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From the initial operation of the line, we have concluded that the process sequence as defined is suitable for automated production, and planning for a large scale facility will begin shortly.

6. FUTURE OF PHOTOVOLTAICS

There are certain technical problems still to be solved for large scale use. Although the efficiency of modules has increased significantly over the past 5-6 years, higher efficiencies are still required for economical large scale deployment. It has been estimated that efficiencies in excess of 18% are required to lower the cost per watt to be commensurate with other electricity costs, e.g., a bus bar power at 15¢/kWh. Also certain auxiliary equipment such as power inverters, batteries, etc., must be developed/improved so that the use of photovoltaic systems can be expanded (e.g., not only dc electricity and not only during daylight).

When these are achieved, PV will fill a significant fraction of the nation's energy requirements.

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Obtention of Polycrystalline Solar Cells from Metallurgical Silicon

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ABSTRACT

A process to obtain solar grade silicon with potentialities of being economically feasible made use of metallurgical grade silicon as a starting material. The first purifying step was accomplished by acid leaching of a silicon powder resulting from the crushing of the raw material employed. Such powder was induction melted into graphite crucibles in a purposely built apparatus. A cylindrical ingot removed from the heating zone. A further purifying effect was derived from solute segregation. The main heat extraction from the base of the crucible caused a crystallographic microstructure consisting of almost longitudinally disposed crystalline grains, favouring the photovoltaic phenomenon. In the silicon wafers, the bottom region of the ingot was p-type while the central and top regions were n-type. Wafers of the n and p-type were diffused from a NaCl_2 liquid source at 800°C, resulting a n^+p layer with 50 Ω sheet resistance. In order to evaluate the material's quality, junctions of the p^+n , n^+p and Sn/p (n /Si) type were prepared using several quality. Junctions of the p^+n , n^+p and Sn/p (n /Si) type were obtained and the photovoltaic parameters were determined. Efficiencies of 4.01, 2.01 and 3.7% were measured with the p^+n , n^+p and Sn/p (n /Si) structures respectively, showing the process to be promising.

1. INTRODUCTION

The availability of the solar energy by the photovoltaic effect relies upon the use of monocrystalline electronic grade silicon (MG-Si) wafers, its degree of purity being typically 99.9999%. The technological processes involved in its obtention are the same employed for the silicon used in the manufacturing of semiconductor devices, resulting in a high cost/watt ratio when compared with the so-called conventional methods of large scale energy conversion. Nevertheless, for a number of terrestrial applications, such as water pumping for irrigation and the supply of electrical energy in remote located countries, a comparatively downgraded silicon would exhibit a suitable performance, provided the cost of its obtention would be lower.

Brazil is one of the countries where the photovoltaic energy finds the most promising conditions of extensive application, due to its large extension with favourable insolation and an economy with a strong agricultural basis [1]. Furthermore, high quality quartz (crystalline SiO_2) deposits abound, from which metallurgical grade silicon (MG-Si) with a degree of purity as high as 99.9% is produced by reduction with charcoal in electrical furnaces. The high standard of quality of the Brazilian MG-Si is recognized worldwide [2].

The research work here presented, still in laboratory stage, consists of a sequence of alternative processes of silicon production for solar cells whose main objective is to supersede the expensive methods of MCP-Si processing.

Starting with crushed high purity MD-Si, a first purifying step is accomplished by acid leaching, which is described elsewhere [1]. The subsequent process of polycrystalline ingot growth by unidirectional solidification, and solar cells fabrication, are now detailed. The resulting material will be referred as solar grade polycrystalline silicon (SGP-Si), its full characterization having not been attained yet.

2. UNIDIRECTIONAL SOLIDIFICATION

A polycrystalline silicon ingot is obtained by first melting the previously leached silicon powder into a crucible, in a induction furnace, under an inert gas atmosphere. Further, a solidification front is established by slowly removing the crucible from the heating zone.

The work of Fisher and Pachander [2], and Roy et alii [3], showed the influence of the polycrystallinity of silicon on the performance of solar cells. The grain boundaries act as centers of recombination of minority charge carriers, and as barriers for the majority carriers, elucidating the low efficiencies observed in conventionally solidified silicon. The essential features of polycrystalline wafers are so decurrent:

a) The grain size must be larger than 100 μ m, assuring full reception of the minority carriers.

b) Grain boundaries perpendicular to the majority carriers flow must be avoided.

