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EVALUATION AND VERIFICATION OF EPITAXIAL PROCESS SEQUENCE FOR SILICON SOLAR-CELL PRODUCTION

D. Redfield
RCA Laboratories
Princeton, New Jersey 08540

QUARTERLY REPORT NO. 2

JULY 1981

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

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Prepared under Contract No. 955825 for

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PREFACE

This Quarterly Report, prepared by RCA Laboratories, Princeton, NJ 08540, describes the results of work performed from April 1, 1981, to June 30, 1981, in the Energy Systems Research Laboratory, B. F Williams, Acting Director.

The Project Scientist is D. Redfield, and the Project Supervisor is A. H. Firester, Head, Process and Applications Research. R. V. D'Aiello also participated in the research (cell processing) for this report.

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SECTION I

GOALS AND OBJECTIVES

The goal of this program is to evaluate the applicability of solar-cell and module processing sequences previously developed for single-crystal silicon under the sponsorship of the LSA project, to be used now on lower-cost epitaxial silicon wafers. These process sequences have been shown to be of potentially low cost and to perform effectively when applied to the high-quality silicon crystals for which they were developed. The present program is intended to verify the extent to which such process sequences can also perform effectively when applied to lower-cost thin-film solar cells formed by epitaxial deposition of Si on potentially inexpensive substrates of upgraded-metallurgical-grade (UMG) Si. Therefore, maximum use is being made of process steps developed under the LSA project, and of epitaxial-Si wafer development being performed at RCA Laboratories under the SERI Exploratory Development program.

SECTION II

INTRODUCTION

After much preparatory work was done during the first quarter, the efforts during this quarter generated the first sets of results of substance. Because evaluation of the cell-process sequence is the principal goal, it has occupied the largest part of these efforts. Also important, however, is the influence of substrate quality on the processing success and on cell performance. Most of the substrate and epitaxial growth work of relevance here is being performed under the allied SERI Exploratory Development (ED) contract [1]. Salient results from that program which pertain to this contract are summarized in the next section under Task 1.

Design of the minimodules has been completed. But since good epitaxial cells have not yet become available for them, module fabrication has begun with other cells used to permit assembly of a complete trial module.

1. "Exploratory Development of Thin-Film Polycrystalline Photovoltaic Devices," Solar Energy Research Institute Contract XS-09100-3.

SECTION III

DATA AND RESULTS

A. TASK 1 - SILICON SUBSTRATE MATERIALS

1. Epitaxial Substrates

Evaluation is continuing on two different upgraded-metallurgical-grade (UMG) Si substrates: HEM material from Crystal Systems, Inc., and UMG from Hemlock Semiconductor Corp., a subsidiary of the Dow-Corning Corp. Although HEM material is expected to be the eventual choice for epitaxial substrates, the ED epitaxial program [1] has encountered serious problems in cell performance when HEM material solidified from MG-Si obtained from early choices of feedstock suppliers is used. Therefore, evaluation of different feedstock materials was undertaken before extended commitments to HEM were made. For that reason, the purchase order for HEM wafers to be used in this contract has been postponed. In the meantime, Dow-Corning wafers were used for epitaxial growth and cell processing.

The evaluation of various HEM materials by the ED epitaxial program has produced two major findings: (1) that the use of well-selected MG feedstock can provide substantial improvement in solar-cell properties; and (2) that double solidification can improve the material further, provided much of the particle-containing top is removed after the first solidification. The performance of epitaxial solar cells made on substrates of these improved HEM wafers has been quite good.

A number of cells of various sizes were made on epitaxial wafers whose HEM substrates were solidified twice by the use of South African MG-Si feedstock. The numbers of particulate inclusions in these substrates are much lower than in previous HEM substrates, for which other feedstocks were used, and the cell performances are correspondingly better. For 20-cm^2 cells with evaporated metals, efficiencies of more than 10% have been obtained with good yields. Also on these substrates, cells of 4.5-cm^2 area with screen-printed metals displayed equally good efficiencies. Cells of larger sizes are now being processed on these materials. There appear to be good prospects for finding alternative sources of better-quality MG-Si in the United States and for avoiding the need for a second HEM solidification.

