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CHEMICAL VAPOR DEPOSITION GROWTH

Quarterly Report No. 3

R. P. Ruth
H. M. Manasevit
R. E. Johnson
L. A. Moudy
W. I. Simpson
J. J. Yang

January 1977

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Electronics Research Division
Rockwell International Corporation
Anaheim, California

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy

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ABSTRACT

The technical objective of this contract is the development of chemical vapor deposition (CVD) techniques for the growth of large areas of Si sheet on inexpensive substrate materials, with sheet properties suitable for fabricating solar cells meeting the technical goals of the Low Cost Silicon Solar Array Project. The work of the fourth quarter is summarized.

Over 20 different suppliers have now submitted substrate materials for consideration and/or evaluation. Surfaces of many of these materials have been characterized — primarily by surface profilometry and SEM examination. In general, the lower the purity of a polycrystalline ceramic the poorer the surface quality, even after polishing. Some ceramics, such as mullite and zircon, appear to consist of crystallites of the primary material embedded in a glasslike matrix. It has also been found that refiring of polycrystalline aluminas, to produce enlarged grains, generally results in only limited grain enlargement unless the individual wafer surfaces are kept out of contact with other surfaces during the firing process.

Repeated evidence of some type of impurity contamination of Si films deposited on various glass substrates, as well as on the companion sapphire monitor substrates, has required a preliminary investigation of possible causes. In the limited tests conducted to date, no detectable differences have been found in either full- or partial-coverage films of Si deposited by SiH_4 pyrolysis in He onto glass substrates cleaned by three different controlled procedures.

Deposition experiments during the past quarter have been concentrated on 1) production of p-type polycrystalline Si films in a range of B doping concentrations on glasses and polycrystalline aluminas and 2) early-stage island-growth experiments on these same substrate materials. It was found that more uniform Si film growth rates can be achieved by reducing both He and H_2 carrier gas flow rates to 1.5 lpm, at typical SiH_4 flow rates of 10 ccpm. Preliminary data have been established for available carrier concentrations in polycrystalline Si films vs B concentration (in the form of 46 ppm B_2H_6 in He) added during growth in He in the 850°C range.

Several unexpected phenomena have been observed for growth on various glasses. Growth rates, both on the glass and the companion sapphire, have been significantly depressed relative to the expected values for the parameters used, and are generally larger on the glass than on the sapphire. Evidence of some discoloration of the sample pedestal surrounding the glass substrates was noted, and in several instances there was interference with the orderly growth of the Si layer on the companion sapphire. Electrical measurements indicated a higher carrier concentration in the film on glass than in that on the sapphire, in most cases. Spreading resistance measurements as a function of distance into the film have provided data consistent with the possibility of a compensating donor impurity entering the film from the substrate, for the case of Corning Code 1715 glass, but films grown on Owens-Illinois GS211 glass have not shown this effect.

Analysis of x-ray diffraction line intensities for Si films 15 μm or more in thickness on various glass substrates has shown that very strong {100} preferred orientation occurs in polycrystalline films deposited on Corning Code 1715 glass at $\sim 850^\circ\text{C}$, and strong (but less dominant) preferred orientation of the same planes occurs in films on Owens-Illinois glasses GS211, GS210, and GS186. Post-nucleation island growth experiments with normal CVD parameters have indicated that essentially complete Si coverage of single-crystal sapphire or large-grained polycrystalline alumina substrates is achieved in ~ 0.1 sec for growth in H_2 at $\sim 1025^\circ\text{C}$. Shorter deposition times result in partial coverage, and wide differences in the area density of Si islands on individual grains of polycrystalline alumina substrates have been observed, indicating a possible dependence of initial nucleation density on crystallographic orientation. Islands tend to congregate at grain boundaries and — to a smaller degree — at steps in the surfaces of individual grains in regions removed from the grain boundaries. Similar deposition experiments to date with glass substrates at $\sim 850^\circ\text{C}$ in He have provided evidence that is inconclusive. Some experiments indicate that deposition for times the order of 0.1 sec results in complete coverage of the substrate by a layer of extremely fine-grained or possibly amorphous Si, while other experiments have raised doubts as to the integrity of a Si film grown for as long as 6 sec.

Measured carrier concentrations in epitaxial films grown on single-crystal sapphire substrates at 1025°C in H_2 have been used as a measure of the B concentrations added during growth to polycrystalline films grown simultaneously on alumina substrates. For B concentrations of $\sim 5 \times 10^{14} \text{ cm}^{-3}$ the measured active carrier concentrations in the polycrystalline films are in the low- to mid- 10^{12} cm^{-3} range. Above the mid- 10^{16} cm^{-3} B concentration range a very rapid increase in measured carrier concentration occurs as the impurity concentration is increased, until at 10^{19} cm^{-3} the B impurity density and the carrier concentration are essentially the same. These and related data are being developed to establish the impurity additions required for obtaining polycrystalline Si films of proper carrier concentrations for solar cell fabrication.

B-doped polycrystalline Si films on four different glasses and one polycrystalline alumina, as well as epitaxial films on sapphire, have been prepared and submitted to OCLI for solar-cell fabrication and evaluation. Included were two double-layer p/p⁺ Si films, the p⁺ layer in each case doped to $\sim 10^{19} \text{ cm}^{-3}$ to evaluate the possible improvement in photovoltaic performance that might accrue from the presence of the gettering sublayer. Initial results indicate improvement has occurred, so the composite structure will now be tested with polycrystalline films on other substrates.

Conclusions and recommendations are summarized and plans for the next quarter are outlined.

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1. INTRODUCTION

This contract began 29 December 1975, and is of 18-month duration. This quarterly report covers the three-month period from 1 October through 31 December 1976.

The purpose of the contract is to explore the chemical vapor deposition (CVD) method for the growth of Si sheet on inexpensive substrate materials. The work is carried out at the Rockwell Electronics Research Division in Anaheim, and also involves some experimental solar cell fabrication and evaluation by the Photoelectronics Group of Optical Coating Laboratory, Inc. (OCLI), in City of Industry, California.

The formal objective of the contract is development of CVD techniques for producing large areas of Si sheet on inexpensive substrate materials, with sheet properties suitable for fabricating solar cells meeting the technical goals of the Low Cost Silicon Solar Array Project (LCSSAP). The techniques developed are to be directed toward (1) minimum-cost processing, (2) production of sheet having properties adequate to result in cells with terrestrial array efficiency of 10 percent or more, and (3) eventual scale-up to large-quantity production.

The CVD method as applied to Si sheet growth involves pyrolysis or reduction of a suitable Si compound at elevated temperature and (approximately) atmospheric pressure in a flow-through (open-tube) system. A carrier gas is used to transport the reactants to the deposition chamber, in which the substrate is mounted on a SiC-coated carbon pedestal heated by rf from outside the chamber. The properties of the Si sheet are determined by deposition temperature, reactant concentrations, the nature of the carrier gas, the Si source compound used, growth rate, doping impurities (added by introduction of appropriate compounds into the carrier gas stream), and the properties of the substrate.

The specific technical goals established for the contract include the following:

Si sheet area (per sample)	30 cm ²
Si sheet deposition rate	5 μ m per min
Si sheet thickness	20 to 100 μ m
Si sheet crystal structure	100 μ m average grain size
Intragrain dislocation density	<10 ⁴ per cm ²

The principal technical problems to be solved are (1) establishing preferred CVD process parameters (temperature, reactant concentrations, carrier gas composition, doping impurities, growth rate) for optimized intragrain properties for the Si sheet grown on various substrate materials; (2) identifying suitable substrate materials that will survive the environment of the CVD process and be potentially inexpensive and available in large areas, yet be as favorable as possible to Si grain growth; and (3) achieving adequate grain size in the Si sheet to provide satisfactory solar cell properties.

Many characteristics of the CVD method indicate that it has considerable promise for achieving the 1985 technical and cost goals of the LCSSAP: (1) it produces only that amount of Si that is actually required for the photovoltaic effect, without the requirement of additional Si for purely structural reasons; (2) it is a relatively low-temperature process and thus is energy-conservative, not requiring melting of Si at any stage;

(3) it does not require refined/purified polycrystalline Si starting material, using instead a high-purity compound of Si that is actually a product of one of the early steps in the preparation of polycrystalline semiconductor-grade Si; (4) it is inherently a large-area process, capable of potential scale-up to areas that are practical for large array fabrication in the LCSSAP; (5) impurity doping for junction formation can be carried out during CVD growth of the Si sheet; (6) thicknesses are closely controllable by reactant flow-rate adjustments; and (7) it has the capability for eventual development of a continuous fabrication process, in which the Si material, the junction or barrier, and the required contacts are all fabricated in a single integrated series of operations in one apparatus.

