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LOW-COST EPITAXIAL TECHNIQUES FOR SOLAR-CELL FABRICATION

Final Report for the Period September 25, 1979—September 24, 1980

By
R. V. D'Aiello
P. H. Robinson

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RCA Laboratories
Princeton, New Jersey

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Solar Energy

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Princeton, New Jersey 08540

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PREFACE

The objective of this work is to extend epitaxial techniques for the growth of silicon films on the lowest cost silicon substrates consistent with the material and device requirements for the fabrication of high-efficiency solar cells. The specific approaches toward this goal are:

- The characterization of several candidate silicon substrate materials to determine impurity level, doping distribution, grain boundary morphology, and defect state;
- Optimization of epitaxial growth parameters in relation to the substrates; and
- Solar-cell and device fabrication and evaluation to provide feedback relating to the epitaxial growth and the substrate quality.

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SUMMARY

This research and development effort was designed to investigate epitaxial growth processes which will allow the use of low-cost forms of silicon for fabricating high-efficiency, cost-effective solar cells. This report covers the results of a 1-year effort which involved characterization of potentially low-cost silicon substrates, epitaxial growth studies, and the fabrication and evaluation of solar cells made in the epitaxial layers.

Three grades of generic metallurgical grade (MG) silicon material designated upgraded metallurgical grade (UMG) silicon were investigated in some detail. These three grades have a wide range of purity, defect structure, and crystallinity, all of which are representative of the characteristics expected in future low-cost silicon. The electrical, physical, and structural properties of this material were measured. An initial epitaxial growth technique was standardized and qualified for application to the growth of diagnostic and solar-cell structures. Such structures were grown on the three UMG grades of substrates, and the properties of these layers were compared to those of the substrates. It was generally found that the defect density in the epitaxial films was lower than in the substrates, but greater aerial variation was observed for the less pure, multicrystalline grades of substrates. Solar cells were fabricated in epitaxial structures grown on all three UMG grades of substrates. With a 15- μm -thick epitaxial structure grown on the purest form of UMG substrate, an average cell AM-1 efficiency of 12.5% was obtained. Similar structures grown on the less pure multicrystalline substrate grades result in efficiencies of 9 to 10.3%. A novel way of slicing these substrates which exposes larger grain areas was implemented and resulted in higher average and peak efficiencies for cells made on such substrates.

Two additional substrate materials which were obtained from other research efforts supported by SERI were briefly explored. On one of these, a silicon ingot solidified by the HEM method applied to MG silicon, epitaxial cells of efficiency as high as 12% were obtained.

The second material was representative of the early stages of a low-cost substrate development program, and peak efficiencies of about 10% were obtained, but material defects resulted in a large variation in cell performance. The limitations experienced with these preliminary materials are pointed out.

The practical aspects of making epitaxial solar cells were explored by growing and fabricating large-area cells. In this work, a significant achievement was the attainment of efficiencies close to 10% with epitaxial cells of 10.8- cm^2 area grown on the lowest grade silicon substrate under study. For larger areas (23.1 cm^2) an efficiency of 7.0% was obtained.

The use of low-cost surface preparation techniques was successfully demonstrated for both epitaxial growth and the resultant solar-cell properties. Some requirements on the surface finish obtainable with chemical etchants which relate to the subsequent application of AR coatings are pointed out.

Variations in the epitaxial growth parameters and in the pre- and post-growth processing were explored in order to indicate the tolerance in the process and the options available for future designs of large-scale epitaxial growth processes. These experiments included surface preparations, slow cooling and gettering, growth with alternate gas sources (silane), and the effect on cell performance of growth temperature and growth rate.

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SECTION 1.0

INTRODUCTION

1.1 BACKGROUND

Previous work [1,2] has demonstrated the feasibility and technical advantages of using chemically vapor deposited (CVD) epitaxy for the growth of silicon solar-cell structures. Silicon solar cells having nearly ideal electrical characteristics and very high open-circuit voltage were fabricated in epitaxial layers grown on high-quality silicon substrates [1]. This technique was also explored for potential application in the low-cost manufacturing of solar cells by the use of epitaxial growth in conjunction with substrates such as edge-defined film-fed growth (EFG) ribbon [3] and several forms of simply purified metallurgical grade silicon [4,5]. This latter work identified the need for a technical qualification and the establishment of supply for a low-cost silicon substrate consistent with high efficiency, good yield, and reproducibility of epitaxial solar-cell fabrication.

1.2 OBJECTIVES AND APPROACH

The major objective of this contract work is to refine and apply epitaxial growth techniques to several candidate low-cost silicon substrates in order to define the growth technique and substrate combination which will allow the fabrication of low-cost and efficient solar cells. The planned approach is:

- Define and characterize several potentially low-cost silicon substrates in terms of physical, chemical, and electronic properties.
- Refine and explore suitable epitaxial growth methods in conformance with the substrate characteristics so that the resultant epitaxial layers can be used in the fabrication of high-efficiency solar cells. The efficiency goal for such cells is 14%, AM-1.
- Fabricate solar cells and diagnostic devices and perform electronic characterizations so that the influence of the epitaxial growth and structure, as well as the substrate, can be evaluated.

1.3 ORGANIZATION OF THIS REPORT

This report is organized in the following manner: SECTION 2 - Physical and Electrical Characteristics and Properties of UMG Silicon Substrates; SECTION 3 - Establishment of Baseline Epitaxial Growth Techniques and Solar-Cell Structures; SECTION 4 - Performance Characteristics and Evaluation of Epitaxial Cells; SECTION 5 - Studies of the Effects of Variations in the Epitaxial Growth Parameters on Cell Performance; and SECTION 6 gives the Conclusions and Recommendations derived from this work.

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SECTION 2.0

CHARACTERISTICS OF UMG SILICON SUBSTRATES

2.1 CLASSIFICATION AND MAJOR IMPURITY CONTENT

The primary substrates* which have been used in this program were formed from upgraded metallurgical grade (UMG) silicon obtained from Hemlock Semiconductor Corporation.** This material was produced by remelting and applying chemical purification techniques to metallurgical grade (MG) silicon as obtained from an arc furnace [6]. Three grades of such material have been studied. These grades differ in the amount of purification or upgrading applied to each, and as a result they differ both in their impurity content and crystallinity. Table 2-1 summarizes the nomenclature associated with each silicon grade, and lists the range of concentration of impurities as obtained from spark source mass spectrographic analysis. Grades 1P and 2P have large-grained multi-crystalline structures as shown by the photograph in Fig. 2-1.

Table 2-1. PROPERTIES OF UMG SILICON

UMG Grade	Crystallinity	Type	Impurities ^a (ppm)						
			<u>Al</u>	<u>B</u>	<u>P</u>	<u>O</u>	<u>C</u>	<u>Cr</u>	<u>Fe</u>
1S	Single Crystal <100> Orientation	p	1-4	36-71	1-5	58-170	3-47	13	<0.03
2P	Large Grain Polycrystalline	p	3-40	48-150	3-11	200-240	10-36	~1	<0.03
1P	Large Grain Polycrystalline	p	0.6-1	46-53	1-4	44-192	4-50	6	<0.03

^aFrom spark-source mass spectroscopy.

Several spark-source analyses were conducted on the UMG substrates. Because of the variation in the precision of this method and because of the suspected spatial inhomogeneity of impurities, these values are valid only in a qualitative sense.

*Two additional substrate materials derived from MG silicon were obtained toward the end of the contract period, the properties of these materials and the performance of epitaxial cells made on them are given in Section 4.4.

**Hemlock Semiconductor Corp., Hemlock, Michigan, a subsidiary of the Dow Corning Corp.

Figure 2-1. PHOTOGRAPH OF THE ETCHED SURFACE OF A 2-in.-DIAMETER WAFER. THE MATERIAL IS UMG 1P

Similar measurements were made on thick (100 μm) epitaxial layers grown on UMG and control substrates. The results show lower levels of most impurities detected; however, the sensitivity of this measurement is only of the order of 1 ppm. The data shown in Fig. 2-2, taken from reference 7, illustrate the concentration dependence of solar-cell performance for various metallic impurities in p-type silicon. It is noted that these impurities adversely affect cell performance at levels well below 1 ppm.

2.2 ELECTRICAL RESISTIVITY

The electrical resistivity of the three substrate grades was measured by two-point spreading resistance. Surface and bulk scans were made on wafers arbitrarily selected from each grade to determine the absolute resistivity and the uniformity across large areas. Typical spreading resistance measurements for the three grades of material are shown in Fig. 2-3, where the average resistivity is seen to be $\sim 0.01 \Omega\text{-cm}$. Variation in resistivity across a 2-in.-diameter wafer was no more than $\pm 15\%$.