Therefore, the ED program and this work are expected to be able to use future HEM material solidified from properly selected feedstock. These results are now nearly adequate to serve as the basis for specifying the HEM material to be ordered for this contract.

2. Epitaxial Growth

In three epitaxial-growth runs performed in the high-throughput reactor, 3-in.-diam Dow-Corning wafers were used as substrates. Fifty-two UMG wafers and seven single-crystal CZ control wafers had epi layers grown in these three runs. The resistivity profiles all were similar to that shown in Fig. 2 of Quarterly Report No. 1; the layer thicknesses were 28 μm for run 39, 19 μm for run 40, and 24 μm for run 41.

Before growth all substrates were etched in the manner described in Quarterly Report No. 1. However, there is now reason to doubt that the amount of material removed in this way was as great as desired. This etching is intended to remove saw damage on the UMG wafers which are neither lapped nor polished. Because saw damage can propagate through an epi layer, this removal is essential for the production of good solar cells. Experience has shown that 2 mils should be removed this way from each sawn surface to achieve the necessary quality. The use of the new batch etching machine and imprecise thickness measurements have resulted in uncertain values for the thickness removed.

As part of the effort to check on the possible presence of residual saw damage at the surfaces of UMG substrates, a series of x-ray topographs were made. These reveal strain patterns in the Si, whether they are caused by isolated dislocations, misfit at epitaxial interfaces, or saw damage. Figure 1 shows three portions of a section topograph of an epi/UMG wafer from epi run 40. The dark band on the right side is the epi layer that contains many misfit dislocations caused by nonuniform doping; their presence is verified by projection topographs. The dots throughout the thickness of the substrate are dislocations and other strain-inducing defects. Along the left surface are numerous dark regions - more than the bulk density can explain - that appear to be remnants of saw damage. Therefore, it appears fair to infer that similar damage existed on the other surface where the epi layer is grown. If insufficient removal of saw damage did occur, then we should expect that all of the

Figure 1. Section x-ray topographs of a Dow-Corning UMG wafer with an epitaxial layer about 20 μm thick on the right-hand face. Dark regions are strained.

properties (J_{sc}, V_{oc}, FF) of the eventual cells would be harmed. As discussed in the next section, another closely related effect may be simultaneously affecting the FF. At this time, therefore, it is difficult to make a positive identification of the causes of the poor FF in the first batch of these epi cells.

Further epitaxial growths on Dow-Corning UMG substrates have been postponed until the questions concerning the poor FF will have been resolved. For the present, only small numbers of epitaxial layers are being grown for test cells for diagnostic purposes.

B. TASK 2 - CELL PROCESSING

Before processing of the epitaxial wafers, a third process lot of 25 semiconductor-grade (SG) wafers was processed, with several subgroups given slightly different treatments in an effort to diagnose the cause of the poor fill factors in the first two lots, whose properties were previously reported. These variations and subsequent work led to the conclusions that (i) the poor FFs were due to inadequate metal-semiconductor contact by the screen-printed metal on the front of the cells (not the back); (ii) the surface texture of the Si substrate affects the quality of the contact; and (iii) the surface conductivity of the diffused layer is high enough to make fairly good contact with the screen-printed silver.

The first of these conclusions was reached by several different etching treatments of the metals that consisted of dipping the cells into 2% HF solution. This type of treatment is known to improve the contact properties of poor screen-printed Ag on Si, although it causes other problems, as described below. By masking the backs of some wafers and the fronts of others before this etch, we demonstrated that the effect occurred only when the HF dip acted on the metal of the front of the cells.