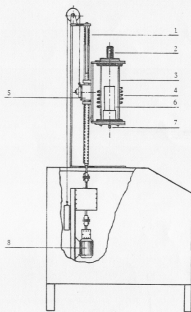
These two requisites are fulfilled by silicon ingots grown by unidirectional solidification, where the main heat extraction occurs at the bottom of the crucible, its side wall being chemically insulated. Ideally, the ingot would consist of longitudinally disposed crystalline grains [4].

A further purifying effect occurs during the solidification due to solute segregation from the solid to the remaining liquid. The governing parameter is the solute partition coefficient in equilibrium K_0^S/K_0^L , where C_0^S and C_0^L are the concentrations of solute in the solid and liquid phases respectively. In silicon all impurities have $K_0^S < 1$, and so are expected to concentrate in the ultimate solid region to be formed.

3. EXPERIMENTAL EQUIPMENT

A purposely built induction furnace was employed for the obtention of silicon ingots by unidirectional solidification, and is shown in figure 1. The leached silicon powder fills a graphite crucible which is placed inside the quartz chamber. The process starts with the crucible surrounded by the induction coil, the silicon being completely melted at about 1,417°C. After a slight overheating, the quartz chamber begins to be slowly moved down by a screw mechanism driven by a d.c. motor. As the crucible is withdrawn from the coil the solidification process takes place. The thermal insulation between the crucible and the quartz chamber assuring a main heat extraction at the base of the ingot being grown.

A continuous flow of argon inside the chamber prevents the oxidation of the



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|--------------------|-----------------------|
| 1 - Screw | 5 - Clamping system |
| 2 - Argon outlet | 6 - Graphite crucible |
| 3 - Quartz chamber | 7 - Argon inlet |
| 4 - Induction coil | 8 - D.C. motor |

Figure 1. Induction Furnace for Obtention of Silicon Ingots

silicon, and temperature readings are made by means of thermocouples.

4. RESULTS OF THE SOLIDIFICATION PROCESS

A longitudinal cross section of a cylindrical ingot obtained when the solidification front progressed with a rate of 2 cm/hour is shown in Figure 2. The structure is composed of grains which solidified from bottom to top of the ingot, although nucleation and grain growth also occurred at the side wall of the crucible. The curved paths present on the observed surfaces were due to the cutting action of a diamond saw.

Figure 3 shows a silicon wafer obtained from a half-ingot, where the grains were observed to have an average diameter well above the minimum size of 100 μ m recommended by Roy [5].

Wafers of the bottom, middle and top regions alongside the ingot were chemically analysed by semi-quantitative emission spectroscopy, the results for a number of elements being given in table 1. We can verify that elements like Fe and Mn, with K_0 in the order of 10^{-6} and 10^{-9} respectively, are effectively pulled to the top of the ingot, while P, with $K_0 = 0.35$ is not affected by segregation.

During solidification silicon crystallizes with the diamond cubic lattice, forming large interstices where impurity atoms can be introduced by diffusion [6]. Such factor could explain the fact that elements like Cu, with K_0 in the order of 10^{-4} , but with high diffusibility in solid silicon, are not removed by solute segregation.



Figure 2. Longitudinal Cross Section of Silicon Ingot. Magnification: 1,6X



Figure 3. Polycrystalline Silicon Wafer . Magnification: 1,6X

Table 1. Chemical Analysis of SiP-Si by Emission Spectroscopy

Element	bottom (ppm)	middle (ppm)	top (ppm)
Al	500	300	500
Fe	150	1000	>1000
Cu	>250	50	150
Mn	9	>250	>250
Ni	<9	25	125
B	9	20	25
P	100	100	100
Tl	9	250	450
Mg	<25	12	25
Ag	<4,5	<4,5	<4,5

5. SOLAR CELLS PROCESSING

The unidirectionally solidified silicon ingot presented regions of opposite

type resistivity. A small part of the bottom portion was p-type. The central and top portions were n-type. In order to evaluate the material's quality, different photovoltaic structures were fabricated, using different parts of the ingot and of the process of upgrading the Si-Ge [6, 8].