2.3 SURFACE AUGER ANALYSIS

For the multicrystalline UMG substrates, data taken by spark source analysis suggest that impurity incorporation might be spatially localized, i.e., in

Figure 2-2. MODEL-DERIVED IMPURITY PERFORMANCE CURVES FOR SINGLE-METAL CONTAMINANTS IN p-TYPE Si. THE CURVES FOR Mo, Ta, W, AND Co ARE CALCULATED FROM RECENT CELL EFFICIENCY AND IMPURITY CONCENTRATION DATA [7]

Figure 2-3. TWO-POINT SPREADING RESISTANCE TRACES MADE ON THE THREE UMG SILICON SUBSTRATES

precipitates and/or at grain boundaries. If this is the case, the density of such impurities, i.e., SiC, Fe, Cr, could be quite high in those regions. We have examined and selected several UMG samples for surface Auger analysis. Specific areas of these samples have been identified and were examined for the presence of SiC and selected heavy metals. Figure 2-4 shows an example of a precipitate on a grade 1P substrate, and Fig. 2-5 shows the intersection of several grain boundaries on grade 2P material. These areas are typical of those selected for analysis.

Figure 2-4. OPTICAL PHOTOGRAPH SHOWING INTERSECTION OF GRAIN BOUNDARIES ON GRADE 2P UMG SILICON

Prior to analysis, the samples were prepared by cleaning to remove organic contaminants and residues from sawing, and then chemically etched ($\text{HF}:\text{HNO}_3:\text{CH}_3\text{OOH}$; 3:3:2) to remove about 50 μm of silicon from the surface.

For the sample of Fig. 2-4, an Auger surface scan revealed the presence of carbon and oxygen at the site of the precipitate. A secondary electron micrograph (SEM) and Auger scanning maps in the region of the precipitate are shown in Figs. 2-6, 2-7, 2-8, with Figs. 2-7 and 2-8 illustrating the oxygen and carbon maps.

The carbon scan in Fig. 2-9 shows excess carbon along the grain boundaries of the sample shown in Fig. 2-5.

Figure 2-5. SEM PHOTOGRAPH SHOWING INTERSECTION OF GRAIN BOUNDARIES ON GRADE 2P UMG SILICON

Figure 2-6. SEM SCAN AT 600X SHOWING PRECIPITATE ON FIG. 2-4

In the vicinity of grain boundaries such as that shown in Fig. 2-5, excess carbon and oxygen in an approximate ratio 1:1 were found. The Auger carbon map is shown in Fig. 2-9. For the above samples and several others, a search was also made for Fe and Cr. These elements were not found; however, the sensitivity of the Auger analysis for heavy metals is about 1/2% so that only large precipitates or clusters of Fe or Cr could possibly be detected.

Figure 2-7. AUGER OXYGEN SCAN OF REGION IN FIG. 2-6

Figure 2-8. AUGER CARBON SCAN OF REGION IN FIG. 2-6

Figure 2-9. AUGER CARBON SCAN OF REGION IN FIG. 2-5

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SECTION 3.0

EPITAXIAL GROWTH TECHNIQUES AND BASELINE SOLAR-CELL STRUCTURES

3.1 EPITAXIAL GROWTH PROCEDURES

The growths were carried out using dichlorosilane in a standard horizontal reactor. The quartz tube had a cross section of 5 x 10 cm and held a silicon carbide-coated graphite susceptor that was 30 cm long. Heating was accomplished by rf induction into the susceptor, which was inclined horizontally, and the walls of the reactor were air-cooled. Hydrogen was obtained from a Pd-Ag diffusion cell. The doping gas was diborane diluted with hydrogen at the 10- to 20-ppm level and further diluted as needed before insertion into the reactant gas stream. Dichlorosilane was metered as a gas directly from the cylinder and temperatures were measured with an optical pyrometer and corrected for emissivity and quartz adsorption effects. Typically, the temperature during growth is 1100°C and the growth rate is 5 $\mu\text{m}/\text{min}$. The epitaxial growth cycle used in our first experiments is listed below.

- (1) Substrates are chem-etched, polished, cleaned, and then spun dry and placed on a susceptor which is inserted into the epitaxial reactor.
- (2) The reactor is flushed with hydrogen, flow rate 30 liter/min, for 10 min. All other lines to be used are flushed to vent line for 5 min and turned off.
- (3) The rf generator is turned on and substrates heated to 1150°C with hydrogen flowing for 5 min.
- (4) Substrates are etched in 1% HCl for 5 min at 1150°C; this removes about 5 μm of material.
- (5) HCl is turned off, and the system is flushed with hydrogen for 5 min.
- (6) Temperature of substrates is reduced to growth temperature of 1100°C.
- (7) Flow rates of gases (SiH_2Cl_2 , AsH_3 , or B_2H_6) to give desired growth rate, doping level, and conductivity type are metered to vent line.
- (8) An automatic timer is set to give predetermined thickness, and growth is started.
- (9) Growth is stopped automatically, and the reactor is flushed with hydrogen for 3 min.
- (10) The rf power is turned off, and the system cools with hydrogen flowing.

This procedure was used successfully in the past to grow solar-cell structures on several different types of silicon substrates. For this reason it was selected as a starting point for the present investigations. The resultant layers and the devices fabricated in them were analyzed as described below, and changes in the above growth procedures, where necessary, were made as dictated by deficiencies which could be related to the epitaxial growth.

3.2 PROPERTIES OF EPITAXIAL LAYERS GROWN ON UMG SUBSTRATES

For purposes of diagnostic measurements described below, 100- μm -thick undoped layers were grown on the three UMG grades of substrates. The objective in growing such layers is to make comparisons of the impurity content and defect structure in the grown layers with that of the starting substrates.

Studies of the defect structure by means of x-ray topography have revealed interesting differences between the grown layers and the substrates. From these studies the following observations were made:

- The crystal perfection of the epitaxial layer on average is significantly better than the starting substrate material. This is seen in the section topograph presented in Fig. 3-1, for the case of 1S material. For the grade 1P and 2P material, there are some grains where no significant improvement in crystal quality was observed, as shown in Fig. 3-2.

EPI
LAYER

Figure 3-1. SECTION OF X-RAY TOPOGRAPH OF A 100- μm -THICK EPITAXIAL FILM GROWN ON GRADE 1S SUBSTRATE

- A network of misfit dislocations near the epitaxial-substrate interface is observed using the single-crystal and polycrystalline UMG substrates. This is shown in Figs. 3-3 and 3-4.
- Grain boundaries present in the substrate material propagate into the epitaxial layer as depicted in Fig. 3-5.

EPI
LAYER

Figure 3-2. SECTION OF X-RAY TOPOGRAPH, GRADE 1P SUBSTRATE

3.3 SOLAR-CELL FABRICATION PROCESS

In this section, the details of the solar-cell fabrication starting from as-grown epitaxial wafers are described.

General Procedures

The general procedures for fabrication of the solar cells and test structures are:

- (1) Grow epitaxial layers.
- (2) Characterize grown layers by spreading resistance.
- (3) Clean wafers - $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$; $\text{H}_2\text{O}_2:\text{NH}_3\text{OH}$; $\text{H}_2\text{O}_2:\text{HCl}$ boiling solutions. For epitaxial structures without a junction layer: POCl_3 diffusion at 875°C for 30 min followed by a slow pull (10 min). Wafers are then stripped of oxide and a four-point sheet resistance measurement is made. Sheet resistance values average $\sim 75 \Omega/\square$ with a junction depth of $\sim 0.3 \mu\text{m}$.
- (4) Metallize by evaporation of Ti/Ag ($0.2 \mu\text{m}/5 \mu\text{m}$) - front and back.
- (5) Spin-on AR coating - bake and sinter.
- (6) Screen-on wax to define cell and test structure areas.
- (7) Etch silicon to form mesa structures delineating cell area.
- (8) Remove wax, rinse, and bake.

These processing steps are described in more detail below.

Figure 3-3. PROJECTION X-RAY TOPOGRAPH OF A 100- μ m EPITAXIAL FILM GROWN ON GRADE 1S SUBSTRATE. CROSS-HATCHED LINES ARE THE STRAIN FIELDS ASSOCIATED WITH MISFIT DISLOCATIONS AT THE FILM-SUBSTRATE INTERFACE

Junction Formation

The n+p junction can be formed into the epitaxial layer at the time of growth or in a later step by ion implantation or gaseous diffusion. In previous work [8], we investigated the epitaxial growth of the junction layer in sequence after the growth of the p-layer. The solar-cell performance achieved with such structures was slightly below that attainable with diffused junctions formed into similar epitaxial p-layers. The small difference in performance was not the main reason for the selection of gaseous (POCl_3) diffusion for this program. The growth and control of the required thin ($\sim 0.3 \mu\text{m}$) n+ junction layer is incompatible with the loose thickness and concentration-profile tolerances found for the p-layer. Thus, adding the requirement of growing the n+ junction layer would remove a major potential simplification of the epitaxial growth system. In addition, when conducted in the same chamber, the possibility of cross-contamination between the n+ and subsequent p-layer growth exists. Furthermore, the projected cost of junction formation by ion implantation or gaseous diffusion appears to be quite low.