The role of surface texture in determining the quality of the metal-Si contact has been established in other places, and was confirmed here by direct comparisons of the properties of cells that were nearly identical except for the nature of the initial surface. The central result is that a highly polished Si surface makes poor contact to screen-printed silver. This result is evidently not understood, and the limits of its validity are not known. Specifically, will a variety of crystallographic orientations in the surface due to polycrystallinity create problems in the surface preparation for this purpose?

One complication that is now troubling this program is the close relation between the improper surface texture and the possible presence of saw damage at the surface. There is clear evidence that each of these can harm cell performance, but it is difficult to distinguish between them at present.

The conclusion that the surface conductivities used here are not the primary source of the poor FFs was reached by modifying the diffusion schedule for some wafers to produce a higher conductivity (~25 Ω/□) without a significant increase in junction depth. At this level of conductivity, it is well established that the silver ink used here can make a good electrical contact. But this increase in conductivity (the former value was ~40 Ω/□) did not succeed in eliminating the problem with poor FFs.

The first epitaxial wafers to be processed into solar cells were 14 wafers from epi runs 39 and 40, which were processed simultaneously with 11 SG single-crystal wafers as Process Lot 4. One of the 14 epi wafers consisted of an epi layer grown on a substrate of p+ single-crystal CZ Si as a control for evaluating the epitaxial growth. The fill factors for these cells before and after the HF dip are shown in Fig. 2 as a function of the wafer position in the group of 25 as they stood in the diffusion furnace. It is obvious that in their initial condition the cells made on UMG substrates had much worse FFs than the others. (There is evidence, shown later, that cell Nos. 24 and 25 at the end of the furnace had lower FFs because of lower surface conductivity.) The fact that cell No. 10, which was the epi control, had a much better FF than all the other epi cells makes it clear that the responsibility for poor FFs is not with the epi growth.

The effects of a HF dip on the FFs of the UMG cell is dramatic; also, most of the SG cells have improved FFs. There is, unfortunately, insufficient understanding of the cause of this improvement to allow its use to diagnose the original trouble with the FFs. There may be two contributions to the limitation in FF: one due to nonoptimum surface textures and one due to some remnant saw damage at the front surface. One further observation in Fig. 2 is that even after the HF dip the FFs are not quite as good as they should be for good cells (~0.75).

That is not the only problem with the use of HF to improve the metal contact. There has been evidence in the past that contacts that need the HF dip become sensitive to moisture after the treatment. In the case of Process

