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EPITAXIAL SILICON GROWTH FOR SOLAR CELLS

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RCA Laboratories
Princeton, New Jersey 08540

QUARTERLY REPORT NO. 1

January 1978

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U.S. Department of Energy.

JPL Low-Cost Silicon Solar Array Project is funded by DOE and forms part of the Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays.

Prepared Under Contract No. 954817

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91103

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ABSTRACT

The work performed during the first quarter included the development of epitaxial baseline solar cell structures grown on conventional single crystal substrates and initial studies of epitaxial growth and the fabrication of solar cells on one type of polycrystalline substrate.

Growth and fabrication procedures for the baseline solar cells are described along with measured cell parameters, and the results. Reproducibility of these results was established and the direction to be taken for higher efficiency is identified.

Growth studies on polycrystalline substrates were started and x-ray topographic studies of the epitaxial layers showed that a substantially lower defect density was in the grown layer. Initial results on epitaxial solar cells fabricated on polycrystalline substrates are discussed along with some limitations associated with the use of this material.

SECTION I

SUMMARY

The work performed during the first quarter included the development of epitaxial baseline solar cell structures grown on conventional single crystal substrates and initial studies of epitaxial growth and the fabrication of solar cells on one type of polycrystalline substrate (Wacker* SILSO**).

Details of the growth and fabrication procedures for the baseline solar cells are given along with measured cell parameters. The results show that solar cells fabricated on epitaxial layers of about one mil thickness can produce AM-1 efficiency of 12%. Reproducibility of these results was established and the direction to be taken for higher efficiency is identified.

Growth studies on polycrystalline substrates were started and x-ray topographic studies of the epitaxial layers showed encouraging results in that a substantially lower defect density was noted in the grown layer. Initial results on epitaxial solar cells fabricated on polycrystalline substrates are discussed along with some limitations associated with the use of this material.

*Wacker Chemical Corporation, Richardson, Texas.

**Brand Name of product manufactured by Wacker Chemical Corporation, Richardson, Texas.

SECTION II

SUMMARY OF EXPERIMENTAL RESULTS

A. EPITAXIAL GROWTH PROCEDURES

1. Epitaxial Reactor

The growths were carried out using dichlorosilane in a standard horizontal reactor. The quartz tube has 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. Doping gases were arsine or diborane diluted with hydrogen at the 10-20 ppm level and were further diluted as needed before they were inserted 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 emmisivity and quartz adsorption effects.

2. Epitaxial Growth

The silicon substrates used for epitaxial growth are:

(1) Cleaned for 10 min in boiling ammonia-peroxide-water mixtures (reagent ratio 4-1-1).

(2) Rinsed in super q water (filtered dionized water with a resistivity greater than 15 MΩ).

(3) Cleaned for 10 min in boiling hydrogen chloride-peroxide-water mixtures (reagent ratio 4-1-1).

(4) Rinsed in super q water.

(5) Substrates are then spun dry and placed on susceptor which is inserted into epitaxial reactor.

(6) Reactor is flushed with hydrogen flow rate 30 liter/min for 10 min. All other lines to be used flushed to vent line for 5 min and turned off.

(7) Rf generator is turned on and substrates heated to 1150°C with hydrogen flowing for 5 min.

(8) Substrates are etched in 1% HCl for 5 min at 1150°C; this removes about 5 μm of material.

(9) HCl turned off and system flushed with hydrogen 5 min.

(10) Temperature of substrates reduced to growth temperature 1100°C.

(11) Flow rates of gases (SiH_2Cl_2, AsH_3 or B_2H_6) to give desired growth rate and doping level and conductivity type are metered to vent line.

(12) Automatic timer set to give predetermined thickness and growth is started.

(13) Growth stopped automatically and reactor flushed with hydrogen for 3 min.

(14) Rf power turned off and system cooled with hydrogen flowing.