Si sheet growth by CVD on inexpensive substrates will almost certainly be polycrystalline, because such substrates will be either amorphous or microcrystalline and will thus provide little or no ordering influence on the growth mechanism. However, the prospects of at least closely approaching the project goal of 10 percent terrestrial array efficiency are considered good. The chances of obtaining sufficient cost reduction per unit area of active cell surface appear strong enough that a cost-per-watt figure within the project goals should be achievable with this process.

The contract program is composed of six main technical tasks: (1) modification and test of an existing CVD reactor system; (2) identification and/or development of suitable inexpensive substrate materials; (3) experimental investigation of CVD process parameters using various candidate substrate materials; (4) preparation of Si sheet samples for various special studies, including solar cell fabrication; (5) evaluation of the properties of the Si sheet material produced by the CVD process; and (6) fabrication and evaluation of experimental solar cell structures (by OCLI), using standard and near-standard processing techniques.

The progress achieved during the fourth quarter is described by task in the following section, followed by a summary of conclusions and recommendations and an outline of the work planned for the next three months. This is followed by the New Technology statement and a listing of references used in this report.

The manpower and funding expenditures to date are summarized in Appendix A, and the Updated Technical Program Plan is included as Appendix B.

2. TECHNICAL DISCUSSION

This section contains a summary of the results obtained during the fourth quarter in performance of the Statement of Work of this contract, with interpretation of the results where appropriate. This discussion is arranged by task, although the interlocking of the tasks is such that this distinction is not always successfully made.

2.1 TASK 1. MODIFICATION AND TEST OF EXISTING CVD REACTOR SYSTEM

The principal planned activity on this task was completed in April 1976. Since that time various additional modifications of a minor nature have been made in the apparatus, and these have been described in previous reports (Ref 1).

No changes were made in the CVD reactor system during the fourth quarter, so the apparatus remains as shown schematically in Figure 2-2 of the Annual Report (Ref 1).

2.2 TASK 2. IDENTIFICATION/DEVELOPMENT OF SUITABLE SUBSTRATE MATERIALS

The 1985 cost goals of the LCSSAP are such that single-crystal materials (other than perhaps Si itself) probably cannot be used for the substrate for low-cost large-area Si solar arrays meeting the technical performance goals of the project. Although future developments could alter this outlook, the requirements of this contract are such that other materials far less favorable to Si crystal growth must be considered and evaluated. This was the starting premise in the search for candidate substrate materials.

2.2.1 Rationale and Procedure for Material Selection

In identifying candidate substrate materials for CVD growth of Si sheet which will meet the technical goals of this contract, several considerations are necessary. First of all, the material must be potentially inexpensive. As an absolute upper limit, in today's market as well as in 1985, it must be less expensive than Si itself for comparable sizes and shapes.

Next, it must be available in relatively large areas - if not now, then at least by 1985. In addition, the properties of the substrate material should be compatible with those of Si. Its linear thermal expansion behavior should duplicate that of Si as closely as possible, from at least the Si sheet deposition temperature down to room temperature.

The importance of the thermal expansion coefficient (TEC) of the substrate material relative to that of Si in the range between room temperature and the Si deposition temperature is emphasized by the data given in Figure 2-1. This shows the TEC as a function of temperature for several glasses and other possible substrate materials, as well as for some other familiar materials for comparison, throughout the range from below room temperature up to Si CVD temperatures. These data provide guidance in the selection of candidate materials for further experimental evaluation.

The Si film must also be chemically stable with respect to the substrate surface, so that any transition layer at the interface does not cause separation or other adverse interaction of the two components. Also, the substrate surface must be stable relative to the carrier gas and the products of Si formation - notably, H_2 when SiH_4 is the source of Si, and HCl when the Si-containing halides are used to produce the Si.

Only a few classes of materials now readily available could be considered initially as candidate substrate materials, based on cost, availability, and reported properties. These include the amorphous glasses, glass-ceramics, and various polycrystalline ceramics. Many glasses are available in large sheet form, and others are potentially susceptible to fabrication into large sheets. It is believed that flat substrates could be produced in most cases by techniques well-known in the glass industry if the need were demonstrated. Some glass-ceramics are also produced in large sheets (the order of square meters), and many low-cost polycrystalline ceramic materials are now available in areas up to about 300 cm².

Figure 2-1. Linear Thermal Expansion Coefficients as a Function of Temperature for Si and Various Other Materials

In contemplating the use of an amorphous glass as a substrate, it is necessary to give special attention to the effect of temperature on the TEC and the viscosity. Convention has identified certain viscosity values with some of the important physical characteristics of glasses: strain point, $\sim 3 \times 10^{14}$ poises; annealing point, $\sim 10^{13}$ poises; softening point, $\sim 10^{7.6}$ poises; and working point, $\sim 10^4$ poises. From room temperature to just below the strain point, which is usually regarded as the upper limit for use of an annealed glass, the TEC for glasses tends to remain nearly constant, increasing only slightly with temperature. However, with further increase in temperature into the annealing range the viscosity decreases and a large and rapid increase in TEC occurs. Although the reduction in viscosity at temperatures above the annealing point might on first examination eliminate a glass from consideration for possible use as a substrate for Si sheet growth in that temperature range, there have been instances of successful Si layer growth on such surfaces in the past (Ref 2). Such a system may have some promise in the present work, as well.

Only two readily available commercial glasses have strain points above the lowest temperatures at which Si growth is considered feasible by CVD techniques; these are the aluminosilicates Corning Code 1720 and Code 1723. However, Si growth by CVD on other glasses could be possible at temperatures between the annealing point of the glass and its softening point, i.e., above $\sim 600^\circ\text{C}$, which is the lowest temperature consistent with growth of Si from SiH_4 . Thus, since it has not yet been determined with certainty what condition of viscosity of a glass surface is best for the formation of Si films of solar-cell quality, glasses remain in consideration. However, previous studies of polycrystalline growth of Si on SiO_2 indicate that higher temperatures lead to larger grain sizes (Ref 3), so early evaluation of glasses has involved those which possess relatively high softening points.

Glass-ceramics are materials which have been converted from their original glassy state to polycrystalline ceramics by controlled nucleation and devitrification. Through variations in composition and heat treatment, glass-ceramics offer a wide range of grain size, crystalline orientations, and TEC values - from high positive values to negative values, including some that are zero over a limited temperature range. Glass-ceramics with TEC's similar to that of Si are being sought for evaluation as substrates for solar cell structures.

The third class of substrate material of initial interest is the polycrystalline ceramic, which is available in many compositions and purities. Based on average TEC values only, likely materials for study include zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$), with TEC $\sim 4.9 \times 10^{-6}$ per deg C (25-900°C); cordierite ($2 \text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$), with TEC $\sim 3.7 \times 10^{-6}$ per deg C (25-900°C); a number of aluminas, with TEC's 7.7 - 8.0×10^{-6} per deg C (25-900°C); and mullite ($2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), with TEC $\sim 4.8 \times 10^{-6}$ per deg C (40-800°C). * In today's market, demand has produced "supersmooth" as-fired surfaces only on certain aluminas. Further studies for producing better surfaces (without polishing) on the other ceramics are necessary; fortunately, such work is in progress in the laboratories of some of the manufacturers.

*In each case, the average TEC value quoted is referred to the temperature at the low end of the temperature range given.

Another type of substrate material considered as a substrate for Si sheet growth is a combination of two of the above classes, namely, a glass film produced on a polycrystalline ceramic, i.e., a glazed ceramic. The typical glaze formed on ceramic offers a surface finish better than that which can be achieved on the ceramic itself (in an as-fired condition) without polishing. The glaze tends to fill in the pores of the surface and can be used with a relatively inexpensive non-smooth substrate of purity lower than, for example, 99.5 percent alumina. Presently, however, the commercial availability of glazed ceramics is very limited, and glazes with low softening temperatures appear to be the rule. This type of composite is attractive, however, and various glazes as well as other types of composite substrate will be evaluated as they become available.

Once a substrate material is identified as a candidate for experimental use in this program, representative samples of it are examined for physical appearance (unaided eye); thickness; surface roughness; surface features at 100X and/or 450X magnification; and (optional) structural properties determined by X-ray diffraction analysis, reflection electron diffraction (RED) analysis, and scanning electron microscope (SEM) examination of the surface.

