</tr>
</tbody>
</table>

- Internal Diameter of the Vessel: 1020mm
- Electrodes Diameter: 175mm
- Length Between Electrodes: 370mm
- Maximum Power: 240kVA
<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>SiC AFTER GRINDING ppmw(*)</th>
<th>QUARTZ</th>
<th>Si HPS RUN #10/2</th>
<th>Si HPS EXPECTED VALUE (*)</th>
<th>DEVIATION FACTOR HPS</th>
<th>Si DAR RUN #12/6</th>
<th>Si DAR EXPECTED VALUE (*)</th>
<th>DEVIATION FACTOR DAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>156</td>
<td>31</td>
<td>340</td>
<td>182</td>
<td>1.9</td>
<td>365</td>
<td>168</td>
<td>2.2</td>
</tr>
<tr>
<td>B</td>
<td>2.1</td>
<td>&lt;0.5</td>
<td>5.8</td>
<td>3.6</td>
<td>1.6</td>
<td>2</td>
<td>3</td>
<td>0.7</td>
</tr>
<tr>
<td>Ca</td>
<td>194</td>
<td>60</td>
<td>153</td>
<td>203</td>
<td>0.8</td>
<td>115</td>
<td>225</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe</td>
<td>290</td>
<td>10</td>
<td>986</td>
<td>504</td>
<td>2.0</td>
<td>615</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td>Mg</td>
<td>45</td>
<td>15</td>
<td>27</td>
<td>48</td>
<td>0.6</td>
<td>14</td>
<td>63</td>
<td>0.2</td>
</tr>
<tr>
<td>p</td>
<td>5.6</td>
<td>5.2</td>
<td>6.1</td>
<td>16</td>
<td>0.4</td>
<td>32</td>
<td>34</td>
<td>1</td>
</tr>
<tr>
<td>Ti</td>
<td>96</td>
<td>5.2</td>
<td>382</td>
<td>120</td>
<td>3.2</td>
<td>270</td>
<td>2.6</td>
<td>10</td>
</tr>
</tbody>
</table>

(*) MEASURED BY ICP - ES

(°) TAKING INTO ACCOUNT THE STOICHIOMETRY OF THE PROCESS

**TABLE III - IMPURITY CONTENT IN Si HPS AND Si DAR OBTAINED STARTING FROM SIMILAR RAW MATERIALS IN THE SAME ARC FURNACE**
<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>FEED-STOCK (ppmw)</th>
<th>CUBE no</th>
<th>9</th>
<th>11</th>
<th>13</th>
<th>15</th>
<th>50</th>
<th>52</th>
<th>54</th>
<th>56</th>
<th>TOP</th>
<th>C1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>170</td>
<td>6.6</td>
<td>8.8</td>
<td>6.4</td>
<td>7.5</td>
<td>4.9</td>
<td>5.3</td>
<td>7.0</td>
<td>275</td>
<td>&gt;5000</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.9</td>
<td>2.8</td>
<td>2.9</td>
<td>2.5</td>
<td>2.8</td>
<td>2.6</td>
<td>2.7</td>
<td>3.0</td>
<td>3.1</td>
<td>8.7</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>77</td>
<td>126</td>
<td>84</td>
<td>212</td>
<td>40</td>
<td>183</td>
<td>314</td>
<td>171</td>
<td>330</td>
<td>&gt;1500</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>490</td>
<td>3.7</td>
<td>5.6</td>
<td>6.2</td>
<td>4.8</td>
<td>1.8</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>640</td>
<td>&gt;6000</td>
<td>0.006</td>
</tr>
<tr>
<td>Mg</td>
<td>14</td>
<td>34</td>
<td>28</td>
<td>32</td>
<td>15</td>
<td>12</td>
<td>23</td>
<td>19</td>
<td>31</td>
<td>250</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>3</td>
<td>3.8</td>
<td>6</td>
<td>10</td>
<td>5.2</td>
<td>5.3</td>
<td>7.1</td>
<td>10</td>
<td>16</td>
<td>300</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>190</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>240</td>
<td>&gt;1500</td>
<td>&lt;0.005</td>
</tr>
</tbody>
</table>

(*) - HALF OF THE VALUES REPORTED IN TABLE III

TABLE IV - IMPURITIES DISTRIBUTION MEASURED IN THE INGOT W 271

(FEEDSTOCK: # 10/2 50% AND Si EG 50%)
<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>ppmw</th>
<th>CUBE nº</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1.5</td>
<td>3.0</td>
</tr>
<tr>
<td>B</td>
<td>2.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Ca</td>
<td>27</td>
<td>47</td>
</tr>
<tr>
<td>Fe</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Mg</td>
<td>21</td>
<td>16</td>
</tr>
<tr>
<td>P</td>
<td>2.1</td>
<td>2.5</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

**TABLE V - IMPURITIES DISTRIBUTION IN THE INGOT W 273**

**GROWN USING INGOT W 271 AS FEEDSTOCK**
TABLE VI - PHOTOVOLTAIC PROPERTIES OF SOLAR GRADE SILICON PRODUCED BY HPS PROCESS.
WAFERS FROM INGOT n° W 273