Mask Design

The contact mask used to delineate the metallization pattern for all cells reported here is shown in Fig. 3-6. The large cell is 2.1 x 2.1 cm, having 11

Figure 3-4. PROJECTION X-RAY TOPOGRAPH OF A 100- μm -THICK EPITAXIAL FILM GROWN ON GRADE 1P SUBSTRATE

current collecting fingers and a single bus-bar with a total 7% metal area coverage. The two small cells and ten diodes are for diagnostic purposes such as the measurement of lifetime and area dependence of electrical characteristics. The parallel bar structures A and A' are included for measurement of surface-layer sheet resistance and metal-to-silicon contact resistivity, and the line structure B is for the measurement of metal sheet resistance.

Metallization

Metallization was done by E-gun evaporation of 0.2 μm of titanium followed by 5 μm of silver. These metals are evaporated over the entire front and back of

Figure 3-5. SECTION X-RAY TOPOGRAPH OF A 100- μ m-THICK EPITAXIAL FILM GROWN ON GRADE 1P SUBSTRATE. FILM GROWTH IS SEEN (ARROW) TO FOLLOW GRAIN BOUNDARY

3.4 BASELINE SOLAR-CELL STRUCTURES

In order to establish a baseline for the epitaxial film quality and solar-cell performance, the structures shown in Fig. 3-7 were grown on high-quality Czochralski (CZ) single-crystal p⁺ substrates. Solar cells were fabricated on each structure as described. The thicker structures (III, IV, and V) were included to assess the effect of diffusion length on cell performance. The measured AM-1 cell characteristics for cells made in each structure are summarized in Table 3-1.

Figure 3-7. BASELINE EPITAXIAL STRUCTURE DESIGNS

Table 3-1. SUMMARY OF AM-1 PARAMETERS FOR FABRICATED BASELINE EPITAXIAL SOLAR CELLS

Structure	W_{epi} (μm)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	η (%)
I	15	27.0	602	0.801	13.0
II	20	26.8	590	0.790	12.5
III	50	26.2	570	0.785	11.7
IV	75	25.4	550	0.791	11.1
V	100	25.8	560	0.785	11.0

The results show first that a 15- μm -thick epitaxial layer is sufficient to obtain an AM-1 efficiency of 13% with excellent cell characteristics. Second, these data show that with the current epitaxial growth techniques, the performance of solar cells of thickness greater than 20 μm is diffusion-length-limited. This is indicated by the saturation in short-circuit current and the decrease in open-circuit voltage for the thicker structures. Analysis of

spectral response data for these samples yielded an estimate of 30 μm for the diffusion length in the epitaxial layer. Although thin epitaxial structures are desirable for economy in the epitaxial growth, and the above results show that with the thinnest structures solar-cell efficiencies of approximately 13% are obtainable, an increase in diffusion length will raise the level of efficiency for all structures.

Two additional epitaxial solar-cell structures were investigated to determine if differences in the grown doping profile affect the solar-cell performance. A straight-line approximation of the grown profiles extracted from spreading resistance data for two structures are shown in Fig. 3-8 along with baseline structure II. The major differences between the test and baseline structure are the lower average doping level and the rapid drop in doping concentration in the first 3 μm of the grown layer. Three cells of each test structure were fabricated and the results of their measured solar-cell performance in comparison with typical results for structure II are given in Table 3-2.

Figure 3-8. APPROXIMATE CONCENTRATION PROFILES OF TWO EPITAXIAL TEST STRUCTURES AND BASELINE STRUCTURE II

The cell performances of structures A and B are remarkably similar to each other and to that of structure II. Although no improvement in cell efficiency was obtained with these structures, these results show how insensitive the cell performance characteristics are to large changes in the epitaxial doping profile. Since these structures are more difficult to reproduce and offer no performance advantage, the baseline structure was retained for experiments with MG substrates.

Table 3-2. MEASURED SOLAR-CELL PARAMETERS FOR EPITAXIAL STRUCTURES A AND B

Structure	Data	I_{sc} (mA)	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF -	η (%)
A	Ave	115.8	26.0	588	0.807	12.3
A	Max	117	26.3	595	0.810	12.6
B	Ave	116.7	26.2	586	0.800	12.2
B	Max	119	26.7	590	0.801	12.6
II	Ave	119	26.8	590	0.790	12.5
II	Max	117	26.3	598	0.800	12.6

SECTION 4.0

SOLAR-CELL PERFORMANCE FOR EPITAXIAL CELLS ON MG SUBSTRATES

The performance of solar cells reported in this section is for structures and cells fabricated using the baseline processes described in Section 3. Experiments conducted to improve material properties or cell performance by modifying the epitaxial techniques or by addition or changes in cell processing are described in Section 5.

4.1 EPITAXIAL CELLS ON UMG SUBSTRATES

Solar cells fabricated in baseline epitaxial structures I and III were used to evaluate the epitaxial layers and substrates for each of the three grades of UMG material. For comparative purposes, solar cells were also fabricated directly into each of these substrates by forming the junction by diffusion.

A summary of the measured AM-1 solar-cell parameters accumulated during this study is given in Table 4-1. For each structure, the data on the first line give the parameters for the cell having the highest measured efficiency and the second line lists the average value for at least four cells.

The salient features shown by these data are:

- Aside from the slightly ($\sim 4\%$) reduced short-circuit current density, the performance of the epitaxial cells made on the grade 1S substrates is comparable to that of the control samples made on high-quality CZ silicon.
- An efficiency of 10.3% was achieved with one of the multicrystalline substrate grades.
- There is a relatively large variation from sample to sample in the open-circuit voltage and fill-factor for the multicrystalline cases.
- Solar cells made on the epitaxial layers have significantly higher efficiencies than those made directly in the substrate material.

It is interesting to note that there is little difference in the efficiencies obtained with the epitaxial cells on grades 1P and 2P substrates even though the 2P material is less pure than 1P. In fact, among the multicrystalline samples, the highest efficiency (10.3%) was obtained with a 15- μm -thick epitaxial cell made on a grade 2P substrate. In contrast, for the cells made by diffusion directly into the UMG substrates the order of efficiencies and cell performance parameters is as might be expected on the basis of impurity levels and crystallinity.

Both the multicrystalline structure and the impurities play a role in affecting the performance of the epitaxial cells. Some indication of these effects was obtained by measuring the spectral response of several representative cells with both a large and small light spot. These data (Fig. 4-1) show the expected lower average quantum efficiency for the epitaxial cells on grade 2P material

Table 4-1. SUMMARY OF THE CHARACTERISTICS OF SOLAR CELLS MADE IN UMG SUBSTRATES

Substrate	W_{epi} (μm)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF -	$\eta^{\text{a,b,c}}$ (%)	Data
P+ Control CZ	15	28.2	605	0.810	13.2	Max
P+ Control CZ	15	27.0	575	0.778	12.3	Ave
P+ Control CZ	50	28.5	593	0.806	13.1	Max
P+ Control CZ	50	27.6	570	0.785	12.3	Ave
UMG Grade 1S	15	26.5	604	0.792	12.6	Max
UMG Grade 1S	15	25.9	600	0.790	12.4	Ave
UMG Grade 1S	50	27.1	592	0.800	12.9	Max
UMG Grade 1S	50	26.7	581	0.791	12.3	Ave
UMG Grade 1P	15	24.7	550	0.713	9.7	Max
UMG Grade 1P	15	23.6	550	0.720	9.5	Ave
UMG Grade 1P	50	23.8	533	0.731	9.3	Max
UMG Grade 1P	50	22.3	526	0.743	8.7	Ave
UMG Grade 2P	15	24.8	570	0.734	10.3	Max
UMG Grade 2P	15	23.1	545	0.767	9.3	Ave
UMG Grade 2P	50	26.0	540	0.655	9.2	Max
UMG Grade 2P	50	24.0	530	0.712	9.0	Ave
UMG Grade 1S	0	15.0	550	0.740	6.1	
UMG Grade 1P	0	15.3	480	0.584	4.3	
UMG Grade 2P	0	12.9	430	0.476	2.6	

^a Measured using ELH lamp at $100 \text{ mW}/\text{cm}^2$

^b AR coating TiO_2 from spin-on liquid source

^c Cell area = 4.45 cm^2

Figure 4-1. SPECTRAL RESPONSE CURVES FOR EPITAXIAL AND BULK CELLS FABRICATED ON UMG SUBSTRATE

when compared to that on grade 1S substrates. In addition, the data taken in the 2P cell with the light spot focused inside one of the better responding grains show a lower quantum efficiency than the 1S cell even at wavelengths greater than $0.8 \mu\text{m}$, indicating that a somewhat lower diffusion length is obtained in the epi layer grown on the 2P material. That the diffusion length achieved in the epi layers is greatly improved over that of the substrate can be seen by comparing the spectral response of the bulk n^+/p cell also shown in Fig. 4-1 with that of the epitaxial samples. For this cell, the base diffusion length was estimated from the long wavelength spectral response and found to be only about $3 \mu\text{m}$, while the epi layer on the 1S material has an L of $50 \mu\text{m}$.