Substrates of interest are then subjected to exploratory Si CVD growth in both H₂ and He atmospheres at temperatures consistent with the reported properties of the material. For example, for free-standing glasses deposition temperatures below the softening point are used; for glazes on ceramics, higher than softening temperatures may also be used; and for the high-temperature-stable ceramics, temperatures up to about 1200°C can be considered, depending upon the properties of the Si-containing compounds in the carrier gas atmosphere.

A thick ($\geq 20\mu\text{m}$) Si film usually is grown on the substrate, in the presence of a small wafer of sapphire; the latter helps in monitoring the test substrate material stability in the carrier gas and growth atmosphere, as revealed by any obvious contamination pattern in the Si growth on at least the part of the sapphire nearest the substrate. The thick Si film also helps to determine if the difference in TEC between the Si and the substrate leads to detectable bowing of the composite, due to the differential stresses developed upon cooling to room temperature. The Si film also helps reveal some kinds of nonuniformities in some of the substrates.

2.2.2 Candidate Substrate Materials Obtained for Evaluation

By the end of the fourth quarter over 20 different companies had supplied samples of materials for evaluation as possible substrates for the deposition of Si films for low-cost solar cells. Follow-up contacts have continued by telephone with these and other potential suppliers of substrate materials that were contacted or visited personally during the second contract-supported vendor trip in August 1976. Suppliers have all been encouraged to submit their specialty materials noted in Table 2-1 of the Annual Report (Ref 1).

During the fourth quarter, two grades of alumina (97 and 99.5 percent purities) were submitted to the Ferro Corporation, Specialty Glass Products Division (Cleveland), for application of several different glazes to be considered as possible substrates for Si film deposition. The 97-percent alumina was produced by dry pressing, the 99.5-percent, by a tape process. Two different glazes produced on

samples of each of the two aluminas were recently received for testing. These glazes are made from existing (but proprietary) frits, which are described as both soda-free and Pb-free in one case and Pb-free and alkali-containing in the other, with thermal expansion coefficients compatible with alumina.

A variety of other candidate materials has also been received. Samples of mullite and porcelain were received from Metsch Refractories, Inc. (Chester, WV), and Associated Ceramics and Technology (Sarver, PA) supplied pieces of extruded alumina (96-percent purity) and pressed alumina and steatite. Materials Research Corporation (Orangeburg, NY) supplied additional samples of its highest-purity Superstrate alumina and a new 96-percent-purity Superstrate alumina. Plessey-Ceramics Division (Frenchtown, NJ) submitted samples of No. 4462, a 94-percent-purity alumina body containing some MnO. Saxonburg Ceramics (Saxonburg, PA) supplied samples of two different types of dense steatite - a general use material (L-3) and a spray-dried version of a low-loss steatite - and samples of their dense cordierite (S-213). Corning Glass (Corning, NY) has also provided additional samples of Code 1715 substrates, in the form of 3/4 x 3/4 in. plates, but they are very thick (0.130 in.) and must be ground thinner and polished before use.

Corning is also planning to supply soon a different experimental glass with thermal properties "slightly better" (for Si CVD) than those of Code 1715. It will also require polishing before use. Owens-Illinois (Toledo, OH) is still considering supplying three additional glasses to Rockwell, but it will be necessary to produce polished substrates in-house from the materials to be supplied. These glasses have anneal points in the temperature range 775-815°C and average TEC's (referred to 25°C) between 3.1 and 4.2×10^{-6} per deg C. In addition, Saxonburg Ceramics is considering preparing some mullite substrates for evaluation, as well as some refired S697 (97-percent purity) alumina, subjected to as many as six refiring steps beyond normal to effect grain size changes.

2.2.3 Substrate Characterization

The surfaces of a number of additional candidate substrate materials were characterized during this quarter, mainly by Dektak profilometer scans to determine surface roughness and by SEM examination for further surface characterization and to determine an apparent grain size range from the dimensions of surface features. The materials examined include as-fired, refired, and polished ceramics of various compositions. Results of the examinations are given in Table 2-1 and in Figures 2-2 through 2-8, described in the following paragraphs.

2.2.3.1 Polished Ceramics

SEM analysis of a number of polished substrate surfaces showed nonuniform surface structure on many of the materials. As previously found for MRC Superstrate alumina and shown in Figure 2-13, Quarterly Report No. 2 (Ref 4), a number of small voids (pits) are also typically present in the highest-purity (99+ percent) aluminas from other manufacturers - such as ASM772 and ASM838 from 3M Company and ADS995 from Coors Porcelain, as shown in Figure 2-2. The lower the purity, the greater the size of the voids and the coarser the structure, generally. In Figure 2-3, Saxonburg S697 (97 percent) appears to be slightly more compact than ASM614 (96 percent, dry press) from 3M, and the latter has smaller crystals than ASM614ASB (96 percent, tape process) both as-fired and refired.

Table 2-1. Surface Characteristics of Various Candidate Substrate Materials
Evaluated during Fourth Quarter

Substrate Identification	Material (Nominal Purity, percent)	Surface Roughness (Peak-to-Valley, μm)		Apparent Grain Size* Range (μm)	
		First Side	Second Side	First Side	Second Side
Comco No. 5	Alumina (96)	0.5-2.5	NM†	NM†	NM†
Comco No. 2	Alumina (96)	0.5-2	NM†	NM†	NM†
Comco No. 3	Alumina (99.5)	0.5-3	NM†	4-12	NM†
Ceramislik (Plessey)	Alumina (99.7)	<0.5	NM†	NM†	3-15
Saxonburg S697	Alumina (97.5)	1-5	NM†	NM†	NM†
MRC 960	Alumina (96)	0.5-1	NM†	1-4	1-4
Magneco	Alumina (96)	0.5-3.5	0.5-4.5	2-10	3-15
Associated Ceramics (Extruded)	Alumina (96)	0.5-5	1-8	2-5	2-5
	Pressed alumina	1-6	NM†	NM†	NM†
	Pressed steatite	2-6	NM†	NM†	NM†
ASM805 Refired 1 time**	Alumina (99.9)	<0.3	NM†	10-30	15-60
		<0.3	NM†	(large areas)	
		<0.3	NM†	5-20	10-40
Corning 9608	Glass-ceramic	<0.1	NM†	(large areas)	

†NM = Not measured

*Dimensions of surface features measured in SEM photographs

**These substrates were separately supported (not stacked) during refiring process.

(a)

(c)

(b)

(d)

Figure 2-2. SEM Photographs of Polished Commercial Grade of 99+ Percent Alumina.

(a) ASM838, As Fired (3M); (b) ASM838 Refired (3M); (c) ADS772, As Fired (3M); (d) ADS995, As Fired (Coors).

(a)

(c)

(b)

(d)

Figure 2-3. SEM Photographs of Polished Commercial Grades of 96-97 Percent Alumina.
(a) S697 (Saxonburg); (b) ASM614, Dry Press (3M); (c) ASM614ASB (3M); (d) ASM614ASB, Refired (3M).

From Figure 2-4 it can be seen that polished zircon (ASM475 from 3M) consists of grains of a number of different sizes (1-20 μm across) in a binder that is not specifically identified. Mullite (Figure 2-4b and c) shows a more uniform grain size and structure than the zircon, but the grains again appear to be dispersed in a "sea" of some material that appears non-crystalline. Polished cordierite (ASM701 from 3M) shows very little grain structure, with some irregular pits in the surface (Figure 2-4d). It is not known how these pits are generated.

2.2.3.2 As-fired Commercial Ceramics

Comparisons were also made (by SEM examination) of the uniformity of the individual grains of several as-fired aluminas obtained since the second contract trip to visit potential suppliers. These include Ceramislik alumina (99.7 percent) from Plessey, alumina (99.5 percent) from Comco (Sun Valley, CA), and 96-percent aluminas from MRC, Magneco (Addison, IL), and Associated Ceramics (extruded alumina). Both surfaces of each substrate were examined.

The surfaces are shown in Figures 2-5 and 2-6. All of the surfaces are obviously quite rough, and apparent grain sizes are variable. There is also not very much difference in the two sides of the substrate in a given case. Such is not the case, however, for the two sides of refired substrates, as discussed in the next section.