Some n- and p-type wafers were selected and used to fabricate n⁺-p-SiO₂/n-Si and p⁺-n structures. Figure 4 shows schematically the different structures tested and the corresponding energy band structures. The fabrication processes follow. An acid solution was used to remove a thin layer of damaged surface. All wafers were diffused from a POCl₃ liquid source at 900°C, obtaining a n⁺ layer having 50 Ω/cm sheet resistance on the two faces of the wafers. The n⁺ layer of one face was chemically etched. On the p-type silicon wafer a n⁺-p rectifying junction was aluminum was deposited. In order to provide a good ohmic contact on the back side, successive evaporation of Ti, Pd and Ag. Finally, a SiO₂ antireflective coating was deposited by chemical spray. Junctions of the n⁺-p type were obtained by this process. In the n-type wafers the phosphorus diffusion provided an ohmic contact. In these wafers two different structures were made: 1) the SiO₂/n-Si structure was prepared as follows. On the front side of the wafer a 150 Å SiO₂ layer was deposited. Front grid and back contacts were made in the same way as in the first cell. 2) to produce the p⁺-n structure, aluminum was deposited and annealed on the back side. In this case the illumination was made through the n⁺-n ohmic contact. On this face a SiO₂ antireflective coating was deposited by chemical spray. Front grid and back contacts were made in the same way as in the other cells.

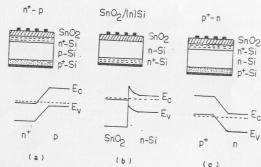


Figure 4. Schematic Representation of the Solar Cells and Their Energy Band Structures

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6. SOLAR CELLS PERFORMANCE

All cells were measured in the dark and under AMG conditions (100 mW/cm²). Current vs. voltage plots were obtained and the photovoltaic parameters were determined. Figure 5 shows the open circuit voltage, short circuit current, fill factor and efficiency of the fabricated structures. Efficiencies of 4.01, 2.04 and 3.74 were obtained in the p⁺-n, n⁺-p and SiO₂/n-Si solar cells, respectively.

The performance of the cells could not be compared with each other, due to different properties of each silicon wafer. The type and resistivity of the material changed along the ingot. The structural properties like crystallinity and grain orientation also were different along the ingot. In addition the area of the cells were not the same.

The p⁺-n barrier was illuminated through the n face because the p⁺ layer is too abundant, decreasing greatly the efficiency of the cell. The other two cells were illuminated in the conventional way.

The open circuit voltage of a good solar cell of each one of these structures should be approximately equal to each other. In the case of the present work there was a great difference. This is because of the differences in the properties of each silicon slice, such as resistivity, grain orientation and the fabrication process. For example, in the fabrication of a SiO₂/n-Si solar cell the sprayed tin liberated during the reaction [10]. The short circuit current is higher in the p⁺-n solar cell (25 mA/cm²). Probably this wafer had a higher diffusion length and/or a higher carrier lifetime.

To enhance the performance of solar cells the Si-Ge processing and cells fabrication technology must be optimized. First of all the Si-Ge needs to suffer a good lifetime of the carriers, which will contribute to increase the diffusion length. Junction interfaces might be acoustically treated to increase the short circuit current and the open circuit voltage. In the fabrication of solar cells the silicon could also be intentionally doped to produce a material with an optimized resistivity (about 1 Ω·cm). The present results show an improvement when compared with those achieved in a previous work [6], especially in the making of large area solar cells.

7. CONCLUSIONS

- The conclusions of this work are the following:
1. The proposed process for producing solar grade polycrystalline silicon, built for such purposes, can be considered promising, since large area solar cells with a efficiency of about 4.0% were so obtained.
 2. The produced silicon, due to its variable characteristics, allowed the research with a number of different process of solar cells fabrication, in order to attain the best performance.
 3. Both processes above referred are subject to further improvements, intended to provide greater efficiencies of the cells.
 4. The cost effectiveness of the process will be evaluated when, after optimization, a larger than the present laboratory stage production will be possible.

ACKNOWLEDGMENTS

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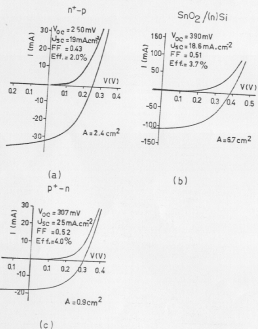


Figure 5. Current vs. Voltage Plots and Photovoltaic Parameters of Different Solar Cells. a) n^+-p , b) $\text{SnO}_2/(\text{n})\text{Si}$, c) p^+-n

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