From the above experiments and analyses, it is difficult to separate the effects of defects and impurities on cell performance from those due to the presence of grain boundaries. However, it is clear from the spectral response data and from the comparative performance of the solar cells on the controls and the different grades of UMG material that adequate diffusion length is obtained in the epitaxial layers, and that grain-boundary effects play an important role in reducing cell performance.

The effects of the grain boundaries on cell performance were further investigated with the aid of atomic hydrogen passivation experiments. The details and results of these experiments are given in the appendix to this report. In the next section, a method is described for obtaining improved performance for the case of epitaxial cells on multicrystalline substrates.

4.2 A METHOD FOR OBTAINING IMPROVED PERFORMANCE FOR MULTICRYSTALLINE SUBSTRATES

When silicon of multicrystalline structure is used in the fabrication of solar cells, two attributes of the grains considered to be important for achieving high cell efficiency are large grain size and columnar structure [9].

Since grades 1P and 2P have a multigrained structure, the size, distribution, and geometry of the grains can be important both in the epitaxial growth and in the final solar-cell performance. We have observed that the size and geometry of the grains in wafers cut from this material are considerably different depending upon the direction of the cut relative to the direction of solidification of the ingot. Photographs of typical sections of the grade 1P material cut both longitudinally ($\parallel$) and ($\perp$) to the direction of solidification are shown in Figs. 4-2 and 4-3. For the perpendicular cut, the grain sizes vary from about 1 mm to 5 or 6 mm in maximum length. In contrast, the longitudinal cut exposes grains of greater length (several cm) because of the columnar nature of the grain formation in the direction of solidification of the ingot. This can be utilized to advantage in the case of epitaxial cells since the growth of the active film will replicate the surface grain geometry resulting in columnar grains which are then transverse to the original direction, but of considerably larger area.

We have explored this condition by the growth and fabrication of solar cells on both transverse and longitudinally cut sections of grade 2P material. The pattern of solar cells used in these experiments and the typical geometry of the grains which resulted from parallel and perpendicular cuts are shown in Figs. 4-4, 4-5, and 4-6. Four samples of 15- μ m-thick epitaxial structures were prepared and fabricated into solar cells for each of the two directional cuts. The range and typical values of the solar-cell parameters obtained for the large- and small-area cells are given in Table 4-2. The average efficiency for all cells in each category listed under comments shows that an almost one percent increase (10.5% vs 9.6%) is obtained when the 2P ($\parallel$) substrates are used. Individual values of the cell parameters can vary greatly among the cells on the same substrate. The data in Table 4-3 for the individual samples shown in Figs. 4-4 through 4-6 form an interesting comparison, especially for the small-area (0.40 cm²) cells, since their linear dimensions are of the order of the maximum grain size, so that some of these cells are located in areas containing only one or two grain boundaries. One such case (Fig. 4-4) is sample C2, on which cell C2-R contains one grain boundary, and has the highest set of solar-cell parameters of the group, contrasting with C2-L which is the lowest in the group.

4.3 LARGE-AREA SOLAR CELLS

Having achieved efficiencies of over 10% in 4.45-cm² area cells, solar cells of nominal areas of 10 and 25 cm² were then fabricated to explore the range of efficiencies obtainable in practical-size solar cells. This will also provide a preliminary indication of any limitations imposed by the substrate material parameters or the epitaxial growth process when large areas are used.

For this purpose, a portion of a grade 2P UMG ingot was cut in the $\parallel$ direction and sliced to form rectangular wafers 1 x 2 in. and 2 x 2 inches in cross section. Similar wafers were prepared from grade 1S material in order to

Figure 4-2. UMG SUBSTRATE SLICED PERPENDICULAR TO THE DIRECTION OF SOLIDIFICATION

Figure 4-3. UMG SUBSTRATE SLICED PARALLEL TO THE DIRECTION OF SOLIDIFICATION

Figure 4-4. EPITAXIAL SOLAR CELL FABRICATED ON $\perp$ CUT GRADE 2P. (SAMPLE A-1)

Figure 4-5. EPITAXIAL SOLAR CELL FABRICATED ON || CUT GRADE 2P. (SAMPLE C-2)

Figure 4-6. EPITAXIAL SOLAR CELL FABRICATED ON || CUT GRADE
2 P. (SAMPLE C-1)

Table 4-2. SUMMARY OF SOLAR-CELL DATA FOR 15- μ m-THICK EPITAXIAL STRUCTURES ON 2P ($\perp$)^a AND 2P ($\parallel$)^b SUBSTRATES

Substrate	Cell Area	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF -	η (%)	Comment
Dow Grade 2P ($\perp$)						
MAX	4.45	24.8	570	0.734	10.3	
TYP	4.45	23.1	545	0.729	9.2	
MAX	0.40	23.2	570	0.730	9.6	
TYP	0.40	23.1	545	0.729	9.2	
< >		23.55	557	0.731	9.6	Ave η = 9.6%
Dow Grade 2P ($\parallel$)						
MAX	4.45	24.4	578	0.750	10.6	
TYP	4.45	23.7	552	0.760	9.9	
MAX	0.40	25.5	565	0.791	11.4	
TYP	0.40	23.5	570	0.745	9.9	
		24.28	567	0.761	10.5	
		+3.1%	+1.8%	+4.1%		

a $\perp$ = Ingot cut transverse

b $\parallel$ = Ingot cut longitudinally

Table 4-3. COMPARISON OF SOLAR-CELL PARAMETERS FOR SPECIFIC SAMPLES ON 2P (||) and (⊥) SUBSTRATES

Sample	Cell Area (cm ²)	J _{sc} (mA/cm ²)	V _{oc} (mV)	FF -	η (%)
<u>2P (⊥)</u>					
A1 - L	0.40	21.5	555	0.771	9.2
A1 - R	0.40	22.0	540	0.749	8.9
A1	4.45	23.5	550	0.740	9.5
<u>2P ()</u>					
C2 - L	0.40	21.7	534	0.703	8.2
C2 - R	0.41	25.5	565	0.791	11.4
C2	4.45	24.0	555	0.755	10.0
C1 - L	0.40	23.2	568	0.782	10.3
C1 - R	0.40	22.7	542	0.740	9.1
C1	4.45	23.4	540	0.720	9.1

compare the multicrystalline to the single-crystal case. The wafers were chemically etched to remove 50 μm from each side and cleaned. Using our standard growth procedure, we then grew 20-μm-thick epitaxial layers on these substrates and on control p+ Czochralski (CZ) wafers.

To check the areal uniformity of growth, one of the 2 x 2-in. samples grown on a grade 2P substrate was sectioned and spreading resistance traces were made at four places. These traces were compared to each other and to similar data taken on a control wafer grown in the same run. The results are shown graphically in Fig. 4-7. It can be seen that there is very little variation in the epitaxially grown resistivity profile within the 2 x 2-in. wafer and between the sample wafer and the control. For example, traces 2 and 4 were taken in locations over 2 inches apart, are in different grains, and yet show almost identical profiles.

Six cells were fabricated on the 1 x 2-in. size substrates and three on the 2 x 2-in. size for each substrate grade. Evaporated Ti/Ag metallization and spray-on AR coatings were used to complete the cells. The final cell areas are less than the wafer dimensions because the device areas are delineated by a mesa etch to clean the junction at the edges. The actual cell areas were measured and are given below along with the characteristics of the cell performances.

A summary of the measured AM-1 solar-cell characteristics for the large-area cells made on both grade 2P and 1S substrates is given in Table 4-4. For comparison, the average and peak values of 4.45-cm² cells, which had been the standard cell size for our work to date, are also listed. Average values for the 23.1-cm² area cells are not shown since only three samples were made with each substrate in this size.