2.2.3.3 Refired Commercial Ceramics

Several substrate materials have been prepared by the 3M Company for this program by refiring two of its standard highest-purity aluminas (ASM838 and ASM805) a number of times. The substrates were refired both as single wafers or plates and in a stacked configuration. Optical examination of the stacked substrates showed an "imprint" of some substrates on others, and it was concluded that such stacking during refiring probably would not lead to substrates with uniform grain sizes or other properties, since only the substrate on top of the stack appeared to be similar to the substrates that were fired singly. Therefore, SEM photographs were taken only of those substrates that were singly fired.

The photographs are shown in Figures 2-7 and 2-8. A comparison of Figure 2-11 in the Annual Report (Ref 1) with Figure 2-7 indicates that a single refiring causes a major increase in the grain size of ASM805 alumina on both sides of the substrate. ASM838 (Figure 2-8) appears to require several additional refiring cycles before grain sizes similar to those found in refired ASM805 are produced.

(a)

(c)

(b)

(d)

Figure 2-4. SEM Photographs of Polished Zircon, Mullite and Cordierite.
(a) ASM475 Zircon (3M); (b) ASM832 Mullite (3M); (c) Mullite (Honeywell); (d) ASM701 Cordierite (3M).

(a)

(c)

(b)

(d)

Figure 2-5. SEM Photographs of Commercial Grades of 99+ Percent Alumina
 (a) Comco 995, Side a; (b) Comco 995, Side b;
 (c) Ceramislik (Plessey), Side a; (d) Same, Side b

(a)

(c)

(e)

(b)

(d)

(f)

Figure 2-6. SEM Photographs of Commercial Grades of 96 Percent Alumina.
 (a) MRC960, Side a; (b) Same, Side b; (c) Magneco, Side a; (d) Same, Side b;
 (e) Associated Ceramics and Technology (Extruded Alumina), Side a; (f) Same, Side b.

(a)

(c)

(b)

(d)

Figure 2-7. Photographs of Refired ASM805 (3M).
 (a) Side a, Refired Singly 1 Time; (b) Side b, Refired Singly 1 Time;
 (c) Side a, Refired Singly 3 Times; (d) Side b, Refired Singly 3 Times.

(a)

(c)

(b)

(d)

Figure 2-8. SEM Photographs of Refired ASM838 (3M).
(a) Side a, Refired Singly, 1 Time; (b) Side b, Refired Singly 1 Time;
(c) Side a, Refired Singly 5 Times; (d) Side b, Refired Singly 5 Times.

2.2.4 Substrate Surface Preparation

It is obvious that the condition of the substrate surface will affect the properties of the film grown on that surface. In many cases the properties obtained in as-manufactured substrates, even though not optimum, are sufficient for the intended application. For substrates to be low in cost, a minimum of surface preparation is preferred. For glasses, a nascent, as-produced surface can be flat, uniform, and clean. For aluminas, the as-fired surfaces have been (in most cases) grossly rough compared with those on the glasses, yet Si films grown on some of the as-fired aluminas have had surface characteristics similar to those obtained on polished aluminas (Figures 2-28 and 2-29, Quarterly Report No. 2, Ref 4).

However, the glasses being evaluated in this program are not "run-of-the-mill" glasses, but are specially processed into substrates with polished surfaces. These surfaces then may be handled and contaminated by fingerprints, oils, less-than-electronic grade water, embedded polishing agents, and other impurities, and therefore must be cleaned before use. The manufacturers of the glasses suggest that acids and bases not be used in cleaning processes; what might be good for cleaning one glass of a given composition is not necessarily good for cleaning another. This dilemma has led to the use of only organic solvents as cleaning agents in the surface preparation of the glasses used for Si CVD experiments to date. Also, in the absence of an extensive investigation of possible organic solvents, the reagents used were trichloromethane, acetone, and Freon, in that order.

Experimentation showed that most of the glass substrates appeared to be contaminating the Si films grown on the companion sapphire substrates, as is discussed further in later sections. It is not known if the apparent contamination is the result of dirty surfaces, decomposition of the substrates, or some reaction of the substrates with the Si deposit - especially in partially obscured locations where the Si film is relatively thin compared with the deposit on surfaces directly exposed to the growth atmosphere.

Any non-organic chemicals used in cleaning a glass substrate surface may also change it, by leaving a residual film or etching the surface; this may provide a surface that enhances nucleation and larger grain growth. An extensive study of surface preparation procedures is not planned at this time, but some limited studies might lead to important results. Therefore, an investigation was initiated this quarter to compare nucleation and early film growth on glass surfaces treated in several different ways.

Similarly, the polycrystalline aluminas have been given a sapphire surface cleaning treatment before use. These lower-purity materials may be reactive to the cleaning procedure used for sapphire, and the reagents used may not be completely removed from the crevices and other defects on the ceramic surfaces. In any case, the aluminas tested have been found on many occasions to move about on the pedestal surface during the pre-deposition heating period, to impart a yellow-orange color to the burning H_2 exhaust flame and to contaminate the neighboring sapphire substrate. Corrections in substrate processing before Si film growth are clearly necessary, and various alternatives are being examined.

In order to obtain an indication of the probable condition of the glass surfaces just prior to Si deposition, several glasses were exposed to flowing He carrier gas for 15 min at deposition temperatures (~850 -900°C). Four glasses from Owens-Illinois and one from Corning were used. SEM examination of the surfaces of the glass samples after this exposure and of the surfaces of other parts of the same original wafers that had not been subjected to the He treatment indicated little, if any, change in the surfaces of GS211, GS213, GS186, and Corning Code 1715 glasses.

The surface of Owens-Illinois GS210 may have been improved by the annealing; the lapped back surface of the GS210 sample (which was in direct contact with the SiC-covered carbon pedestal) actually became much smoother during this annealing period. SEM photographs of the GS210 surfaces with and without the anneal are shown in Figure 2-9. These results are consistent with the fact that GS210 has the lowest softening point (869°C) of the glasses being evaluated. (Unfortunately, Owens-Illinois has still not provided strain and annealing temperature data for the glasses it has supplied for use in this program.)

The SEM examinations also showed that the poorest polished surfaces were those found in certain areas of the Corning Code 1715 samples, as shown in Figure 2-10. Holes, scratches, and grooved areas are sufficiently prevalent to affect light scattering from the surface when viewed with the naked eye.

(a)

(b)

Figure 2-9. SEM Photographs of Back of Owens-Illinois GS210 Wafer a) As Supplied by Manufacturer and b) after Anneal in He at 850-900°C (in contact with sample pedestal).

Figure 2-10. SEM Photographs of Surface of Corning Code 1715 Glass, as Polished by Corning, at Two Magnifications.

2.3 TASK 3. EXPERIMENTAL INVESTIGATION OF Si CVD PROCESS PARAMETERS

During the fourth quarter 41 Si deposition experiments were done on this program in the CVD reactor system. The major emphasis was in two different areas: (1) production of relatively thick p-type polycrystalline Si films with various B doping concentrations on glasses and aluminas and (2) nucleation and early-stage growth studies on these same substrate materials. The p-type doped films were used for establishing a correlation between added doping impurity and available carrier concentration in polycrystalline Si films and for potential fabrication into solar cell structures. The electrical properties and the growth conditions used for these films are discussed under Task 5. The results of the post-nucleation growth studies are shown in Figures 2-11 through 2-13 and are discussed in Section 2.3.3.

2.3.1 Effect of Carrier Gas Flow Rate on Film Growth Uniformity

Early in the quarter a change was made in the carrier gas flow rate used in film growth studies. As reported previously (Refs 1, 5) Si films grown in He carrier gas at flow rates of 4-8 ℓ pm have generally not had uniform thickness. By changing the total He carrier gas flow rate to 1.5 ℓ pm the film thickness uniformity was improved considerably. For example, growth on a single-crystal sapphire wafer at 850°C produced a film 34 μ m thick which varied by only three percent in thickness across about 80 percent of its 2 in. diameter and about 10 percent in thickness for the other 20 percent.

At 1.5 ℓ pm He flow rate, however, the formation of deposits on the reactor wall is increased considerably, and a turbulent brown "smoke" is evident in the reactor during film growth. The role of the products of this smoke during growth of polycrystalline films is not yet known, but its presence did not seem to impede epitaxy on sapphire and spinel single-crystal substrates during work performed previously at Rockwell on another program (Ref 6). X-ray and other analyses of the films grown at the low flow rates as well as of those grown at higher flow rates will help determine if the smoke is in any way hazardous to the film growth process. Such evaluations are in progress, but in the meantime carrier gas flow rates of 1.5 ℓ pm are being used regularly for films grown in both He and H₂ atmospheres.