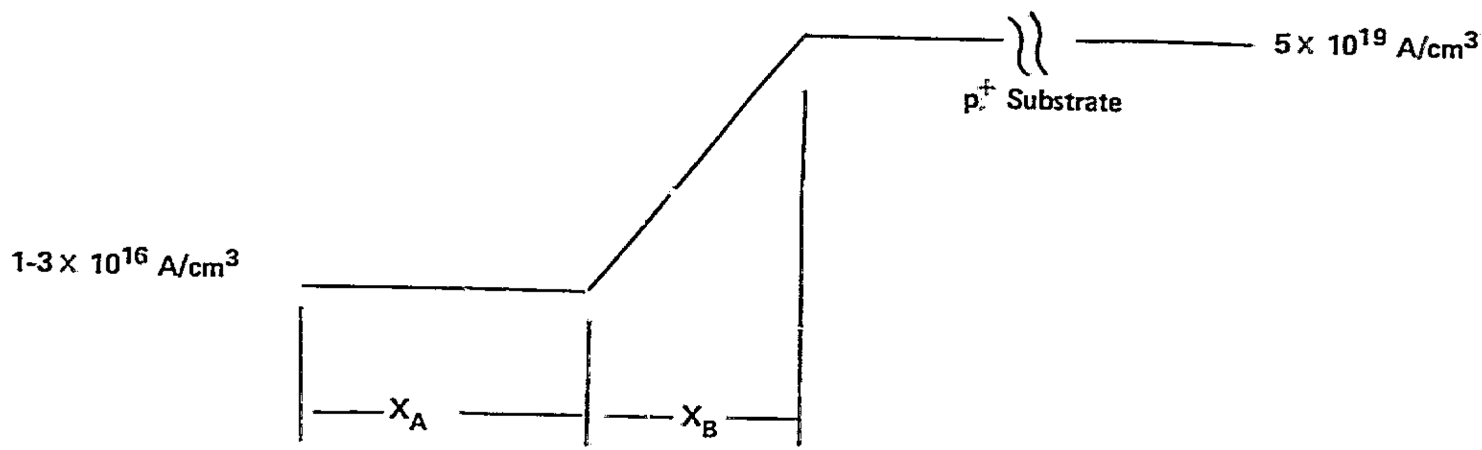
B. EPITAXIAL SOLAR CELLS ON SINGLE CRYSTAL SUBSTRATES

Since most low-cost silicon substrate forms developed to date are p-type (aluminum or boron residual impurity), a first step in our program plan involves the development of $n/p/p^+$ epitaxial structures. The work performed during the first two months of this contract was directed toward establishing the efficiency level and performance characteristics of $n^+/p/p^+$ epitaxial solar cells grown on high quality (conventional) single crystal p^+ substrates. The best of these structures will then form a baseline for later comparison to cells grown on low-cost silicon.

Initial studies were performed on p/p-graded$/p^+$ structures not containing a grown junction. The growth of junction or surface layers will be addressed separately, since we wish to separate and compare conventional, diffused junctions with epitaxially grown junctions. The general structure which we have selected is shown in Fig. 1 with the specific thickness values of the layers given in the inset. The layer X_B is included to provide a "buffer" between the substrate and the layer X_A, with the exponential doping gradient associated with X_B providing a built-in electric field to move photogenerated carriers away from the substrate and toward the junction.

Representative samples of the three structures of Fig. 1 were fabricated into (4.4 cm^2) cells by diffusing a shallow (0.2 μm) junction layer using a $POCl_3$ gaseous source at 875°C and a contact metal (Ti/Ag) pattern was then evaporated. A summary of the measured AM-1 (simulated light-source*) cell parameters are given in Table 1. Illuminated I-V traces representative of the three structures are shown in Figures 2, 3 and 4.

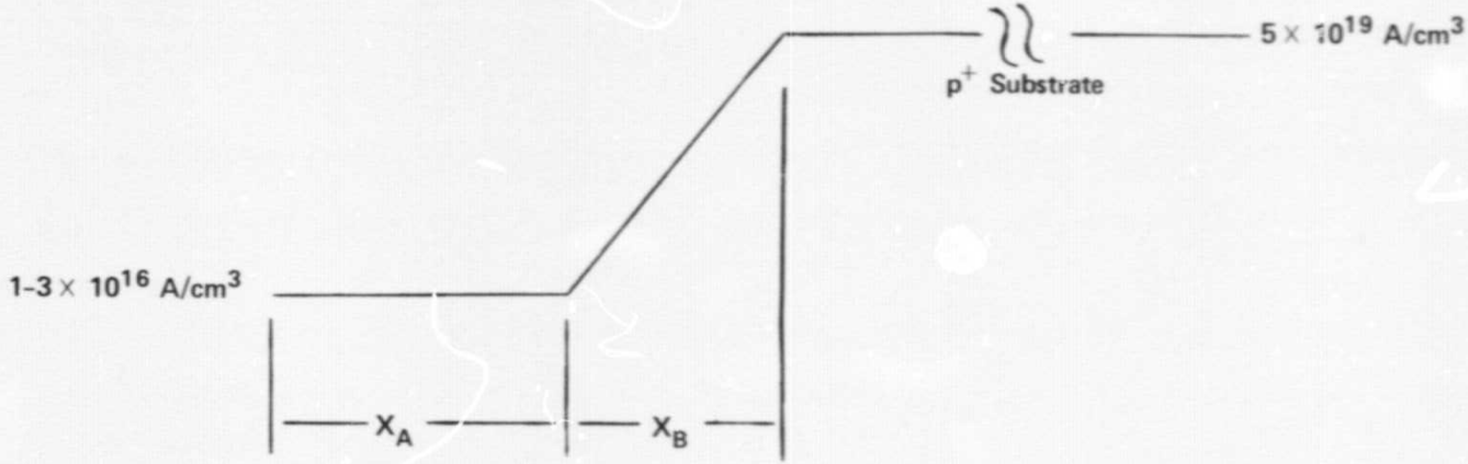
*ELH-Lamp AM-1 simulator--97 mW/cm^2.



