Abstract: Large area polycrystalline silicon substrates were prepared by the unidirectional solidification of metallurgical silicon on graphite. The silicon was first purified by continuous heating with aqua-regia and then gittered with P2O5 at 1050 °C. Substrates had elongated silicon grains, up to several centimeters long. X-ray diffraction and spreading resistance measurements showed that the substrates were 0.03 Ωm.cm, n-type of (110) orientation. P+ - n junction solar cells were fabricated by chemical vapor deposition from trichlorosilane. The front contact was formed by vacuum deposition of a Ti/Ag layer through a metal mask. A thin film of SnO2 was used as an AR coating. The cell efficiency under AM1 conditions, open circuit voltage, short circuit current, and fill factor were measured to be 9.75 %, 568 mV, 23 mA/cm², and 0.76, respectively, for a 30 cm² cell with AR coating. Heat treatment in hydrogen at 900 °C was found to improve the cell efficiency by 15 - 20 %.
I. INTRODUCTION

Single crystalline silicon is too expensive to use in the commercial production of solar cells for terrestrial applications. Different techniques have been introduced to economically produce a good quality silicon, termed "solar-grade silicon", from metallurgical grade silicon for manufacturing solar cells. These include casting and controlled cooling [1], chlorine treatment of molten silicon [2], solvent refining of silicon [3], edge-defined film-fed (EFG) [4], ribbon-to-ribbon (RTR) [5], dendritic web [6], and silicon-on-ceramic [7] growth techniques. These methods are characterized by being either highly energy intensive, and/or not economical or not suitable for large scale production.

In this paper we report a low cost process for the economic production of large area rectangular polycrystalline silicon solar cells. The process reported is simple, is not energy intensive, and is compatible with large scale production.

II. THE ACID EXTRACTION PROCESS

The starting material is pulverized metallurgical grade (MG) silicon (purity ~ 98%). Heavy metallic impurities in the MG silicon are very harmful to the solar cell operation, considerably degrading the minority carrier lifetime. Typical concentrations of these impurities in the starting silicon are 1500, 650, and 10 ppm atomic, for iron, aluminum, and copper, respectively. The metallic impurities are highly soluble in molten silicon, but have very low solubilities in solid silicon [8]. Therefore, a lot of these impurities accumulate at grain boundaries in the form of silicides and other silicon compounds when silicon is solidified during the preparation of metallurgical grade silicon. Pulverization of metallurgical silicon takes place mostly at grain boundaries, therefore treatment of pulverized MG silicon with acids should be effective in reducing the content of the harmful metallic impurities.

The size of the starting pulverized MG silicon was 0.75 - 2.00 mm and the initial iron content was 0.35% [9]. 1.5 kg of the pulverized silicon was heated continuously under reflux conditions for 3 - 4 days in a 3 l flask with 1.5 liters of acid, then the heating was stopped and the acid replaced with fresh acid after thoroughly cleaning with deionized water. The process was repeated 2 - 3 times, and atomic absorption was used to measure the concentration of iron in silicon as well as in the extracted acid by comparison with standard solutions. The acids used were hydrochloric, aqua regia, and a 1 : 1 mixture (by volume) of sulphuric and nitric acids. Aqua regia was found to be the most effective in reducing the iron content in the silicon. Figure 1 shows the results of this experiment. The final iron content in the silicon was about 300 ppm.
III. GETTERING

Improvement in the electronic quality of semiconductor materials has been reported using various gettering techniques, for single crystalline [10,11] and for polycrystalline [12] silicon.

In order to further purify the acid-treated silicon it was mixed with 5% (by weight) P₂O₅ powder and deionized water was added to form a thick paste which was then heated in a quartz container in air at 1050 °C for 4 days. The resulting charge was dissolved in diluted HF acid to remove the phosphosilicate glass, which acted like a sink for much of the metallic impurities in the silicon. The iron content in the gettered silicon was measured to be 150 ppm [9].

IV. SUBSTRATE PREPARATION

Unidirectional freezing of molten silicon was reported for the production of single crystal ingots from chemically-upgraded metallurgical-grade silicon [13], and more recently directly from metallurgical silicon [14].

To prepare the substrates cleaned acid-treated and gettered silicon was uniformly loaded on a 12 x 6 x 3/4 " cleaned pure graphite plate which functioned as a mechanical support and as the electrical back contact to the solar cell, in addition to its excellent coupling to the 450 kHz rf heating used in the cell preparation. The top surface of the graphite plate was sandblasted to increase its ability to hold the molten silicon by increasing the interfacial tension. The loaded graphite was then placed inside a fused quartz tube at a small tilt angle and rf heated in pure hydrogen until all the silicon melted. The spacing between the turns of the rf coil had been adjusted to result in a 150-180 °C linear temperature gradient along the length of the substrate, as shown in figure 2. The input power was then gradually decreased to initiate solidification from one end of the substrate to the other, while monitoring the solid-liquid interface using an optical pyrometer. The hydrogen flowrate was also increased to initiate solidification at the surface of the silicon rather than at the graphite-silicon interface. Optimum results were obtained when the solid-liquid interface was linear. Because it was difficult to obtain a linear temperature gradient with the large-diameter rf coil a simple apparatus was constructed using flexible rf power feed cables and a simple mechanism to move the coil linearly along the length of the substrate at any desired rate. The spacing between the turns of the coil was adjusted to be uniform all through except for a narrow (2" wide) higher temperature zone. The apparatus is shown in figure 3. This setup has the advantages that the substrate is stationary, therefore reducing the effect of mechanical vibrations on the crystal growth, and that better control over solidification conditions is achieved. Also only a narrow zone was kept molten in the silicon instead of the whole charge, therefore reducing the impurities introduced due to contact between molten silicon and graphite, and also reducing energy consumption. Using high purity helium, which was more economical than hydrogen, over the surface of the substrate the molten zone
was moved from one and of the substrate to the other by moving the coil mechanically at a controlled rate.