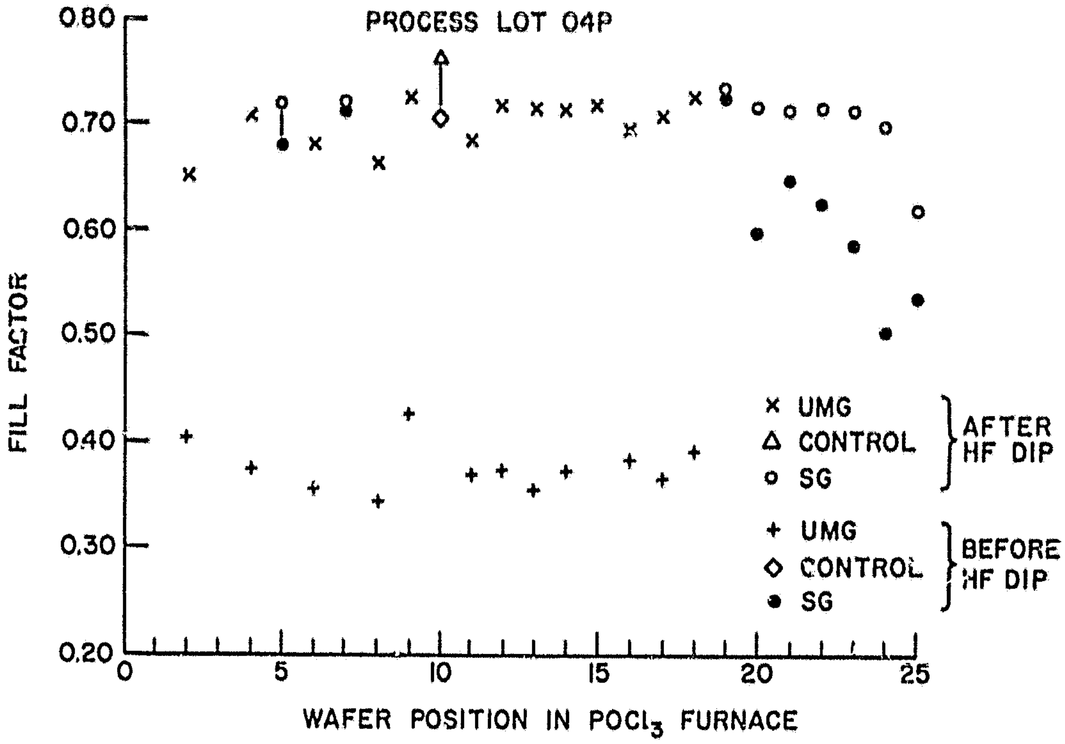

Figure 2. Fill factors of cells in Process Lot 4 in their original condition and after HF treatment to improve the metallization. The wafer position number is its location in the boat during diffusion, with the lowest numbers at the end near the gas entrance.

Lot 4, this effect appeared prominently upon subsequent application of an AR coating as shown in Fig. 3. The FFs dropped back to values comparable to their initial values. The AR coating used here - a sprayed-on suspension of TiO_2-based particles - contains a great deal of water when it is applied.

Also shown in Fig. 3 are the measured values of the sheet resistivity of the diffused layers in all of these cells. These data were obtained by 4-point-probe measurements on the front surfaces after diffusion, and before further processing. It can be seen that this diffusion process results in layers with somewhat higher resistivities near the end of the boat, i.e., at the downstream end as determined by the direction of flow of the gases. Among the SG cells, some correlation apparently exists between low resistivity and higher FF. However, this cannot explain the very poor FFs of the UMG cells, many of which have quite low resistivities.