Figure 4-7. COMPOSITE OF SPREADING RESISTANCE DATA ON LARGE-AREA EPITAXIAL SOLAR CELL

Table 4-4. SUMMARY OF SOLAR-CELL PERFORMANCE FOR LARGE-AREA EPITAXIAL CELLS ON UMG SUBSTRATES

Substrate	Cell Area (cm ²)	J _{sc} ave (mA/cm ²)	V _{oc} ave (mA)	F F ave —	η ave (%)	BEST CELL				WORST CELL			
						J _{sc}	V _{oc}	F F	η	J _{sc}	V _{oc}	F F	η
UMG 2P (II)	10.8	24.0	560	0.671	9.01	24.3	580	0.697	9.83	23.0	535	0.652	8.02
UMG 2P (II)	4.45	24.2	567	0.761	10.43	24.4	578	0.750	10.58				
UMG 2P (II)	23.1					20.8	540	0.623	7.0	20.7	530	0.620	6.80
UMG 1S	10.8	24.2	595	0.746	10.73	24.7	600	0.766	11.3	22.6	588	0.73	9.70
UMG 1S	4.45	26.0	592	0.789	12.14	26.5	600	0.792	12.6				
UMG 1S	23.1					22.4	580	0.730	9.6	22.9	570	0.600	7.83
SINGLE-CRYSTAL (CZ)	4.45	26.4	598	0.790	12.47	26.8	600	0.796	12.8	25.5	585	0.781	11.65

The performance obtained for the large-area solar cells is very encouraging for the usefulness of epitaxial technology for the fabrication of practical devices. The highest efficiency achieved on the grade 2P substrates was 9.83% with a 10.84-cm² cell. The illuminated electrical characteristics for the cell are shown in Fig. 4-8, and a photograph of the cell is shown in Fig 4-9. As expected from our previous experience, the efficiencies for epitaxial cells made on grade 1S single-crystal UMG substrates were higher, with the highest value for a 10.8-cm² area cell at 11.3%.

Some difficulties were experienced with the largest area (23.1 cm²) cells. The evaporated metallization, 0.2- μ m Ti/5- μ m Ag, was too resistive for the length of the bus-bars causing excessive series resistance. This is the major cause of the low values of fill factor. Also, because of the square geometry and the somewhat rough texture of the etched surfaces, our normal method of applying a spin-on liquid TiO₂ base AR coating was abandoned in favor of a spray-on process. This method [10] has proven to be very satisfactory for single-crystal silicon cells with smooth etched surfaces. However, for the cells made on grade 2P (II) substrates, the etch (HF:HNO₃:CH₃COOH;1:2:2) left the surfaces of some of the grains with a textured-like finish which caused these grains to be only partially covered by the spray process. As a result, short-circuit current densities of the coated cells were lower than normally achieved.

In this regard, it should be noted that the uncoated short-circuit currents were measured, and their average values for 4.45-, 10.8-, and 23.1-cm² cells on the grade 2P substrates were 17.6, 17.5, and 17.1 mA/cm². Similarly, for the cells on the 1S material, these values are 18.1, 18.0, and 18.0 mA/cm². The slight area dependence of the short-circuit current density for the 2P material may be explainable on the basis of the grain-size and defect density characteristics of this material. The magnitude of these short-circuit current densities should be compared with the typical value of 18.7 mA/cm² which is routinely obtained with the control cells having the same epi layers grown on single-crystal CZ silicon substrates. The average values obtained for the cells made on the grade 2P substrates are between 6 and 9% below that of the controls.

4.4 ADDITIONAL SUBSTRATES

Toward the end of the contract period, two additional substrate materials were supplied for evaluation. These materials were obtained through SERI from two subcontracts* devoted to exploring means of producing low-cost silicon substrates.

*Crystal Systems Inc., "Low-Cost Silicon Substrates by Directional Solidification," Subcontract No. XS-0-9171-1 and Motorola, Inc, "Sequential Purification and Crystal Growth for the Production of Low-Cost Silicon Substrates," Subcontract No. XS-9-8119-3.

Figure 4-8. ILLUMINATED I-V CHARACTERISTICS FOR 10.8-cm² EPITAXIAL SOLAR CELL ON GRADE 2P (11) UMG SILICON

Figure 4-9. OPTICAL PHOTOGRAPH OF 10.8-cm² CELL

4.4.1 Crystal Systems Inc. (CSI) Substrates

Seven wafer samples of Heat Exchange Method (HEM) [11] directionally solidified silicon derived from metallurgical grade silicon were evaluated. These samples (3 cm x 3 cm in cross section) were selected from a central section of ingots from two experimental solidifications conducted at Crystal Systems. A two-digit code scribed on the wafer identified the ingot run and the location of the slice relative to the top (last to freeze) or bottom of the ingot. For example, 25 refers to a slice taken near the top of the ingot from run 5, while sample 73 would be a slice taken near the bottom of ingot-run 3. A photographic example of this designation and a description of the experimental conditions used in the HEM process can be found in reference 12.

It should be stressed that the samples evaluated here (ingot runs 3 and 5) are from early runs conducted under experimental conditions designed to explore for optimum conditions to solidify MG silicon.

The slices were chemically etched in a HNO₃-HF (6:1) mixture to remove 2 mils from each side. After etching, it was noted that sample 23 was polycrystalline and contained many (~100) large inclusions and etch pits, while sample 25, in contrast, had a smooth surface, no visible inclusions, and was essentially a

single crystal. Photomicrographs of sections of these samples taken after cell processing are shown in Figs. 4-10 and 4-11.

Figure 4-10. PHOTOMICROGRAPH OF SAMPLE 23

Figure 4-11. PHOTOMICROGRAPH OF SAMPLE 25

Epitaxial solar-cell structures 20 μm thick were grown on the CSI samples and on single-crystal CZ control wafers. Because of the small size of the wafers, two solar cells of dimensions 1.1 cm x 2.0 cm were fabricated on each sample. Results of the measurement of the AM-1 parameters are given in Table 4-5. The cell performances correlate quite well with physical appearance and the presence or absence of inclusions in the samples. For example, in each case where a severe shunt was noted (samples 23 and 73), large inclusions were found within the cell area (see Fig. 4-10). Although the physical/chemical composition of these inclusions was not determined during this work, from discussions with personnel at CSI it appears that they are either unreacted carbon or, more likely, SiC.

4.4.2 Motorola Substrates

These substrates were obtained through SERI from an ingot representing the preliminary results of a low-cost substrate development contract at Motorola. This material was received in as-sawed wafer form, 3 inches in diameter. The wafers were prepared by chemical etch-removal of 2 mils from each side. It should be noted that after etching, this material had in general a high density of etch pits and many inclusions of undetermined composition. These conditions were most severe on wafers identified as coming from the tang end of the ingot where the grain size was also noted to be smaller than in wafers from the seed end.

In separate runs, thin (15 μm) and thick (30 μm) epitaxial structures were grown on 3 each of wafers from the seed and tang ends as shown below.

SEED		TANG	
Thin Epi	Thick Epi	Thin Epi	Thick Epi
S-1	S-2	T-1	T-2
S-8	S-9	T-8	T-5
S-15	S-14	T-11	T-10

After epitaxial growth, the surface appearance was not significantly improved and the solar-cell performance generally correlated with surface defects as noted in the comments given along with the solar-cell data in Table 4-6.

Table 4-5. SUMMARY OF SOLAR-CELL CHARACTERISTICS FOR CELLS ON CSI SUBSTRATES

<u>Sample No.</u>		<u>I_{sc}</u> (mA)	<u>J_{sc}</u> (mA/cm ²)	<u>V_{oc}</u> (mV)	<u>FF</u>	<u>η^a</u> (%)	<u>Comment</u>
R-4		58	26.3	596	0.800	12.6	Control, typical for group
23	1	51.5	23.4	550	0.675	8.7	85-Ω shunt
23	2	51.1	23.2	435	0.349	3.5	Severe shunt ~15 Ω
33	1	54.0	24.6	575	0.773	10.9	
33	2	54.3	24.7	576	0.775	11.0	
33-A	1	54.9	25.0	565	9.774	10.9	
33-A	2	52.5	23.9	552	0.682	9.0	85-Ω shunt
73	1	52.0	23.6	558	0.729	9.6	300-Ω shunt
73	2	53.5	24.3	205	0.250	1.2	4-Ω severe shunt
73A	1	53.1	24.1	570	0.763	10.5	
73A	2	54.6	24.8	580	0.760	10.9	230-Ω shunt
25	1	55.9	25.4	590	0.798	12.0	
25	2	55.6	25.3	590	0.801	11.9	
35	1	56.1	25.5	582	0.801	11.9	
35	2	54.1	24.6	581	0.792	11.3	

^aAR coated.