2.3.2 B Doping Experiments with Glass Substrates and He Carrier Gas

Since no extensive study of B doping of CVD Si films using B₂H₆ in a He carrier gas had previously been undertaken in the program, it was necessary to establish some reference data by growing several doped films on single-crystal sapphire substrates using selected parameters. A range of B₂H₆ dopant gas (46 ppm in He) flow rates from 5 to 500 ccpm was used for these experiments, each of which involved an observed substrate temperature of ~850°C (see Ref 1, pp 53-56).

The resulting film growth rates on the single-crystal sapphire substrates were in the range 0.41 to 0.76 μ m/min for SiH₄ flow rates of 10 ccpm and He carrier gas flow rates of 1.5 ℓ pm; the average growth rate for these parameters is about 0.5 μ m/min. Preliminary results for measured carrier concentrations in the non-epitaxial Si films as a function of the added B concentration indicated values ranging from $\sim 10^{18}$ cm⁻³ for B₂H₆ flow rates of 500 ccpm down to $\sim 10^{12}$ cm⁻³ for the lowest B₂H₆ flow rates of 5 ccpm (of Figure 2-49, Ref 1).

(a)

(b)

Figure 2-11. SEM Photographs of Early Growth of CVD Si on Alumina. (a) Deposit on Single-crystal (0112)-oriented Sapphire; (b) Deposit on 4-times-refined Polished Vistal (Polycrystalline Alumina). (SiH₄ flow rate 10 ccpm for ~0.1 sec at 1025°C in H₂ carrier gas.)

(a)

(b)

Figure 2-12. SEM Photographs of Early Growth of CVD Si on Polished 4-times-refired Vistal (Polycrystalline Alumina). Area shown in (b) Marked by Rectangular Outline in (a). (SiH_4 flow 10 ccpm for <0.1 sec in H_2 carrier gas, at 1025°C)

Figure 2-13. SEM Photograph of Early Growth of CVD Si on Polished 4-times-refired Vistal (Polycrystalline Alumina).
(SiH_4 flow rate 2 ccpm for 0.1 sec at 1025°C in H_2 carrier gas)

Separate experiments were then performed on a number of glass substrates in the presence of a companion piece of sapphire, using the growth parameters normally employed for sapphire. P-type films were grown on Corning Code 1715 glass and four glasses from Owens-Illinois - GS186, GS210, GS211, and GS213. Film growth on Corning Code 1715 appeared to progress well, and the resulting films were clean and uniform in appearance. At high dopant flow rates the observed growth rates were significantly reduced with respect to the expected value, for both the sapphire and the glass substrates.

In experiments with GS211 glass the film growth rate on the companion sapphire substrates was drastically reduced (to $\sim 0.2 \text{ m/min}$), while that on the glass was also depressed considerably below the $0.5 \mu\text{m/min}$ value established in the preliminary experiments. In these experiments it was noted that after the run a prominent border of discoloration was present on the pedestal surface surrounding the glass substrates. It is presumed that some chemical reaction involving the glass or the outgassing of some impurity or glass constituent had occurred during the deposition cycle.

In experiments with substrates of Owens-Illinois GS213 glass the observed growth rates on sapphire were only about $0.2 \mu\text{m/min}$ while those on the GS213 glass were 0.35 and $0.32 \mu\text{m/min}$ - nearly identical to those found for GS211 glass. The heavily doped films on GS213 glass and its companion sapphire were clean and uniform. In an experiment involving a lower B concentration there was evidence of some interference with the film growth process on the sapphire, presumably caused

by an impurity or other constituent of the glass substrates being transferred to the sapphire surface.

Experiments with GS210 and GS186 glasses, using the same CVD parameters (SiH_4 flow rate 10 ccpm, He flow rate 1.5 lpm), also resulted in depressed growth rates. The film growth rates observed when GS210 glass was used (along with a companion sapphire substrate) were similar to those found for Corning Code 1715 glass and sapphire, the rate on the glass being about twice that on the sapphire and the latter being much lower than would be expected for the deposition parameters used.

When GS186 glass was used with sapphire the growth rate on the glass was again greater than on the sapphire, but both were depressed relative to the expected or "normal" rate for the conditions used. For both GS210 and GS186 glasses there was no obvious indication of the type of impurity contamination on the companion sapphire substrate that was observed when GS213 was used, as mentioned above.

The cause of these departures from the normal film growth process is not clear at this time. The electrical properties of the films are reported in the Task 5 discussion. Additional evaluation is in progress, and attempts are being made to identify the source of the difficulties evident in these experiments.

2.3.3 Nucleation and Island-growth Experiments

It is important to study the early growth of Si on the substrates of interest in order to observe the effects of growth conditions on individual island formation and growth behavior at the Si-substrate interface. It is known that remelting of polycrystalline Si can lead to large grain sizes (Refs 7,8), but the melting point of Si (1425°C) is higher than the softening point of the glasses used here and reactivity at such temperatures is very extensive with the ceramics, such as alumina. Therefore, the initial experiments with early growth phenomena were directed toward determining conditions that would lead to only partial coverage of the substrate under "normal" growth conditions.

It was determined that essentially complete Si coverage of single-crystal sapphire is achieved in ~ 0.1 sec using normal growth conditions (SiH_4 flow rate of 10 ccpm at 1025°C). Figure 2-11a shows a CVD Si deposit on single-crystal (01 $\bar{1}2$)-oriented sapphire after ~ 0.1 sec growth at 1025°C with a SiH_4 flow rate of 10 ccpm in H_2 carrier gas. The individual Si islands have nearly coalesced, so that the layer is nearly continuous. Growth that appears quite similar occurs on refired polished Vistal (large-grained polycrystalline Al_2O_3), with more dense growth occurring at the boundary between two different grains in the substrate (Figure 2-11b).

For less than 0.1 sec of Si film growth, only partial coverage is in evidence (Figure 2-12) for growth on a refired polished Vistal substrate. It is noted that certain grains of the polycrystalline substrate possess a greater density of Si islands than others. That is, the crystallographic orientation of the grains may have a major effect on initial nucleation density. The greatest density of islands tends to occur at the grain boundaries, perhaps due to surface migration of atoms and/or nuclei and subsequent clustering at steps in the surface at the grain boundaries. There is also occasional evidence of island congregation at steps in the surface of a grain in regions removed from the boundaries, as shown in Figure 2-13 for Si growth at a lower SiH_4 flow rate (2 ccpm) at 1025°C .

These observations indicate that refired large-grained Vistal alumina can be used effectively to provide an informative picture of post-nucleation and early-stage growth processes that occur for Si deposited by CVD even on fine-grained low-cost alumina surfaces. This is because the large individual grains of Al_2O_3 in the Vistal tend to provide local conditions that are probably much the same as those existing not only on a larger scale on a single-crystal sapphire surface of that same orientation but also on a smaller scale on an individual grain in a fine-grained low-cost alumina (neglecting effects of impurities escaping from grain boundaries or voids in the polycrystalline case).

Nucleation and island-growth experiments were also performed on glass substrates, using typical growth parameters for Si on glasses - nominally 850°C and a SiH_4 flow rate of 10 ccpm in He carrier gas. On exposure to SiH_4 for 1 sec, growth was evidenced by slight darkening of the substrates. Slight color change was also in evidence after 0.1 sec of growth. However, it was not possible to detect, by normal SEM examination, the presence of the same type of three-dimensional islands as were found for film growth at 1025°C in H_2 on Vistal and sapphire, except in isolated regions where the substrate surface may have been contaminated. It is possible that on the amorphous glass surface at 850°C the early stage of Si growth is also predominantly amorphous, rather than polycrystalline, and that only in thicker films will polycrystalline structure be in evidence. Further investigation of this possibility is planned, using reflection electron diffraction (RED) examination, replica electron microscopy, and normal SEM examination to attempt to obtain corroborative results.

In the experiments with glass substrates there were some indications that the substrate may not have been completely covered even after 6 sec of Si deposition in He at 850°C. A two-step growth process at 850°C (6 sec in He atmosphere followed by 30 min in H_2 atmosphere) led to the same type of needle and whisker growth previously observed on Corning Code 1715 and Owens-Illinois GS211 glasses after Si growth in a H_2 atmosphere (cf Figure 2-31, Annual Report, Ref 1). This suggests that the coverage was incomplete following the first step of the growth process (or that the Si was pervious to H_2). It is obvious that additional studies of nucleation and early-stage growth on glasses will be important to achieving the improvement of Si films grown on these materials.