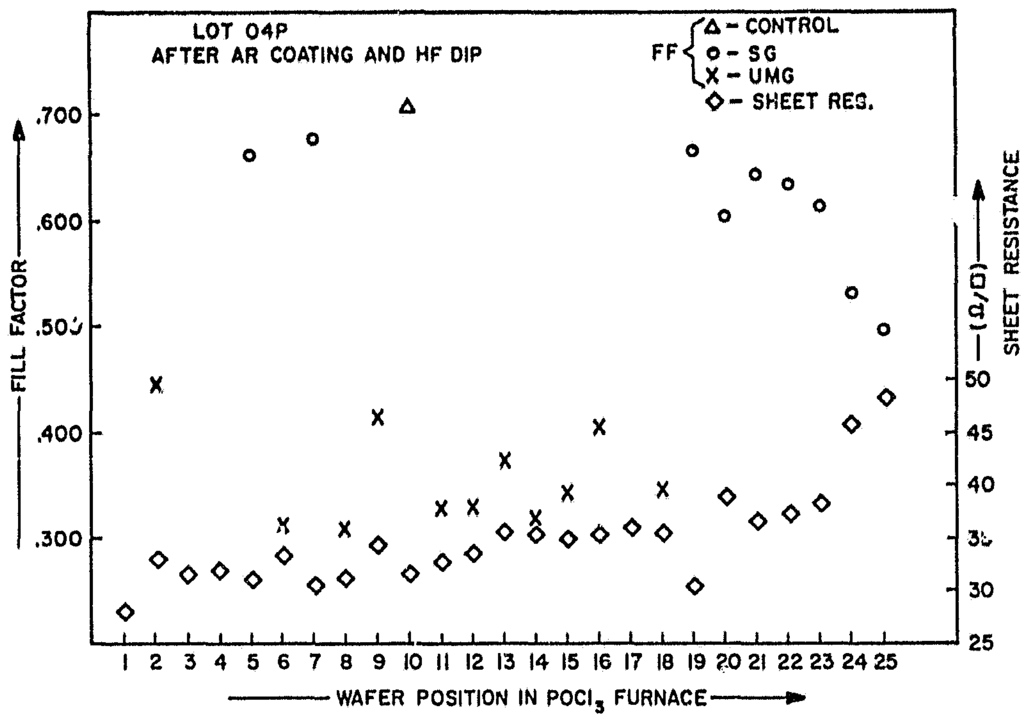

Figure 3. Fill factors of cells in Process Lot 4 after application of a sprayed-on AR coating, and sheet resistances of the diffused layers.

Subsequent measurement of the solar-cell properties of the cells of Lot 4 showed still further degradation of their FFs, presumably due to the action of humidity in the air. This effect is shown schematically for two epi/UMG cells and one SG cell in Fig. 4. Without any further pursuit of this type of observation, it becomes quite clear that the improvement caused by HF on the FF of poor contacts of screen-printed Ag is illusory - it will eventually be lost to natural degradation. On the other hand, contacts that are initially good appear likely to stay that way.

As part of the evaluation of substrates of HEM/South African MG Si, epitaxial solar cells were processed by the use of both evaporated and screen-printed metals. At the same time, two 4.5-cm^2 cells were processed on the wafers from epitaxial/Dow-Corning UMG growth, run 39. These cells had the same screen-printed metals as were used in Process Lot 4. In this small size the two cells, even without any treatment, had good FFs, 0.78 and 0.79, both better than any seen in Lot 4. Other measurements are in progress to explain this result.

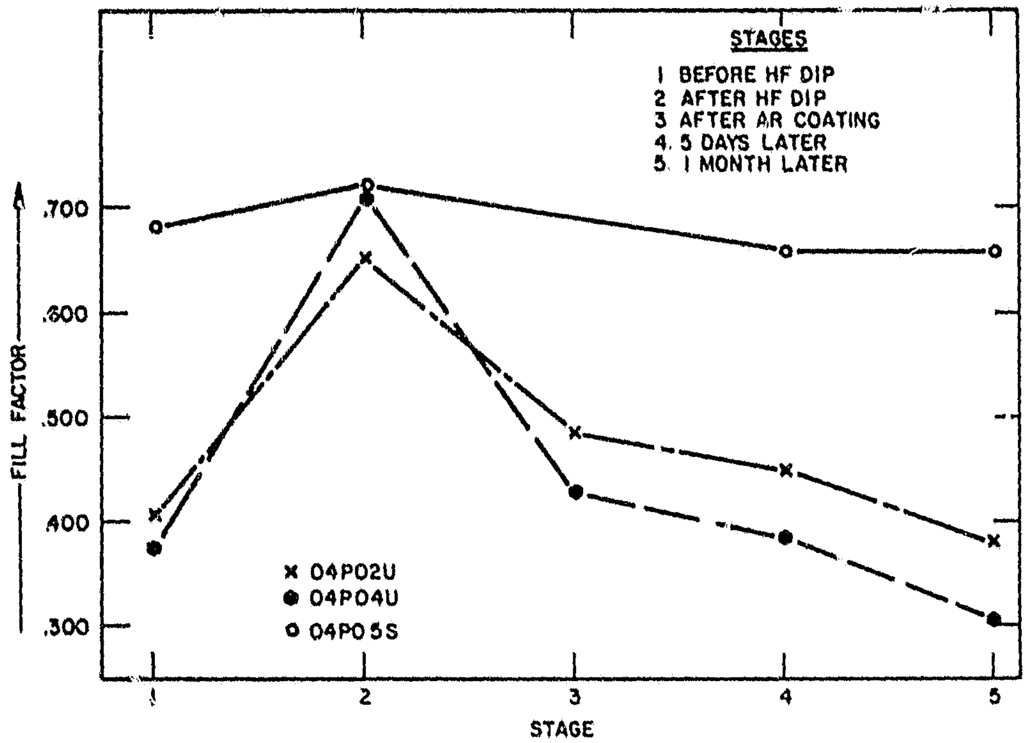

Figure 4. Representation of the variations in FF of three cells of Process Lot 4 at three different stages of their processing and at two subsequent times.