STRUCTURE	X_A	X_B	$(X_A + X_B)$
I	5	12	17
II	10	12	22
III	35	12	47

Figure 1. Concentration profile of epitaxial base layer.

TABLE 1. SUMMARY OF STRUCTURAL CHARACTERISTICS AND SOLAR CELL PARAMETERS FOR THREE EPITAXIAL CELL STRUCTURES



Structure	X_A	X_B	$(X_A + X_B)$	Epi Thickness X_A µm	Epi Thickness X_B µm	Epi Thickness X_T µm	AM-1 Parameters J_{sc} mA/cm	AM-1 Parameters V_{oc} mV	AM-1 Parameters F.F. --	AM-1 Parameters η %
I	5	12	17	5	12	17	28.2	538	0.748	11.7
II	10	12	22	10	12	22	27.2	548	0.778	12.0
III	35	12	47	35	12	47	27.5	550	0.750	11.7

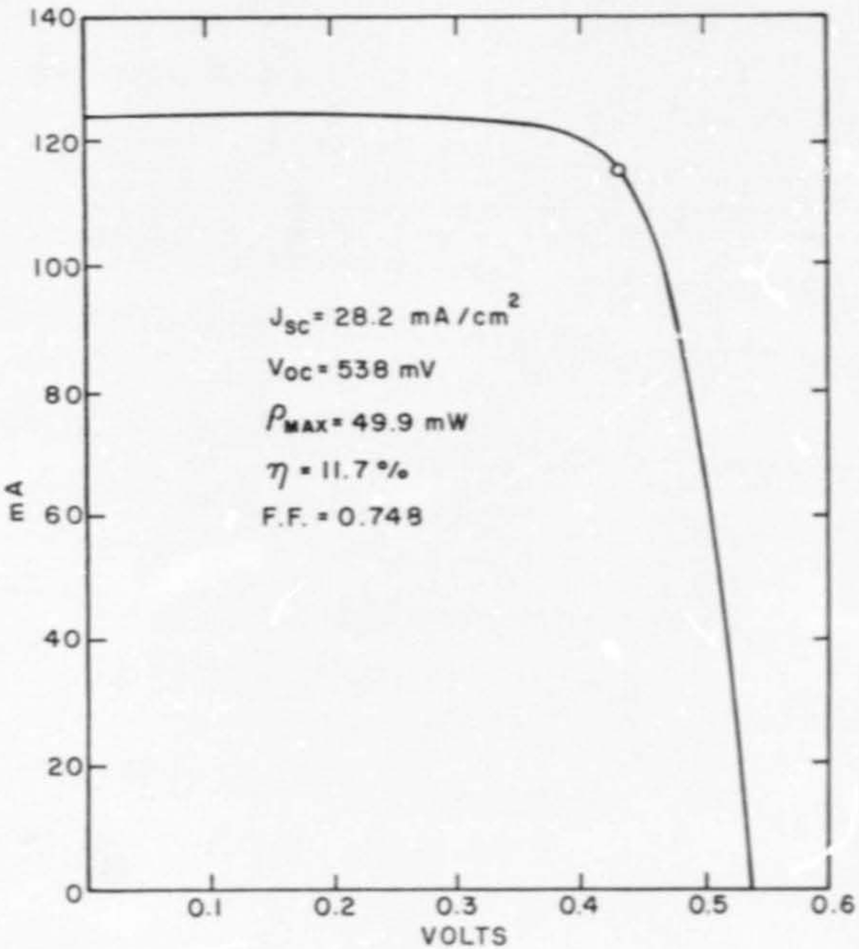


Figure 2. Epitaxial structure I.