2.4 TASK 4. PREPARATION OF Si SHEET SAMPLES

The work of Task 4 is entirely in support of the activities of Tasks 3, 5, and 6. It consists primarily of the preparation of individual samples or groups of samples of CVD Si on various substrates, utilizing established deposition procedures. These samples are intended for use in film characterization studies (Task 5), to examine the variation in Si properties with systematic deposition parameter variations (Task 3), or for use in fabrication of exploratory solar cell structures at OCLI (Task 6). Occasionally, special samples of a non-routine nature are prepared which do not require extensive evaluation of the interdependence of CVD parameters on the resulting properties of the films; such work is also a part of this task. Any samples prepared strictly for demonstration purposes or exclusively for delivery to JPL are also considered part of this task.

Of over 205 Si CVD experiments done in the reactor system during the first 12 months only about 25 have utilized standard procedures strictly for preparation of samples for analysis, processing, demonstration, or delivery to JPL. All other experiments have been exploratory in nature.

In addition to comparing the growth characteristics of films grown on selected glasses from Corning and Owens-Illinois, some experiments in the fourth quarter were designed to provide polycrystalline films on glass for submission to OCLI for solar cell device fabrication and evaluation. The B_2H_6 concentrations chosen were intended to produce p-type films with doping levels in the range $10^{17} - 10^{18} \text{ cm}^{-3}$ in a He atmosphere at relatively low growth temperatures, i. e., $\sim 850^\circ\text{C}$.

In addition, several experiments were designed to prepare single-crystal p-on-p+ Si structures on sapphire for submission to OCLI for solar cell fabrication. The p/p+ films were prepared with two different thicknesses of the p+ film (4 and 7 μm), to determine the effect of p+ film thickness on carrier lifetime properties and subsequent solar cell properties. The results will be used as a baseline reference for similar structures produced on lower-cost substrates and to help develop solar cell fabrication techniques for films grown on low-cost insulating substrates.

To avoid possible contamination of the sapphire by neighboring substrates of other materials, the p/p+ structures submitted to OCLI were produced using only sapphire substrates. Preliminary determination of the conditions necessary to produce the desired p+ and p doping levels with B was made by simultaneous growth on sapphire and high-resistivity Si, followed by measurement of electrical properties with a four-point probe. The p/p+ structure was then formed on sapphire by consecutive Si film growths without removing the substrate from the reactor or exposing the sample to the atmosphere between the two growths.

Three samples were delivered to JPL on November 2, 1976, at the request of the JPL Technical Manager. These were solar cell structures that had been fabricated and evaluated by OCLI and described in the Annual Report (Ref 1, pp. 127-135). These samples (OCLI-13, 17, 18) were used at JPL in surface photovoltage and diode forward characteristics measurements. Prior to delivery to JPL the three samples were further processed at OCLI to produce relatively small mesas in place of the single large mesa initially fabricated.

2.5 TASK 5. EVALUATION OF Si SHEET MATERIAL PROPERTIES

As indicated in Section 2.3 the emphasis of the fourth quarter's work has been on preparation and evaluation of p-type polycrystalline Si films in a range of doping concentrations grown on various glass and alumina substrates and on investigation of the post-nucleation island growth behavior of CVD Si on these same substrate materials. The properties of the films grown in the former case have been determined principally by X-ray diffraction analyses, SEM examinations, Hall-effect measurements, and spreading resistance measurements. The partial-coverage layers prepared in the island-growth experiments have been examined primarily by SEM techniques, as discussed in Section 2.3.3.

2.5.1 Properties of CVD Si Films on Glass Substrates

Following the experiments which provided the preliminary B doping data for He carrier gas and deposition temperatures of $\sim 850^{\circ}\text{C}$ (see Section 2.3.2), a series of experiments was undertaken to grow doped Si films on several candidate glass substrate materials, in each case also employing a single-crystal sapphire monitor substrate for simultaneous Si deposition.

The results of measurements of the electrical properties of some of these films are given in Table 2-2. All of the films in the table were grown under the same deposition conditions (SiH_4 flow rate 10 ccpm, He carrier gas flow rate 1.5 lpm, observed deposition temperature $\sim 850^{\circ}\text{C}$).

As discussed under Task 3, depressed growth rates were observed on the sapphire substrates in all of the experiments and for the glass substrates except in experiments 164 and 171. The apparent growth rate on the glass ranged from 1.2 to over 2.0 times that on the single-crystal sapphire substrate in this series of depositions. Furthermore, the measured carrier concentrations were in most cases larger in the polycrystalline film on glass than in the simultaneously grown film on single-crystal sapphire, by factors ranging from 1.8 (experiment 168) to 5.4 (experiment 164). Only in experiments 171 and 172 were the measured carrier concentrations in the films on the glasses less than those measured in the films on sapphire. Although the Si films grown on sapphire at $\sim 850^{\circ}\text{C}$ were not epitaxial they would, under optimum growth conditions at this temperature, be expected to be fairly strongly oriented crystallographically. It might be expected that a higher free carrier concentration would be found in such films than in highly polycrystalline films simultaneously grown on amorphous glass surfaces. The fact that this was not observed lends some weight to the suspicion that an impurity from the glass substrates used in these experiments adversely affected the Si film nucleation and/or growth process on the sapphire substrates, and probably also influenced the growth process and effective doping concentration in the films on the glasses as well.

Further evidence of such a possibility was obtained in spreading resistance measurements* made on the films grown in experiments 164, 165, and 166. In experiment 164 substrates of Corning Code 1715 glass and single-crystal (0112)-oriented sapphire were used, with a B_2H_6 flow rate of 50 ccpm for 45 min resulting in

*Measurements made by Solecon Laboratories, Costa Mesa, CA.

Table 2-2. Electrical Properties (van der Pauw) of CVD Si Films Grown by SiH₄ Pyrolysis* in He (1.5 lpm) on (0112) Sapphire and Various Glass Substrates

Expt. No.	Obs. Depos. Temp. (°C)	B ₂ H ₆ [†] Flow Rate (ccpm)	Substrate Material**	Film Thick. (μm)	Growth Rate (μm/min)	Resist. (ohm-cm)	Carrier Conc. (cm ⁻³)	Mobility (cm ² /V-sec)
164	850	50	Corning 1715 glass (0112) sapph.	27.2	0.60	8.0	5.4 x 10 ¹⁷	1.4
				16.8	0.37	1.03	1.0 x 10 ¹⁷	61.
165	856	500	Corning 1715 glass (0112) sapph.	14.2	0.32	0.20	2.6 x 10 ¹⁸	12.
				12.0	0.27	0.13	1.4 x 10 ¹⁸	35.
166	858	500	O-I GS211 glass (0112) sapph.	15.4	0.34	0.12	2.8 x 10 ¹⁸	18.
				9.2	0.20	0.081	1.4 x 10 ¹⁸	57.
167	851	50	O-I GS211 glass (0112) sapph.	19.0	0.38	0.37	1.2 x 10 ¹⁸	14.
				10.7	0.21	0.26	3.9 x 10 ¹⁷	61.
168	858	500	O-I GS213 glass (0112) sapph.	15.8	0.35	0.37	1.6 x 10 ¹⁸	10.
				10.0	0.22	0.096	9.0 x 10 ¹⁷	73.
169	856	50	O-I GS213 glass (0112) sapph.	29.0	0.32	6.3	2.5 x 10 ¹⁷	40.
				17.8	0.20	0.44	1.3 x 10 ¹⁷	108.
171	835	50	O-I GS210 glass (0112) sapph.	55.9	0.62	0.26	9.3 x 10 ¹⁷	25.
				27.0	0.30	0.49	1.1 x 10 ¹⁸	11.
172	839	50	O-I GS186 glass (0112) sapph.	38.0	0.42	14.0	1.2 x 10 ¹⁷	3.8
				23.0	0.26	0.65	1.5 x 10 ¹⁷	65.

*SiH₄ flow rate 10 ccpm

**All substrates polished

†B₂H₆ 46 ppm in He

films of approximately 27 and 17 μm thickness, respectively (Table 2-2). A spreading resistance probe scan on a 0.05 rad bevel through the film on the glass substrate (32 μm probe spacing, 20g probe load, 10 μm increment between probe readings) produced the resistivity-vs-thickness plot of Figure 2-14a. The data shown are obtained from the measured spreading resistance data by application of a correction factor based on the behavior of {111}-oriented bulk single-crystal Si; it has been found previously in uniformly doped polycrystalline Si films that the resistivity values obtained by this method are in very good agreement with those obtained on the same films by four-terminal measurements of resistivity made in conjunction with Hall-effect measurements.