One other significant result of this group of cells was the marked difference in FF between cells that had epi layers grown on polished wafers (average FF = 0.56) or on etched wafers (average FF = 0.77). This confirms other observations of the importance of surface finish. This finish is influenced by both the initial amount of saw damage and the surface treatments.

C. TASK 3 - PROCESS SPECIFICATIONS

The set of Preliminary Process Specifications and Procedures contained in the April, 1981, report with that title is still applicable. If problems associated with the screen-printed metal contacts persist, some alternatives may be tried; their specifications will be provided.

D. TASK 4 - MINIMODULE DESIGN

This task is complete.

E. TASK 5 - PROCESS AND DESIGN VERIFICATION

Verification tests and measurements on cells was reported under Task 2. For modules, the acquisition of supplies and materials has been completed with the receipt of the tempered glass ordered to the size specifications in Table 2 of the Statement of Work. Because of the problems with performance of the epi/UMG cells reported under Task 2, the fabrication of operating modules containing such cells has been postponed. In the meantime, however, a group of non-epi cells of 3-in.-diam was obtained and used in the fabrication of a complete trial module. This procedure has established the various steps in cell interconnect, module assembly, and lamination. These processes appear to be well in hand so as to be ready when useful epi/UMG cells will be available.

F. TASK 6 - COST EVALUATIONS AND PROJECTIONS

There has been no change since the submission of the report entitled Initial SAMICS Cost Analysis in April, 1981.

SECTION IV

INTERPRETATIONS OF DATA

There are two principal areas in which available data need careful interpretation for the purposes of this contract. One is the area of epitaxial-substrate quality, which is a vital factor in determining the performance of epi/UMG solar cells. This area is the primary concern of the SERI epitaxial Exploratory Development program, to which this program is closely linked. The second area is that of contact properties of screen-printed Ag now in use for this program.

Current progress in the epitaxial ED program is encouraging for the identification of sources for acceptable feedstock MG Si for use in the HEM process. There appear to be several low-cost options that should lead to satisfactory HEM substrates. Achievement of this goal, however, will necessarily take time and cooperation from some supplier of MG Si. Thus the present outlook is favorable, although with this constraint.

The success achieved by several commercial manufacturers of single-crystal solar cells using screen-printed metals is an important consideration in the interpretation of the present difficulties with such metal contacts. Moreover, the success achieved previously in this laboratory with the use of screen-printed Ag on carefully prepared <100> single crystals was a prominent factor in the selection of the present program. Current work that focuses on surface treatments of the original epitaxial substrate is therefore expected to eliminate the difficulties now being experienced.

SECTION V

TENTATIVE CONCLUSIONS AND RECOMMENDATIONS

Concerning the quality of epitaxial HEM substrates and its impact on epi/UMG cell performance, there now appears to be sufficient evidence of progress to warrant the tentative conclusion that such substrates will be satisfactory for this purpose. That implies success in meeting the cost and performance goals of the SERI program [1], whose 1990 target is $0.50/Wp for the selling price of modules of these cells.

Conclusions regarding the use of screen printing of Ag contacts for these cells appear premature at this point. On the basis of present knowledge we recommend further concentrated effort on resolving the problems of this process before making firm commitments to the related process steps.

SECTION VI

PROGRAM SCHEDULE

Figure 5 displays the planned schedule of activities on the six tasks of this program with solid lines. Accomplishments to date are shown by the shaded bars above their respective solid lines.