Table 4-6. SUMMARY OF SOLAR-CELL CHARACTERISTICS FOR CELLS ON MOTOROLA SUBSTRATES *

<u>Sample No.</u>	<u>Epi Thickness (μm)</u>	<u>I_{sc} (mA)</u>	<u>J_{sc} * (mA/cm²)</u>	<u>V_{oc} (mV)</u>	<u>FF</u>	<u>η* (%)</u>	<u>Comment</u>
S Control	18	112	25.2	591	0.789	11.8	
S-1	18	104	23.4	570	0.755	10.1	Smooth surface, some inclusions
S-8	18	88.2	19.8	300	0.370	2.2	Shunted & rounded IV, pitted surface
S-15	18	103.5	23.2	573	0.763	10.1	
Control	36	117.6	26.4	593	0.801	12.6	
S-2	36	109.9	24.7	564	0.731	10.2	
S-9	36	—	—	—	—	—	Broken
S-14	36	109.2	24.5	570	0.745	10.4	
Control	18	112	25.2	600	0.796	12.0	
T-1	18	98	22.0	528	0.646	7.5	75 Ω shunt
T-8	18	—	—	—	—	—	Broken
T-11	18	97	21.8	490	0.507	5.4	18 Ω shunt, high density of etch pits & inclusions
Control	36	118.3	26.6	597	0.802	12.7	
T-2	36	93.8	21.1	524	0.718	7.9	pitted surface & inclusions
T-5	36	92.4	20.8	518	0.658	7.1	pitted surface & inclusions
T-10	36	84.7	19.1	510	0.703	6.8	pitted surface & inclusions

Cell area = 4.45 cm²

*Measured values were without AR coating; values listed with an asterisk were calculated using $\eta = 1.4\eta_{\text{no AR}}$.

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SECTION 5.0

INVESTIGATION OF THE EFFECT OF EPITAXIAL GROWTH PARAMETERS ON SOLAR-CELL PERFORMANCE

5.1 CHEMICAL ETCHING AND IN-SITU HCl GAS ETCHING

The industry standard method for preparing substrate wafers from silicon ingots involves sawing, etching, lapping, and polishing. The lapping and polishing operations are expensive, and it would be desirable to eliminate them from any low-cost solar-cell production process. The primary purpose of these operations is to provide a reproducible, flat, damage-free smooth surface for epitaxial growth with the flat, smooth finish also being a requirement for subsequent photolithography. In addition, it is customary in epitaxial processing to etch the wafers in-situ with HCl gas at high temperatures just prior to growth. For applying the epitaxial process to solar-cell fabrication, the primary requirement is for a damage-free surface with the need for flatness being secondary; in addition, the degree of HCl etching, if any, is not known. It is envisioned that the source of silicon substrates will be either wafers sawed from ingots or prepared by a sheet-growth technique. For saw-cut wafers the physical damage introduced by the sawing must be removed, and present sheet materials usually also require the removal of surface films and may also require removal of silicon from the surface.

To explore the feasibility of eliminating lapped and polished surfaces, we have conducted several experiments in which chemical etching was used to remove saw damage and prepare the surface for epitaxial growth. In addition, we have compared the results of eliminating in-situ HCl etching from the epitaxial cycle. We used several mixtures of hydrofluoric (HF), nitric (HNO_3), and acetic (CH_3COOH) acid, held at 0°C during the etching. One such mixture ($\text{HF}:\text{HNO}_3:\text{CH}_3\text{COOH};1:2:2$) provided a rapid etching (1/2 to 1 mil/min) but resulted in a partially textured, nonsmooth surface.

Standard 20- μm -thick epitaxial solar-cell structures were grown and cells made on single-crystal control and UMG substrates in accordance with the test matrix shown in Table 5-1. For the cases in which HCl etching was eliminated, the wafers were maintained in hydrogen at the growth temperature for an extra 5 min prior to growth.

The results of these experiments along with comments concerning the individual samples are given in Table 5-2. The major implications of these data to epitaxial solar-cell processing are:

- The combination of chemical etching and in-situ HCl etching is adequate to provide a good surface for the growth of the solar cells. This is arrived at from the good and consistent values of V_{oc} and FF among the various samples in this group. The problem relating to the AR coating is discussed below.
- Removal of the HCl etching step from the epitaxial cycle results in erratic performance for the UMG substrates, but has no effect on the polished controls.

Table 5-1. TEST MATRIX OF SURFACE PREPARATIONS

<u>Substrate</u>	<u>Chem Etch</u>	<u>HCl Etch</u>	<u>Polished</u>
Control (CZ)		✓	✓
Control (CZ)			✓
UMG 1S	✓	✓	
UMG 1S	✓		
UMG 1P	✓	✓	
UMG 1P	✓		
UMG 2P	✓	✓	
UMG 2P	✓		
UMG 2P (II)	✓	✓	
UMG 2P (II)	✓		

- The microscopic roughness introduced by the chemical etching technique used here prevented the uniform application of an AR coating by our standard spin-on technique. The use of alternate etchants such as sodium hydroxide or slower acid etches, and/or application of the AR coating by spray-on methods should provide a solution to this problem. Also, these methods are preferred from a cost standpoint.

5.2 SLOW COOLING AND GETTERING.

Two techniques were applied to the epitaxial process in an attempt to improve the electronic properties of the grown layer. Slow cooling from the growth temperature is a method often used to maintain or improve diffusion length in high-temperature processing of silicon minority-carrier devices. Gettering with a high concentration phosphorus source on the back of the wafers is also often employed to reduce the concentration of unwanted impurities in the active region of silicon devices.

Slow-cooling capability was added to our epitaxial reactor system by providing a voltage ramp on the power supply output to the rf generator. This allows the wafers to be cooled at a rate of 3°C/min from the growth temperature (1100°C) down to 800°C.

In separate experiments, a heavily doped n⁺ layer was incorporated on the back of the substrate wafers prior to epitaxial growth. The substrate preparation consisted of a POCl₃ deposition on the backside of a standard p⁺ epitaxial wafer. A 10-μm polycrystalline silicon layer was then grown over the POCl₃ deposition to seal the back surface and reduce autodoping effects. The front surface was then re-polished. Several n⁺pp⁺ epitaxial structures were then grown using these substrates in order to provide some gettering during growth. The n⁺ region on the back of the cell was removed by etching prior to completing the solar cells.

Table 5-2. RESULTS OF EXPERIMENTS WITH DIFFERENT SURFACE PREPARATIONS

Sample	Substrate	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF —	η (%)	Comment
SERI 7 (CHEM ETCH + HCl ETCH)						
T	Control	26.1	591	0.803	12.3	Polished + HCl
TD1	1S	22.5	591	0.811	10.8	AR Problem
T-2	1S	22.5	596	0.804	10.8	AR Problem
S	Control	25.6	588	0.790	11.9	Polished + HCl
S-1	1P	21.5	562	0.756	9.1	AR Problem
S-2	1P	21.7	563	0.745	9.1	AR Problem
U	Control	26.5	600	0.794	12.6	Polished + HCl
U-1	2P	21.8	560	0.722	8.8	AR Problem
U-2	2P	—	—	—	—	Broken during Processing
V	Control	26.1	595	0.801	12.4	Polished
V-1	2P (II)	21.8	585	0.769	9.8	AR Problem
V-2	2P (II)	22.5	576	0.750	9.7	AR Problem
SERI 8 (CHEM ETCH, NO HCl ETCH)						
XD	Control	26.1	600	0.805	12.6	Polished Only
XD-1	1S	21.3	602	0.809	10.4	AR Problem
X-2	1S	21.1	590	0.775	9.7	AR Problem
W	Control	26.4	606	0.808	12.9	Polished Only
W-1	1P	20.7	540	0.742	8.3	AR Problem
W-2	1P	21.6	540	0.738	8.6	AR Problem
Y	Control	26.5	601	0.800	12.7	Polished Only
Y-1	2P	22.0	550	0.602	7.3	Shunted, AR Problem
Y-2	2P	20.9	500	0.688	7.2	Rounded Knee
Z	Control	26.5	600	0.792	12.6	Polished Only
Z-1	2P (II)	21.3	572	0.751	9.2	AR Problem
Z-2	2P (II)	20.5	495	0.693	7.0	AR Problem, Low V_{oc}

Both of these techniques were applied to the growth of thick (50 to 100 μm) epitaxial solar-cell structures because these structures are more sensitive to increased diffusion length than thin (15 to 20 μm) structures.