Measurement of resistivity in another portion of this same film by the van der Pauw method indicated a value of 8 ohm-cm (Table 2-2), but it is clear that there is a large variation in resistivity with thickness beginning $\sim 8 \mu\text{m}$ below the surface and covering a range from ~ 1 ohm-cm to over 10^3 ohm-cm in the vicinity of the Si-glass interface. A similar resistivity plot obtained on another Si film grown on Corning Code 1715 glass under essentially the same conditions except for the B_2H_6 flow rate, which was 500 ccpm in this experiment, is also shown in Figure 2-14a. (The increment between probe readings was only 5 μm for this sample.) Although the deposition time was the same in both experiments there was a significant difference in the growth rate, so the film thicknesses are different in the two cases, as indicated in the figure.

Of significance is the fact that the resistivity of the more heavily doped film (order of magnitude difference in the measured carrier concentrations in the companion films on sapphire, as shown in Table 2-2) is much more uniform as a function of distance from the interface, although there is still nearly an order of magnitude difference between the value in the upper 6 or 7 μm (~ 0.1 ohm-cm) and that at the interface (0.8-1.0 ohm-cm). Furthermore, the probe values for this sample are consistent with the result obtained by the four-terminal method (0.2 ohm-cm), as given in the table.

Figure 2-14b shows the resistivity as a function of distance from the interface, obtained by spreading resistance measurement on two different bevels on the same sample, for the polycrystalline film grown on sapphire simultaneously with that on glass in experiment 164 (upper curve, Figure 2-14a). One set of points was obtained at the edge of the sapphire substrate that adjoined the glass substrate during the deposition, while the other was on another edge, perpendicular to the first, at a point removed from the location of the first measurement by $\sim 6 \text{ mm}$ (and thus that much farther from the glass substrate during the experiment). Comparison of the plots for the two films shows several features of interest. First, the resistivity in the region of the interface is essentially the same for the film on glass as it is for the film on sapphire at the location nearest the glass substrate. Second, the resistivity at the interface in the film on sapphire is considerably larger in the region near the glass substrate than it is in the other region. Third, at both locations in the film on sapphire the resistivity drops rapidly beyond 2 or 3 μm from the interface, decreasing to ~ 1 ohm-cm at a distance of 5 or 6 μm from the sapphire surface and then slowly decreasing through the remaining 10-11 μm to a value of 0.3-0.4 ohm-cm at the surface. This value is somewhat less than that obtained by the four-terminal method, results of which are given in the table; the latter measurement provides a value that is an average over a significant part of the thickness of the film, accounting for the magnitude obtained. The resistivity variation with depth in the film on glass, however, becomes significant only a few micrometers below the surface, as indicated earlier.

(a)

(b)

Figure 2-14. Spreading Resistance Probe Scans through Thickness of Doped CVD Si Films on (a) Corning Code 1715 Glass, and (b) Single-crystal Sapphire Substrates, for Two Different Boron Impurity Additions

In experiment 166 substrates of Owens-Illinois GS211 glass and single-crystal sapphire were used, again with a B_2H_6 flow rate of 500 ccpm, and films of about 15 and 9 μm , respectively, were obtained. (See Table 2-2.) Measured carrier concentrations (van der Pauw method) were nearly the same - on both substrates - as those obtained in experiment 165, and there were only slight differences in resistivities as measured by the four-terminal method. The spreading resistance measurement on the film grown on sapphire in this experiment showed only slight variation in resistivity with depth into the film, ranging from ~ 0.1 ohm-cm at the surface to an average of ~ 0.06 - 0.07 ohm-cm throughout most of the film, in very good agreement with the four-terminal value of 0.08 ohm-cm (Table 2-2). No excursion to very high resistivity at the interface was observed. Measurement of spreading resistance in the companion film on GS211 glass was not complete at time of preparation of this report.

The spreading resistance results for the experiments with Corning Code 1715 glass appear to be consistent with the possible presence in the CVD Si film of some compensating donor impurity that might enter the film from the substrate, in the case of the film on glass, or indirectly from the glass through the vapor phase, in the case of the film on sapphire. This glass is a calcium aluminosilicate known to contain additional minor amounts of various other impurities. However, it is not clear which of these impurities - if any - would be likely to produce the observed effects in Si films deposited at temperatures of $\sim 850^\circ\text{C}$ for relatively short times. The possibility of this as well as other causes of the results described above, such as residual surface contamination on the glass surface or charge depletion effects associated with the presence of the insulating substrate, is still being investigated.

The fact that the effects appear to be much more pronounced with 1715 glass substrates than with GS211 glass substrates is being carefully evaluated, as are the forthcoming results of similar measurements on films deposited on the other glasses of interest. Future work in the program with glass substrates may be strongly influenced by the conclusions of these studies.

X-ray diffraction analysis to determine line intensities was used for identifying preferred orientation tendencies in doped polycrystalline Si films grown on these glasses in the 850°C temperature range. In an experiment (181) in which a mixture of 1.5 ℓpm of He and 1.5 ℓpm of H_2 was used as the carrier gas, to test the stability of two of the glasses in such an atmosphere at $\sim 860^\circ\text{C}$, with a SiH_4 flow rate of 10 ccpm and a B_2H_6 flow rate of 50 ccpm, Si films were grown on polished substrates of Corning Code 1715 and Owens-Illinois GS211 glasses and single-crystal sapphire for 45 min, to produce films approximately 20 μm thick. X-ray analysis showed the film on the 1715 glass to be very strongly preferentially oriented with $\{100\}$ planes parallel to the interface. There was also a moderate $\{111\}$ preferred orientation, although it was much less prominent than the $\{100\}$ dominant orientation, and the $\{110\}$ planes were present but the line intensity (the $\{220\}$ line) was weaker than that of the $\{311\}$ planes. Thus, the distribution of principal low-index planes is quite similar to that found earlier in the program (Refs 1,4) for undoped Si films grown on this glass in the 850 - 860°C temperature range.

The film grown on GS211 glass in this experiment also showed strong $\{100\}$ preferred orientation, although it was not as dominant as in the film on 1715 glass. Also, there was not the evidence of $\{111\}$ preferred orientation seen in the film on 1715 glass. The $\{110\}$ planes, which had been found as a strong preferred orientation in an undoped film grown on GS211 glass earlier in the program (Refs 1,4), were

present but only to about the extent representative of a randomly-oriented sample. Thus, the orientation tendencies of this doped film on GS211 glass appear to be different from those seen earlier in an undoped film.

In another experiment (178) involving just the customary He carrier gas (at 1.5 lpm), Si was grown simultaneously on GS211 glass and single-crystal sapphire substrates at $\sim 860^{\circ}\text{C}$, with a B_2H_6 dopant flow rate of 300 ccpm. Again a strong $\{100\}$ preferred orientation was found by X-ray diffraction analysis, and again the diffraction line indicative of $\{110\}$ planes was present in about the relative intensity representative of a randomly oriented film. It has not yet been determined if the B impurity concentration added to these films influences the crystallographic orientation habit; some evidence of such an effect has been observed earlier in doped polycrystalline films grown on polycrystalline alumina (viz, Vistal) substrates (Ref 1), but no evidence for this has been found to date in the films on glass.

A doped Si film grown on a substrate of Owens-Illinois GS210 glass (experiment 171) at a temperature of 835°C , with a SiH_4 flow rate of 10 ccpm, He carrier gas flow rate of 1.5 lpm, and B_2H_6 dopant gas flow rate of 50 ccpm, was found by X-ray analysis also to exhibit strong $\{100\}$ preferred orientation. This orientation tendency was not as strong as that observed in the films on GS211 glass and far less than that characteristic of films grown on Corning 1715 glass in this same temperature range. The film on GS210 glass referred to here is listed in Table 2-2; the deposition was continued for 90 min, resulting in a $56\text{ }\mu\text{m}$ film on the glass but only about half of that thickness on the companion sapphire substrate. It is interesting that the film grown simultaneously on the sapphire substrate in this experiment exhibited orientation characteristics not greatly different from those of a randomly-oriented film; only a slight tendency toward $\{100\}$ orientation was noted.