<table>
<thead>
<tr>
<th>WAFER SIZES:</th>
<th>10cm x 10cm x 0.04cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TYPE:</td>
<td>P</td>
</tr>
<tr>
<td>RESISTIVITY:</td>
<td>$\bar{p} = 0.13 \Omega \times \text{cm}$</td>
</tr>
<tr>
<td>DIFFUSION LENGTH:</td>
<td>$L_D = 40 \mu\text{m}$</td>
</tr>
<tr>
<td></td>
<td>(best value = 50 $\mu\text{m}$)</td>
</tr>
<tr>
<td>CONVERSION EFFICIENCY:</td>
<td>$\bar{\eta} = 6.2%$</td>
</tr>
<tr>
<td>(100mW/cm$^2$, 25ºC)</td>
<td></td>
</tr>
<tr>
<td>BEST VALUE of $\eta$</td>
<td>$\text{Isc} \times \text{Voc} \times \text{FF} = $</td>
</tr>
<tr>
<td></td>
<td>$1.83 \text{Amp} \times 0.549V \times 0.69$</td>
</tr>
<tr>
<td></td>
<td>$= 6.9%$</td>
</tr>
<tr>
<td>ACTIVE AREA EFFICIENCY:</td>
<td>$\eta_a = \frac{6.9}{0.8} = 8.6%$</td>
</tr>
<tr>
<td>RELATIVE EFFICIENCY:</td>
<td>$\frac{\eta}{\eta_0} = \frac{6.9}{9.85} = 0.77$</td>
</tr>
<tr>
<td>TOTAL NUMBER OF MEASURED CELLS</td>
<td>$= 43$</td>
</tr>
</tbody>
</table>
FIGURE n. 1 - SCHEME OF REACTIONS OCCURRING INSIDE THE ARC FURNACE
FIGURE n. 2 - VERTICAL SECTION OF THE ACHESON FURNACE USED FOR THE SiC SYNTHESIS
ACHESON
SIC
CRUSHING &
LEACHING
ARC FURNACE
SiO₂ + 3C → SiC + 2CO
SiO₂ + 2SiC → 3Si + 2CO
GRINDING Ø 5mm.
ACID LEACHING
1st DIRECTIONAL
SOLIDIFICATION
S.G.
SILICON
FEEDSTOCK
2nd DIRECTIONAL
SOLIDIFICATION
WAFERS FOR SOLAR CELL PRODUCTION

FIGURE n. 3 - SCHEMATIC FLOW CHART FOR THE HPS PROCESS
FIGURE 4 - Picture of the arc furnace during the smelting of silicon
Figure 5 - Schematic view of the arc-furnace used for Si-metal smelting experiments.
FIGURE n. 6 - SILICON METAL PRODUCTION IN 240 KVA ARC FURNACE UNDER CONTINUOUS OPERATION CONDITIONS IN HPS PROCESS
FIGURE n. 7 - VERTICAL SECTION OF THE INGOT W 271 GROWN FROM HPS 10/2.

NUMBERED CUBES SUBJECTED TO CHEMICAL ANALYSIS REPORTED IN TABLE IV ARE SHOWN
AULICH: Do you feel that by eliminating impurities from the environment that you can obtain a material with low enough boron and phosphorus to make good solar cells without the addition of electronic-grade silicon?

RUSTIONI: We hope so, because we can demonstrate that in some cases the boron concentration is only 2 ppmw. In the run that I described, we could operate the arc furnace for 5 or 6 days, and we obtained 1 MT of this kind of metallurgical silicon with 2 ppm boron. But this is not sufficient, and we must improve to get < 1 ppmw boron. This is a real problem.

LUTWACK: Did you obtain cell efficiency data from baseline cells manufactured from semiconductor-grade silicon so that you could compare the cell data obtained for cells manufactured from your silicon?

RUSTIONI: Yes. The baseline cells made from electronic-grade silicon had efficiencies of 9 to 10%.

LUTWACK: Then the comparison is 6% with about 9%?

RUSTIONI: Yes, and it's not so bad. Now, Pragma is improving the quality of production.

WRIGHT: Using carbon black as the primary carbon source in the arc furnace operation, you ran 5 to 6 days before shutting down. On a much larger scale, say 1000 MT/year (which was what the Solarex plant was capable of producing), the use of carbon black as the primary source will tend to clog the furnace, so you will be forced to use a different carbon source. Then, the decrease in quality of the carbon product with an increase in the productivity of the arc furnace needs to be looked at so that there will be a dilution factor. The tradeoffs of each particular type of submerged arc furnace operation should be investigated.

RUSTIONI: It's possible to change the quality of the quartz lumps used in the carbothermic reduction with silicon carbide. Instead of using single-crystal quartz from Venezuela, we can use very high-purity quartzite. Silicon carbide and quartz powder can be leached, and briquettes can be prepared from silicon carbide and silica to improve the arc furnace operation. Of course, the cost of this type of processing must be considered.

MAYCOCK: I assume that the cell efficiencies you gave were for cells without anti-reflection coatings.

RUSTIONI: That's correct.