The results of these experiments along with the characteristics of two representative baseline cells are summarized in Table 5-3. The data for the case of slow cooling show that little or no improvement in solar-cell performance was obtained. In the cases where a POCl_3 diffusion-gettering was used, the resulting diffusion lengths and short-circuit currents are lower than even the baseline cases where no slow cooling or gettering was applied. A likely explanation is that the 10- μm -thick polycrystalline layer used as a cap over the diffused region did not effectively seal the back of the wafers during the epitaxial growth. Under these conditions the diffused layer becomes a source of phosphorus which is then incorporated in the growing boron-doped layer, resulting in compensated doping in the active layer.

Since the slow-cooling resulted in no measurable improvement in the performance of cells made on UMG substrates, and because this procedure would add considerable time and cost to the epitaxial process, it was not pursued further.

5.3 EPITAXIAL GROWTH WITH SILANE

We have explored the use of silane as the silicon source in the epitaxial growth of solar-cell structures. Silane is chemically simpler and can be lower in cost than other commonly used silicon gas sources. Also, growth with silane can be conducted at temperatures 100 to 200°C lower than presently possible with higher order chlorosilanes. This could be important in reducing the diffusion of impurities from low-cost substrates into the grown layer.

However, epitaxial systems using silane are less tolerant to trace quantities of oxygen and usually require more extensive cooling of the reactor walls. Other potential disadvantages in the use of silane for the growth of solar cells include a relatively low growth rate (0.5 to 1 $\mu\text{m}/\text{min}$) and a tendency for the formation of surface defects for the growth of layers thicker than 5 μm .

In the first experiments, baseline solar-cell structures 20 and 50 μm thick were grown on single-crystal, CZ, p+ substrates at a temperature of 100°C. After growth, the wafers were examined and a considerable degree of surface imperfections in the form of slip and haze was noted especially for the thicker structures. However, the solar-cell characteristics were quite good for three of the four epitaxial runs made. These data are summarized in Table 5-4. Except for run T-154, the efficiencies and cell parameters are comparable to those obtained in typical runs using dichlorosilane for the baseline cases.

The use of silane was then applied to Dow UMG 1P polycrystalline substrates with chemically etched surfaces (2 mils etched from each side to remove saw damage). This substrate material was cleaned in ammonia-peroxide, HCl-peroxide mixtures, HCl etched in situ and a 20- μm epitaxial solar-cell structure grown at 1000°C at a growth rate of 0.5 $\mu\text{m}/\text{min}$. Solar cells were fabricated, and their performance is summarized below.

Table 5-3. SUMMARY OF DATA ON SLOW COOLING AND GETTERING

Sample	Epi Thickness (μm)	Process	QE $\lambda = \mu\text{m}$				L^a (μm)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF -	η (%)	Substrate
			0.4	0.6	0.8	0.9						
III	50	Baseline	32	88	79	58		26.2	570	0.785	11.7	Single-crystal CZ
V	100	Baseline	-	-	-	-		25.8	560	0.785	11.0	Single-crystal CZ
E ³	50	Slow Cool	28	94	86	61	55	27.9	564	0.774	12.2	Single-crystal CZ
F ²	100	Slow Cool	31	92	74	53	48	26.2	553	0.750	10.9	Single-crystal CZ
O	50	POC ₂	29	91	51	26	15	21.6	540	0.790	9.2	Single-crystal CZ
P	50	POC ₃	35	97	72	45	35	24.4	550	0.784	10.5	Single-crystal CZ
MC	50	Slow Cool	42	92	76	53	50	26.3	562	0.766	11.3	Single-crystal CZ
M	50	Slow Cool	36	90	72	48	40	25.8	564	0.784	11.4	Dow grade 1S
L	50	Slow Cool	45	92	68	46	35	23.9	530	0.712	9.0	Dow grade 2P
K	50	Slow Cool	49	80	54	31	20	22.3	526	0.743	8.7	Dow grade 1P.

^aDiffusion length obtained from curve fit to spectral response data.

Table 5-4. SOLAR-CELL PARAMETERS FOR SILANE-GROWN STRUCTURES

<u>Epi-Run</u>	<u>Epi Thickness (μm)</u>	<u>I_{sc} (mA)</u>	<u>J_{sc} (mA/cm²)</u>	<u>V_{oc} (mV)</u>	<u>FF -</u>	<u>η (%)</u>	<u>Comment (Surface Condition)</u>
T-114	20.4	123	27.6	598	0.767	12.7	Slip and haze
T-115	20.1	124	27.8	584	0.776	12.6	Slip, slight haze
T-115	20.1	124	27.8	582	0.770	12.5	Slip, slight haze
T-153	50	121	27.1	570	0.761	11.8	Slip, haze and small Surface pits
T-153	50	122	27.4	575	0.777	12.3	Slip, haze and small Surface pits
T-154	50	96	21.6	520	0.690	7.7	Surface very rough and pitted
T-154	50	87	19.6	375	0.490	3.6	Surface very rough and pitted

A summary of the measured AM-1 characteristics for the cells fabricated from the layers grown with silane on the UMG grade 1P substrates is given in Table 5-5. No AR coatings were applied to the cells made in 1P material because of the nonsmooth surface which resulted both from the surface preparation by chemical etching and from surface pits formed during the growth. Typical values for cells grown using dichlorosilane at 1100°C are also listed in Table 5-5 for comparison.

The data show that while the efficiencies measured for the samples grown with silane on the UMG substrates are comparable to those obtained with dichlorosilane, the cell parameters for the two cases are somewhat different. For the silane group, the short-circuit currents are higher, but the open-circuit voltages and fill factors are lower. The higher values of short-circuit current may be misleading because of the partially textured surface which resulted from the growth with silane. The lower values of V_{oc} and the FF are most likely due to the surface defects mentioned above since such defects can contribute to excess dark current which would lower both V_{oc} and the fill factor.

5.4 EFFECT OF GROWTH TEMPERATURE AND GROWTH RATE ON SOLAR-CELL PERFORMANCE

In studies relating to the determination of the optimum growth parameters, a series of 20- μ m-thick epitaxial solar-cell structures were grown at 950°C, 1000°C and 1050°C, 1100°C, and 1150°C on all three grades of UMG substrates. Spreading resistance measurements of their carrier concentration profiles showed that no problems of doping incorporation were encountered as the growth temperature was reduced. At the growth temperature of 950°C, the surface quality was severely degraded.

A second series of experiments were performed on all three grades of UMG substrates in order to determine the effect of epitaxial growth rate on solar-cell performance. In these runs the growth rate was varied from 1 to 10 μ m/min while the growth temperature was kept at 1100°C. At each growth rate it was necessary to adjust the dopant introduction in order to achieve the same doping profile. The resulting data shown in Figs. 5-1 and 5-2 are averages for all cells including controls.

In the case of growth rate, 1 to 10 μ m/min represents a very large range for epitaxial growth and the data show only a slight variation with a small increase in cell parameters at the lowest growth rate.

The variation with growth temperature is very large but not unexpected since the general experience with the chlorosilanes indicates poor growth for temperatures below 1100°C. This was observed here in the form of surface haze and pits, seen in increasingly pronounced fashion as the growth temperature was lowered. However, from a reactor design viewpoint, the data in Fig. 5-2 show that variation in growth temperature between 1100°C and 1150°C had little effect on cell performance.

Table 5-5. SUMMARY OF SOLAR-CELL CHARACTERISTICS FOR SILANE-GROWN SAMPLES

Epi Run/ Sample No.	Substrate	AM-1 Characteristics					Comment
		J_{sc} (mA/cm ²)	V_{oc} (mV)	FF	η (%)	η_{AR} *	
T-238/D1-1	Control CZ	27.5	582	0.780	12.5	—	With AR Coating
T-238/D1-2	Control CZ	26.9	560	0.737	11.1	—	With AR Coating
T-238/D1-3	UMG 1P	18.3	520	0.719	6.8	9.5	No AR Coating
T-238/D1-4	UMG 1P	17.9	521	0.726	6.8	9.5	No AR Coating
T-238/D1-5	UMG 1P	17.9	516	0.717	6.6	9.3	No AR Coating
SERI 7/S-1	UMG 1P	16.3	552	0.744	6.7	9.4	No AR Coating — Grown with Dichlorosilane
SERI 7/S-1	UMG 1P	16.5	553	0.750	6.8	9.5	No AR Coating — Grown with Dichlorosilane

*Efficiency estimated by $\eta_{AR} = 1.4 \eta$.