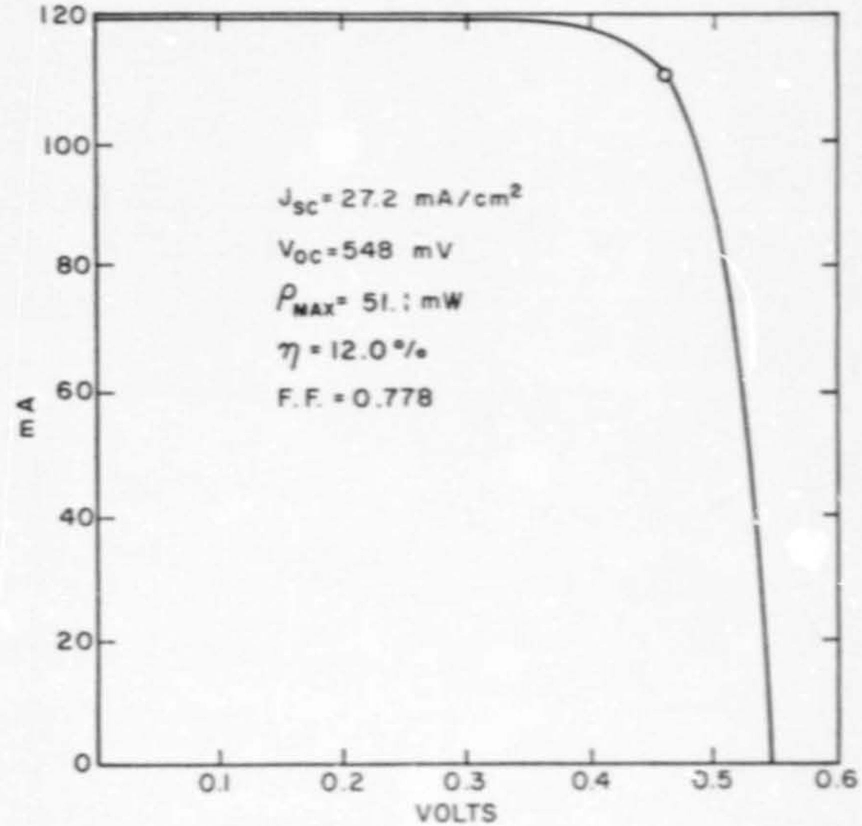


Figure 3. Epitaxial structure II.