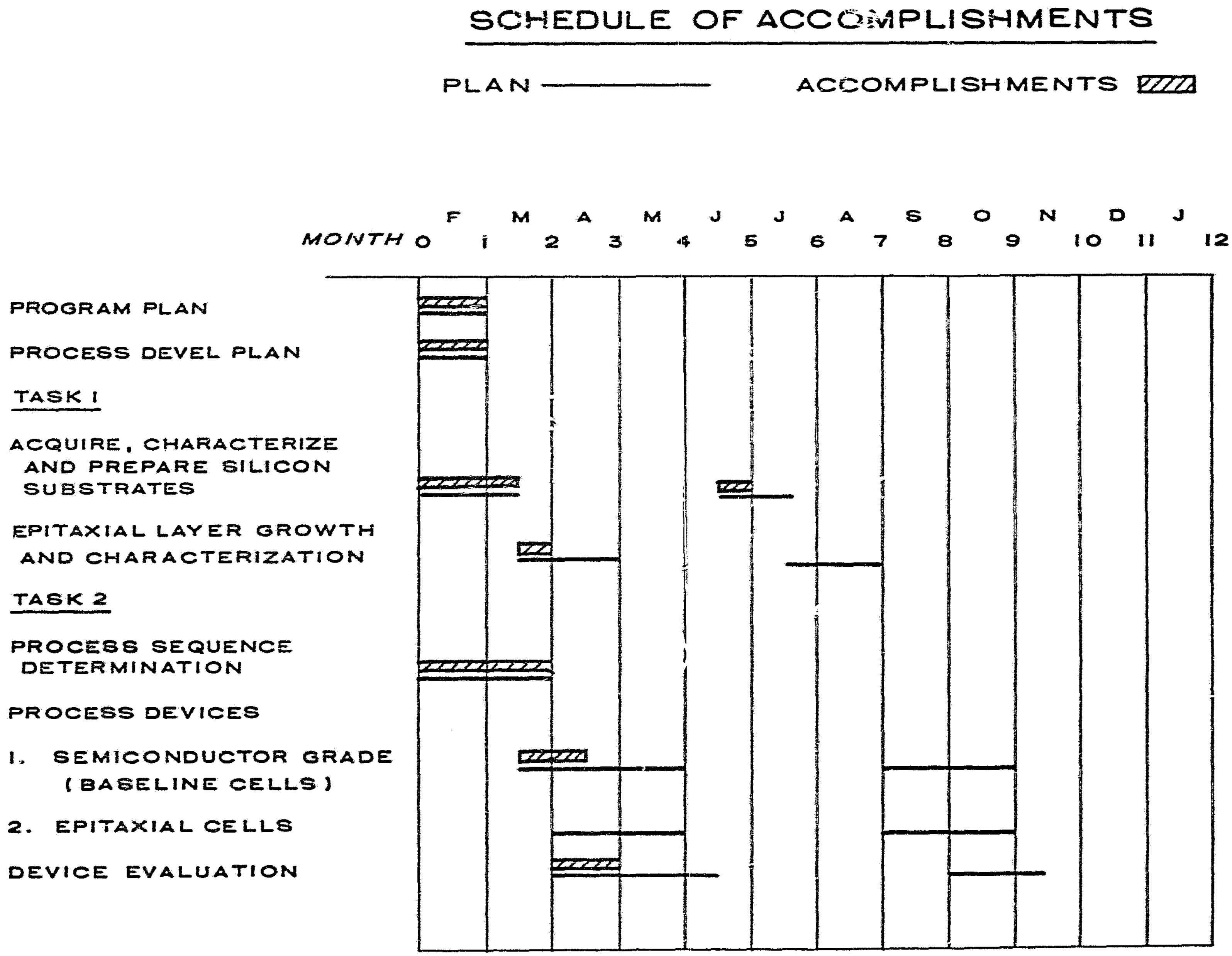

Figure 5. Program schedule.