Figure 5-1. MEASURED CELL PERFORMANCE PARAMETERS AS A FUNCTION OF EPITAXIAL GROWTH RATE

Figure 5-2. CELL EFFICIENCY AS A FUNCTION OF THE EPITAXIAL GROWTH TEMPERATURE

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SECTION 6.0

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The main objective of this contract was to investigate epitaxial growth processes which will allow the use of low-cost forms of silicon for fabricating high-efficiency, cost-effective solar cells. To accomplish this objective, the following four areas were investigated.

- (1) Selection and characterization of low-cost silicon substrates.
- (2) Determination of optimum pregrowth treatments.
- (3) Development of epitaxial growth techniques compatible with the low-cost substrates and with the fabrication of high-efficiency solar cells.
- (4) Investigation of test cells to define the limitations imposed by the quality of the silicon material.

Of the above four areas, items 1 and 3 are key to achieving and furthering the main objectives of this program while items 2 and 4 provide vehicles for improvements and cost reductions of the overall process.

The major conclusions drawn from this work are:

- Silicon substrates prepared from MG silicon by potentially low-cost purification techniques form satisfactory substrates for epitaxial growth and the fabrication of 10 to 12% efficient solar cells. One such substrate on which 12% epitaxial cells were demonstrated is that produced by the HEM directional solidification of MG silicon.
- No major deleterious effects on cell performance could be correlated to the presence of the residual heavy metal impurities in the substrates. However, the presence of large amounts of C and Fe in MG feedstock can cause particulate formation during solidification. These were found in one HEM ingot and were the cause of shunted cells. In the case of the grade 2P UMG substrates, Auger analysis revealed trace amounts of SiC at grain boundaries, but no direct correlation of cell performance with the presence of SiC was noted.
- The allowable range of variation in the key parameters of the epitaxial process and cell structures, such as resistivity of the active layer, thickness, growth rate, and growth temperature was determined; it was found that a greater variation in these parameters is possible for solar cells compared to those required for epitaxial devices now produced in the semiconductor industry. This will allow a relaxation in the major constraints of present epitaxial reactor designs and should result in increased capacity and throughput for future scaled-up epitaxial reactors dedicated to the production of solar cells.

- Thin-film epitaxially grown solar cells were reproducibly demonstrated with efficiencies of over 10%. A scale-up to practical-sized cells was shown to be feasible by fabricating cells of 10-cm² area with almost 10% efficiency.

Other major accomplishments of this work are:

- (1) Discovery of an optimum slicing direction for directionally solidified ingots. It was found that by slicing such ingots parallel to the direction of solidification, a greater grain area and a more uniform geometric grain structure is obtained. This resulted in an increase in the average cell efficiency from 9.5 to 10.5%.
- (2) It was demonstrated that epitaxial growth results in improved crystal quality of layers grown on low quality silicon.
- (3) Cost-effective surface preparation techniques such as chemical etching were found adequate for good epitaxial growth and solar-cell performance.
- (4) The use of silane as a possible alternate silicon-containing gaseous source in the epitaxial growth was successfully demonstrated.

6.2 RECOMMENDATIONS

A net result of this program and of the work that preceded it strongly indicates that the epitaxial growth process for fabricating cells on generic metallurgical grade material can become a viable process for producing solar cells at the costs projected by DOE. To accomplish this, the following recommendations which have been drawn from the present work should be pursued in future programs:

Substrate Development

- MG silicon should continue to be pursued as the feed-stock for low-cost purification techniques.
- Purification methods should be directed toward the avoidance or removal of particulate inclusions (SiC).
- Single-crystal or very large grain structure is desirable.

Surface Preparation

- Surface preparation techniques such as wet etching or dry plasma etching need to be tailored for use on multicrystalline substrates which may also be defected. The technical goal should be to obtain surfaces consistent with both the epitaxial growth and subsequent low-cost cell processes such as metallization and spray-on AR coating applications.

Epitaxial Growth

- To proceed to a cost-effective epitaxial process for solar cells, large-scale, high throughput reactors are required. The work conducted here has shown that the performance of the thin-film epi-cell structure is relatively insensitive to variations in the growth conditions. This information along with established design conditions should be used to develop prototype large-scale epitaxial reactors.

Cell Performance and Processing

- The work on large-area cells should be expanded to include larger areas and higher efficiencies consistent with rectangular geometries suitable for efficient module fabrication.
- The question of compatibility of the epitaxial cell-MG substrate with low-cost cell processes already developed for single-crystal cells should be explored.

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SECTION 7.0

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Appendix

ATOMIC HYDROGEN PASSIVATION EXPERIMENT

There have been several recent reports [A-1, A-2] indicating that heat treatment of polycrystalline silicon in the presence of atomic hydrogen can cause a passivation of grain boundaries resulting in a reduction of barrier heights, electrical resistance, and recombination.

As part of another contract effort [A-3] at RCA Laboratories, studies have been conducted of the effect of atomic hydrogen on the electrical properties of grain boundaries in bulk polycrystalline silicon in relation to solar-cell performance in that material. Use was made of that experience and equipment to assess the possible benefits of hydrogen passivation on epitaxial cells made in the multicrystalline grades of UMG silicon described in this report.

An experiment was conducted in which two selected epitaxial solar-cell wafers containing three solar cells each were heated to 400°C in a quartz tube with atomic hydrogen created by a plasma discharge remaining over the samples. The apparatus used is shown in Fig. A-1. The temperature was maintained at 400°C for 3 hours, then reduced and held at 300°C for 1/2 hour. The samples were then allowed to cool to room temperature and removed from the tube. The illuminated I-V characteristics measured prior to and immediately after the hydrogen treatment for solar-cell sample C1 are shown in Fig. A-2. This sample was then heated in vacuum at 500°C for 1/2 hour with the resultant I-V curve also shown in Fig. A-1. During the heat treatment in vacuum, gases evolving from the sample and exiting the tube were analysed, and it was found that hydrogen was predominant among these gases.

Figure A-1. APPARATUS FOR ATOMIC HYDROGEN PASSIVATION EXPERIMENT

The effects of the hydrogen treatment on the solar-cell performance of all cells contained on the two wafer samples are listed in Table A-1. It can be seen from the data that:

- All cells showed an increase in efficiency after the hydrogen treatment.

Figure A-2. ILLUMINATED I-V CHARACTERISTICS

- The cells having the lowest initial efficiency showed the largest increase after hydrogenation.
- The cell fill factor and voltage show large increases and little or no effect was noted on short-circuit current.

The increases in V_{oc} after hydrogenation (15 to 30 mV) imply large reductions in diode leakage or saturation current, which is consistent with the results obtained in references A-2 and A-4. That no significant increase in J_{sc} was noted is not surprising since the grains in our samples are large, and estimates we have made on the basis of laser scans indicate that grain boundary recombination accounts for a loss in J_{sc} of only about 2%.

The improved cell performance was obtained with only 3-1/2 hours treatment. No attempt has yet been made to determine the minimum time/temperature cycle, but it might be expected to be considerably less for these thin epitaxial cells than for the bulk devices [A-1].

Table A-1. EFFECT OF ATOMIC HYDROGEN ON SOLAR-CELL PARAMETERS

Sample	Cell Area (cm ²)	I _{sc} (mA)	I _m (mA)	V _m (mV)	V _{oc} (mV)	FF -	η^a (%)	$\Delta\eta/\eta_0$ (%)	Condition
C ⁺	4.45	79.2	71.5	425	531	0.723	6.83		Before H ⁺ anneal
C ⁺	4.45	79.8	72.5	465	561	0.753	7.58	11.0	After 4-h H ⁺ anneal
C ⁺ - L	0.40	6.8	6.1	485	560	0.777	7.40		Before H ⁺
C ⁺ - L	0.40	6.8	6.25	497	577	0.792	7.77	5.0	After H ⁺
C ⁺ - R	0.40	6.8	6.1	440	537	0.735	6.71		Before H ⁺
C ⁺ - R	0.40	6.8	6.1	470	557	0.757	7.17	6.9	After H ⁺
L ⁺	4.45	79.1	70.0	420	525	0.708	6.61		Before H ⁺
L ⁺	4.45	80.0	72.5	450	548	0.744	7.33	10.9	After H ⁺
L ⁺ - L	0.40	7.8	7.0	420	512	0.736	7.35		Before H ⁺
L ⁺ - L	0.40	7.8	7.05	455	542	0.759	8.02	9.1	After H ⁺
L ⁺ - R	0.40	7.16	6.3	405	510	0.699	6.38		Before H ⁺
L ⁺ - R	0.40	7.20	6.45	435	535	0.728	7.01	9.9	After H ⁺

^aNo AR coating.

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