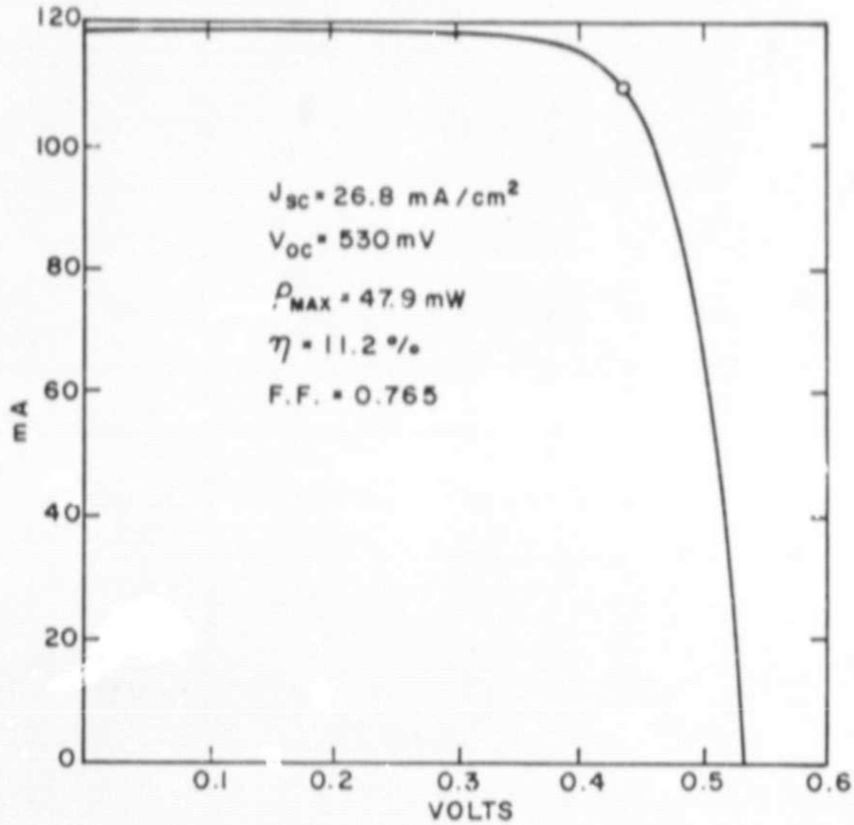


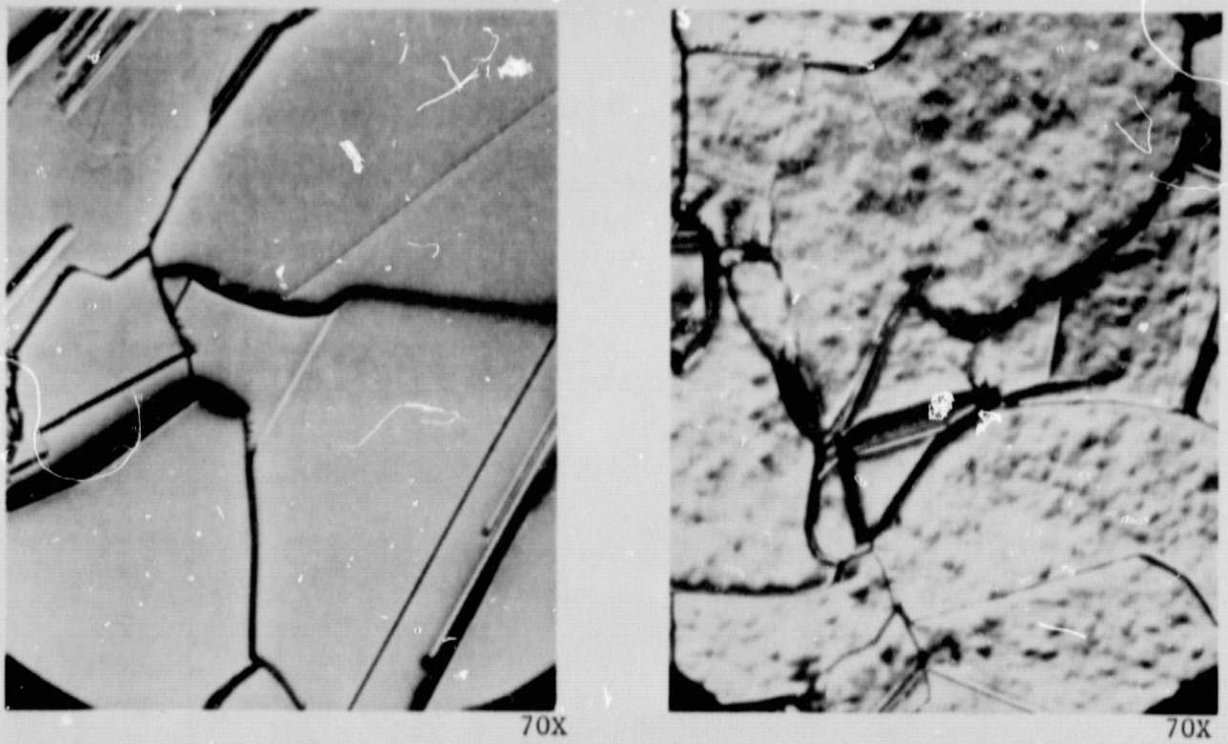
Figure 4. Epitaxial structure III.

C. EPITAXIAL GROWTH ON POLYCRYSTALLINE SILICON

Initial experiments on epitaxial growth on polycrystalline silicon were conducted using Wacker polycrystalline (SILSO) wafers. These are nominally 15-17 mils thick and 4-8 Ω-cm (p-type) resistivity. Since the as-received blanks were saw-cut, comparisons of substrate surface preparation (i.e., etching vs. Quso* polishing) were conducted. Typical layers simulating solar cells structures were grown on such prepared surfaces in order to characterize the bulk and surface properties of the epitaxial layers. Figure 5(a) and (b) shows photomicrographs (70X) of the surface structure of 35 μm thick epitaxial layers grown simultaneously on polished and etched Wacker substrates.

Section and transmission x-ray topographs were taken to evaluate the relative defect density in the epitaxial films as compared to the substrate.

*Registered Trademark of Philadelphia Quartz Co., Valley Forge, Pa.



polished
(a)

EPI/clean etch
(b)

Figure 5. Comparison of the surfaces of 35 μm epitaxial layers grown on a polished (a) and etched (b) Wacker polycrystalline substrate.

In this case, for ease in the x-ray measurement, a 150 μm thick film was grown on a chemically etched substrate. Transmission and section topographs of this are shown in Fig. 6(a) and (b) and an enlarged portion of the section topograph is shown in Fig. 7. The topographs clearly show a greatly reduced defect density in the epitaxial layer.

D. PRELIMINARY SOLAR CELL RESULTS ON POLYCRYSTALLINE SUBSTRATES

The three structures described in subsection B were grown on the Wacker polycrystalline substrates. In each case, both polished and etched surfaces were used, and a control single-crystal sample was included during growth and processed along with the polycrystalline samples. A summary of the measured AM-1 solar cell parameters for samples of each structure are given in Table 2. These results will be discussed in Section III-B.

E. NEW TECHNOLOGIES

There are no new technologies reported in this document.

Figure 6. 150 μm epi on etched poly-silicon #2 projection and section topographs (220)/Mo.