The resulting grains were very large with the smaller size grains at the side where solidification started. The resulting substrate was a smooth surface polycrystalline silicon substrate with very large elongated grains up to 12 - 15 cm long and several millimeters wide. Lower solidification rates (0.5 - 1.9 cm/min) resulted in a smooth substrate surface, while higher solidification rates (3 - 5 cm/min) resulted in a non-planar surface. X-ray diffraction showed that most of the grains had a (110) orientation [15].

The main structural defects in the substrate were grain boundaries and twin planes, as was revealed by Siril etch (CrO3 - HF). The substrate resistivity was measured using the four point probe technique and was 0.03 Ohm.cm.

V. EPITAXIAL PN JUNCTION SOLAR CELLS

The active layers of the silicon solar cell were deposited using the hydrogen reduction of trichlorosilane,

\[ \text{SiHCl}_3 + H_2 \rightarrow Si + 3 \text{HCl} \]

The substrate was loaded into a quartz tube and rf heated in hydrogen to 1200 °C. HCl gas was used for the in situ etching of several microns of the surface of the silicon substrate, then the temperature was dropped to 1100 °C and a 30 µm n-type epitaxial layer of silicon was deposited at a rate of about 1 µm/min using PH3 gas for doping, followed by the deposition of a 1 - 2 µm p-layer using diborane (B2H6) gas diluted in hydrogen for doping.

Figure 4 shows a schematic of the chemical vapor deposition system. The structure of the cells was p'-n/n-acid-treated silicon/graphite. A cross section of the solar cell is shown in figure 5.

The front contact to the cell was formed by the vacuum deposition of 1000 Å of titanium followed by 2 µm of silver on the cell surface through a metal mask. The contact was then annealed for 15 - 20 min. at 525 °C. Anti-reflection (AR) coating was applied by the chemical vapor deposition of a thin layer of tin oxide.

Mechanical lapping and chemical etching were used to delineate the junction in order to measure the junction depth. Four point probe measurement showed that the resistivity of the top layer was 0.002 - 0.004 Ohm.cm, and that of the base region was 0.2 - 0.5 Ohm.cm.

The conversion efficiency of the solar cell, under air mass one (AM1) conditions was measured using a quartz-halogen solar simulator, and was as high as 9.75 %, and the fill factor, FF, was as high as 0.78. for a 26 cm² AR - coated cell. The open circuit voltage, \( V_{oc} \), was 568 mV, and the short circuit current density, \( J_{sc} \), was 23 mA/cm². The illuminated I-V characteristics of a typical cell is shown in figure 6. Current - voltage characteristics for the cell was also measured in the dark and is shown in figure 7. The spectral response of the short circuit current of the cell was measured at several wavelengths using a set of interference filters and comparing with the response of a
reference 4 cm^2 calibrated single crystalline silicon solar cell. The spectral response measured is shown in figure 8.

The minority carrier lifetime in the base region of the solar cell was estimated by measuring the minority carrier diffusion length, L_n, using the surface photovoltage (SPV) technique [16]. L_n measured was as high as 30 μm, from which the hole lifetime can be calculated to be about 0.75 μ sec in the base region. The electron beam induced current (EBIC) technique, reported earlier for the measurement of the minority carrier diffusion length [17], was used to determine the hole lifetime in the base region, and the results were in good agreement with the SPV measurements.

VI. HEAT TREATMENT OF THE SOLAR CELLS

Heat treatment at 850 - 950 °C for 12 - 15 hours in hydrogen and in helium was found to further enhance the performance of the solar cells. This is due to the precipitation of metallic impurities at grain boundaries during the heat treatment, grain boundary passivation [18]. Figure 9 shows the effect of heat treatment on the spectral response of the short circuit current of the cell. There seems to be an optimum annealing temperature above which the enhancement in the cell performance is reduced.

VII. CONCLUSION

Very large area polycrystalline silicon / graphite substrates were prepared by the unidirectional solidification or pulverized acid - treated and patterned metallurgical grade silicon. The structural and electrical properties of the substrates were studied. Epitaxial deposition was used to fabricate p - n junction solar cells on these substrates. The characterization of the solar cells shows that the polycrystalline silicon substrates had very good qualities. The fabricated cells have the advantages of being low cost, rectangular, simple to make, not highly energy intensive, of very good mechanical strength and compatible with large scale production. The effect of heat treatment on the cell characteristics was also investigated and was found to further enhance the cell performance.
REFERENCES


Figure 1. Reduction in the concentration of iron in metallurgical silicon due to treatment with acid.
Figure 2. Unidirectional solidification.
Figure 3. Moving coil set-up for unidirectional solidification of large-area substrates.
Figure 4. Chemical vapor deposition reactor.
Figure 5. A cross section of the pn junction polycrystalline silicon solar cell.
Figure 6. Illuminated current-voltage characteristics of the thin film solar cell.
Figure 7. Dark current-voltage characteristics of a polycrystalline silicon solar cell.
Figure 8. Spectral response of the short circuit current of a polycrystalline silicon solar cell compared with a standard single crystalline silicon cell.
Figure 9. Effect of heat treatment in hydrogen on the spectral response of the polycrystalline silicon cells.