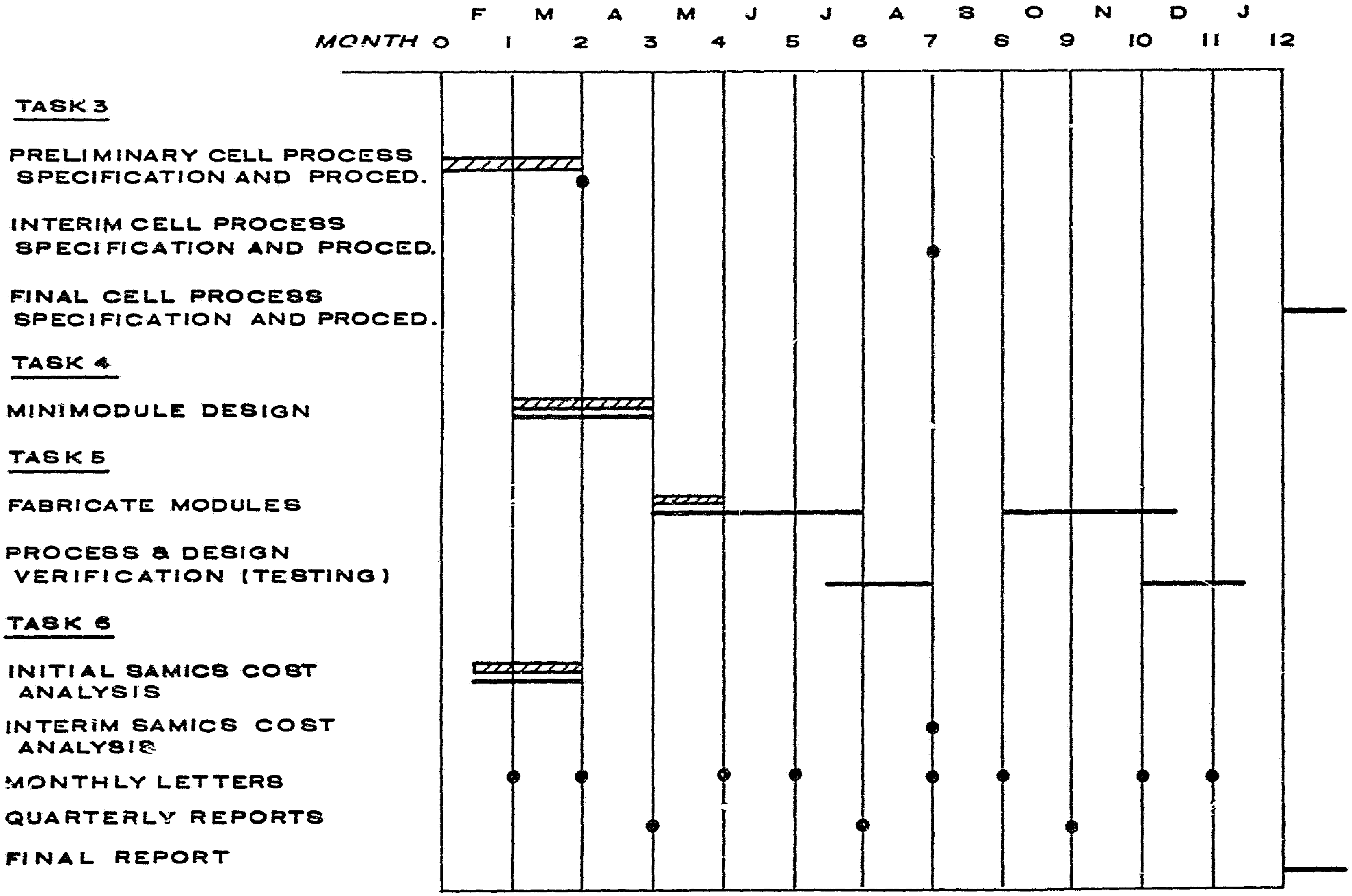

Figure 5. (Continued)