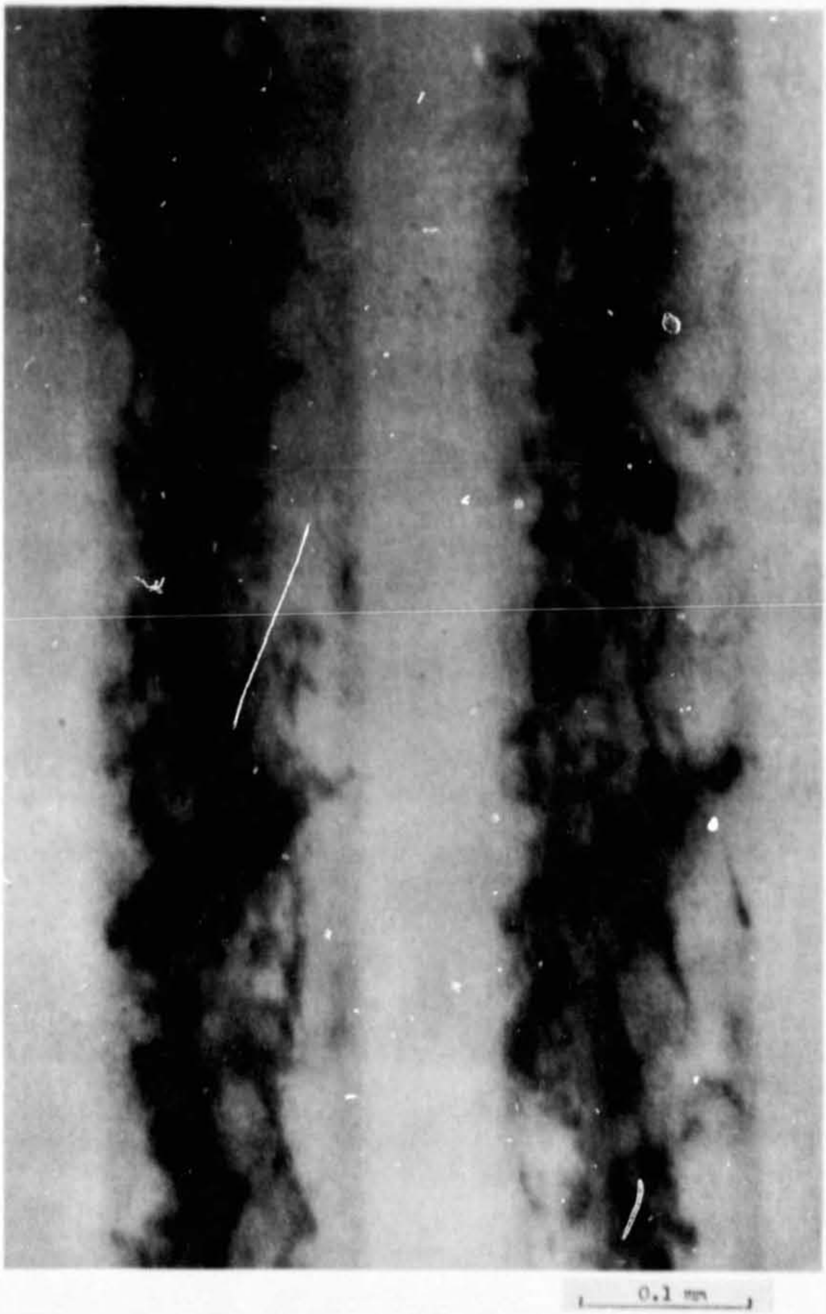


Figure 7. 150 μm epi on etched poly-silicon #1 section topograph (220)/Mo.

TABLE 2. SUMMARY OF SOLAR CELL DATA FOR EPITAXIAL STRUCTURES GROWN ON WACKER POLYCRYSTALLINE SUBSTRATES

Structure/Substrate Surface	AM-1 Solar Cell Parameters*			
	J_{sc}** mA/cm²	V_{oc} mV	F.F. ----	η %
IP/Wacker Etched	25.1	430	0.58	6.5
IP/Wacker Polished	25.9	555	0.777	11.5
I-Control Single Crystal	25.5	495	0.56	7.3
IIP/Wacker Etched	26.8	535	0.633	9.3
IIP/Wacker Polished	26.9	450	0.531	6.6
II-Control Single Crystal	27.3	563	0.772	12.1
IIIP/Wacker Etched	24.9	485	0.654	8.2
IIIP/Wacker Polished	24.9	500	0.683	8.7
III-Control Single Crystal	28.1	575	0.806	13.0

*AM-1 simulation intensity of 97 mW/cm^2

**All cell areas = 4.4 cm^2

SECTION III

DISCUSSION OF RESULTS

A. SOLAR CELL STRUCTURES ON SINGLE CRYSTAL SUBSTRATES

The solar cell performance for the structures grown on single crystal substrates have generally met our objectives of obtaining ~12% efficiency with epitaxial layers of about one mil in thickness. We have grown a sufficient number of these samples to assure reproducibility so that they can form a baseline for comparison with our later work on similar structures grown on low-cost substrates.

Although these results are encouraging, examination of the data of Table 1 shows that there is room for improvement. Specifically, it can be seen that the cell parameters, especially short-circuit current, do not increase as the total epitaxial thickness is increased from 22 μm to 47 μm. This suggests that the performance of these structures is diffusion length limited and that increased minority carrier lifetime should result in improved efficiency. We have taken steps to improve the lifetime by cleaning the epitaxial reactor and gas lines, and by installing new tanks of dichlorosilane and dopant gases. Structure III (~50 μm thick) was then grown on a single crystal substrate and processed into cells. Significant increases in all cell parameters were noted and an efficiency of 13.4% (AM-1) was obtained.

We are establishing experimental methods for the measurement of diffusion length and methods for detecting the limiting factors on lifetime in epitaxial layers.

B. POLYCRYSTALLINE GROWTH AND CELL STRUCTURES

1. Epitaxial Growth

The Wacker polycrystalline substrates were chosen for our initial experiments because of their availability; however, it is not clear at present that this material is representative of low-cost polycrystalline silicon especially with regard to impurity content and defects. This material does contain a sufficient number of grain boundaries so that its use as a substrate allowed us to evaluate potential problems in epitaxial growth on such material.

In our initial growth experiments, a significant finding is that the crystal quality of the grown layers is superior to that of the substrate.

The x-ray topographs shown in Figures 6 and 7 clearly show a significantly lower defect density in the epitaxial layer when compared to the substrate. This indicates that it is possible to improve the quality of silicon grown on a highly defected substrate such as is expected with metallurgical grade silicon. Our experience with epitaxial layers grown on EFG ribbon substrates has shown that such improvements in crystal quality are an important first step in obtaining better devices.

Problems encountered in the epitaxial growth primarily relate to the surfaces and grain boundaries at the surface. X-ray measurements have shown that the grains in this material are randomly oriented, and we have found in some cases, preferential growth resulting in uneven surfaces even when the substrates were polished. This effect is dependent to some extent on the surface treatment prior to epitaxial growth. It was found that removal of about 3-4 mils of silicon from the surface by chemical etching greatly reduced height differences from grain to grain.

2. Solar Cells

From the results given in Table 2, it can be seen that the limiting factors in the epitaxial cells grown on Wacker substrates are the low values of open-circuit voltage (V_{oc}) and fill-factor (F.F.). Preliminary investigations of these devices have given indications that the problem is related to the grain boundaries. Large shunting currents were noted in the junction characteristics and increases in shunt current occurred when the cells were subjected to normal sintering of the metal contacts. Also, the differing heights of the grains mentioned earlier has caused some problem in metalization resulting in excessive series resistance in some cases. Detailed measurements are in progress to determine whether this problem is related to the epitaxial growth or to the nature of the Wacker substrates.

The short-circuit current densities obtained compare favorably with those measured on the single crystal epitaxial control cells, and in spite of the difficulties mentioned above, efficiencies of 6.5-9.3% were obtained.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

The first objective of our program was to develop epitaxial techniques and solar cell structures of one mil thickness having AM-1 efficiency of ∿12-14%. In the first two months of this work, epitaxial solar cells of thicknesses ranging from 17 μm-45 μm, grown on single crystal substrates, have yielded efficiencies ranging from 11.2%-13.4%.

It was noted that improved cell parameters are possible if longer diffusion lengths are obtained in the epitaxial layers. It is recommended that this parameter be monitored and methods for increasing diffusion length be pursued.

Initial growth experiments on polycrystalline substrates (Wacker-SILSO) are encouraging in that a substantial reduction in the defect density of epitaxial layers grown on such substrates was observed. Some difficulties associated with grain boundaries and height differences from grain to grain were observed with epitaxial solar cells fabricated on these substrates. These effects caused low values of open-circuit voltage and fill-factor, however, short-circuit current densities comparable to those for the single crystal case were obtained and AM-1 efficiencies of 6.5-9.3% were measured.

The Wacker polycrystalline material has served as a starting point for our studies of epitaxial growth on low-cost substrates, but this material is relatively pure and of high resistivity. The work next quarter will concentrate on epitaxial growth and the fabrication of solar cells on several forms of metallurgical grade silicon in order to assess the effects of impurities as well as grain boundaries.

SECTION V

PROGRAM PLAN AND ACTIVITIES FOR NEXT QUARTER

Our overall program plan is tabulated below and a milestone chart for this plan is given in Fig. 8. The work for the first quarter has been accomplished on schedule.

Plans for the next quarter include:

1. Evaluation of epitaxial solar cell structures including grown junction layers on both single crystal substrates and polycrystalline substrates.

2. Studies of epitaxial growth on metallurgical grade silicon to include evaluations of defects and electrical properties.

3. Evaluations of solar cells fabricated on metallurgical grade silicon.

4. Establish techniques for the measurements and monitoring of minority carrier lifetime and diffusion length in epitaxial layers.

LARGE AREA SILICON SHEET TASK
EPITAXIAL SILICON GROWTH FOR SOLAR CELLS
PROGRAM PLAN

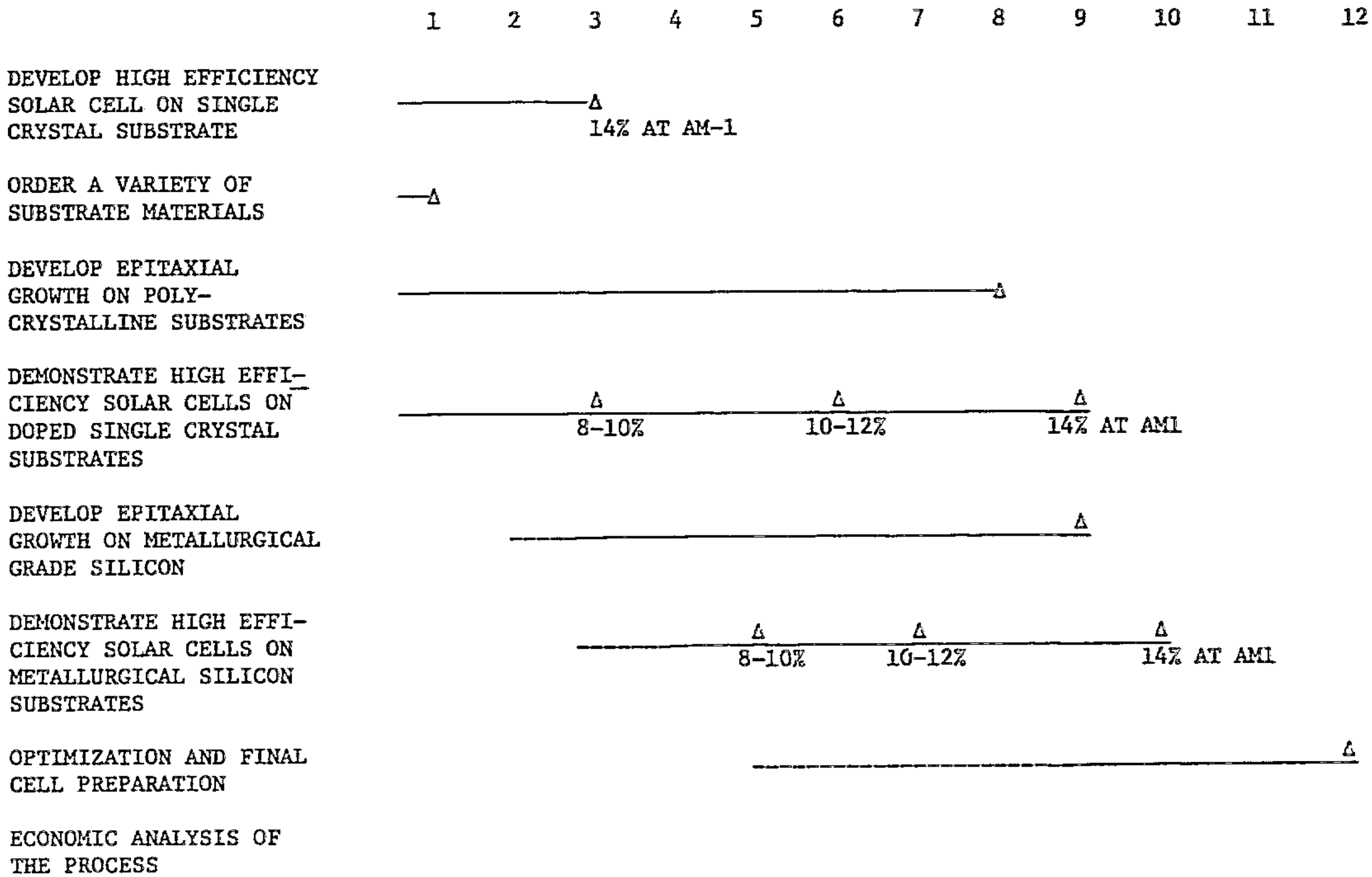


Figure 8. Milestone for overall program plan.