In experiment 172 (see Table 2-2) a $38\text{ }\mu\text{m}$ film was grown on substrates of Owens-Illinois GS186 glass at a temperature of $\sim 840^{\circ}\text{C}$ for a period of 90 min; the SiH_4 and He flow rates had their customary values, and the B_2H_6 flow rate was again 50 ccpm. Once again, very strong $\{100\}$ preferred orientation was observed in the film, and in this instance the diffraction line representative of $\{110\}$ planes appeared somewhat more prominent than it would be for a randomly-oriented film.

The possibility of variations in apparent preferred orientation with azimuth angle in the plane of the film-substrate interface was examined briefly during the quarter for several of the polycrystalline films on glass mentioned above. (Similar measurements were also made with polycrystalline films on alumina substrates and are discussed in Section 2.5.2.) Films on GS211, GS210, and GS186 glasses were analyzed in this way. In all three cases some variations in diffraction line intensity ratios were found as the film was rotated in azimuth 45 and 90 deg from the position used initially for the diffractometer scan. However, in none of the instances was the ratio variation observed to be both systematic with angle and significant in magnitude. That is, the observations concerning preferred orientation tendencies in these films, as given in the preceding discussion, appear to be valid and are not biased by other effects - such as those that would be present if there were a high incidence of very large crystal grains in the films, as produced by Si growth on refired Vistal alumina substrates, for example.

It thus seems clear that CVD Si films grown on various glasses by the SiH_4 pyrolysis reaction in a He carrier gas in the 850°C temperature region tend to crystallize with a strong $\{100\}$ preferred orientation, at least when grown to thicknesses the order of $15\text{ }\mu\text{m}$ or more. Further studies of possible variations in this orientation habit as a function of film thickness as well as deposition temperature are in progress and will be discussed in later reports.

2.5.2 Properties of CVD Si Films on Polycrystalline Alumina Substrates

Measurement of the electrical properties was completed during the quarter on portions of those Si sheet samples from which samples OCLI-20, 21, 22, 23, and 24 were cut for use by OCLI in fabricating solar cell structures late in the third quarter. Measurements were made by both the van der Pauw method and the bridge technique.

Four of the films were on single-crystal sapphire substrates and one on polycrystalline alumina (MRC Superstrate). The results obtained by both methods are summarized in Table 2-3. The Hall bridge results confirm the van der Pauw results for all five samples. As is usually the case, the carrier concentrations determined by the Hall bridge method are somewhat smaller than the values obtained by the van der Pauw method. Similarly, the mobility value obtained by the bridge method is significantly larger than that found by the van der Pauw technique, for each of the samples. (See discussion in Ref 4, pp. 64-67.)

There are at least two significant things to be noted in these results. First, for the four epitaxial films grown on single-crystal sapphire under essentially identical conditions the carrier concentrations estimated from deposition parameters (see Table 2-18, Ref 1) were acceptably close except for experiment 139 (OCLI-20), in which the measured value was found to be an order of magnitude lower than expected (and the resistivity correspondingly higher). Photovoltaic performance of OCLI-20 was also found to be significantly poorer than OCLI-21, for example (Table 2-19), Ref 1); the carrier concentration of OCLI-21 as grown was $5.6 \times 10^{17}\text{ cm}^{-3}$ (Table 2-3), a value thought to be in the acceptable range for p-type single-crystal base material used for solar cell fabrication.

Second, the doped polycrystalline film (experiment 147) grown on polished polycrystalline alumina (MRC Superstrate) was found to have a free carrier concentration ($1.4 \times 10^{13}\text{ cm}^{-3}$) far too low for use as solar cell material, an observation consistent with the fact that the photovoltaic response was almost immeasurably low on sample OCLI-24 (see Task 6 discussion, Section 2.6). The B_2H_6 flow rate used in this deposition experiment had been selected to produce a doping concentration in the epitaxial film on sapphire that would be in the $\text{mid-}10^{16}\text{ cm}^{-3}$ range, based on previous results at higher doping levels. However, the measured carrier concentration in the epitaxial film was found to be only $2.5 \times 10^{15}\text{ cm}^{-3}$. Furthermore, it was not then known how large is the difference in available carrier concentration that actually occurs between epitaxial and polycrystalline Si films doped equally with B in this range during growth. This illustrates the importance of the study that has been in progress to establish the relationship between added B impurity concentration and available carrier concentration in polycrystalline Si CVD films doped during growth at 1025°C in H_2 .

Additional van der Pauw and Hall bridge measurements have been made on other films grown as part of this study of doping vs carrier concentration in polycrystalline

Table 2-3. Electrical Properties of B-Doped Si CVD Films Grown by SiH₄ Pyrolysis* in H₂ (4 lpm) at ~1025°C for Subsequent Fabrication into Solar Cell Structures by OCLI

Expt. No.	Sample Designation (OCLI No. **)	Polished Substrate Material	Obs. Dep. Temp. (°C)	Film Thickness (μm)	Method of Meas. ***	Resistivity (ohm-cm)	Carrier Concentration (cm ⁻³)	Hall Mobility (cm ² /V-sec)
139	OCLI-20	(011̄2) Sapphire	1024	18.8	vdP HB	1.5 1.8	3.0 x 10 ¹⁶ † 2.0 x 10 ¹⁶ †	135. 171.
140	OCLI-21	(011̄2) Sapphire	1027	25.3	vdP HB	0.10 0.10	5.6 x 10 ¹⁷ † 3.7 x 10 ¹⁷ †	105. 168.
141	OCLI-22	(011̄2) Sapphire	1030	21.5	vdP HB	0.12 0.13	5.2 x 10 ¹⁷ † 3.1 x 10 ¹⁷ †	96. 162.
142	OCLI-23	(011̄2) Sapphire	1024	25.2	vdP HB	0.22 0.22	2.6 x 10 ¹⁷ † 1.6 x 10 ¹⁷ †	110. 175.
147	OCLI-24	Poly, alumina (MRC Superstrate)	1030	24.0	vdP HB	5.0 x 10 ⁴ 2.0 x 10 ⁵	1.4 x 10 ¹³ †† 5.1 x 10 ¹¹ ††	8.7 60.

* SiH₄ flow rate 25 ccpm

** Sample sent to OCLI for processing was portion of original sample adjoining measured piece

*** vdP = van der Pauw; HB = Hall Bridge

† B₂H₆ flow rate 10 ccpm

†† B₂H₆ flow rate 2.0 ccpm

Si films, and it is now clear that a large and rapid decrease in free carrier concentration occurs as the added doping impurity is decreased in the range from 10^{18} to $\sim 10^{16}$ cm^{-3} . This result appears to be consistent with some of the conclusions advanced by Seto (Ref 9) for B ion-implanted polycrystalline Si.

There is still a lack of sufficient data for the critical dopant concentration range from 5×10^{16} to 5×10^{17} cm^{-3} , and until additional sample pairs with that B concentration are evaluated the final conclusions about the doping behavior of these polycrystalline films cannot be proposed. However, an indication of the nature of this behavior is given by the data plotted in Figure 2-15. The available carrier concentrations, measured by both van der Pauw and Hall bridge methods, in B-doped p-type polycrystalline Si CVD films deposited by SiH_4 pyrolysis at $\sim 1025^\circ\text{C}$ on polycrystalline alumina substrates are shown as a function of the B impurity concentration added during film growth. The latter was determined by measurements of carrier concentrations in companion epitaxial Si films grown simultaneously on single-crystal (0112)-oriented sapphire substrates; the implicit assumption made is that the available carrier densities measured in the single-crystal Si films adequately represent the added B impurity concentrations throughout the range investigated (10^{14} - 10^{19} cm^{-3}), an assumption subject to further verification.

Figure 2-15. Measured Carrier Concentration in B-doped Polycrystalline Si Films Grown by SiH_4 Pyrolysis at $\sim 1025^\circ\text{C}$ on Polycrystalline Alumina Substrates as Function of B Concentration Added during Growth (determined by measurement of carrier concentration in companion epitaxial Si films).

At very low added B concentrations ($\sim 5 \times 10^{14} \text{ cm}^{-3}$) the available carrier concentration in the polycrystalline films is in the low- to mid- 10^{12} cm^{-3} range. For increasing B impurity additions the available concentration increases but at a slow rate until the mid 10^{16} cm^{-3} range, above which a very rapid rise in the available carrier concentration in the polycrystalline film occurs as the impurity concentration is further increased. At a doping concentration of 10^{18} cm^{-3} the carrier concentration in the polycrystalline film is $\sim 5 \times 10^{17} \text{ cm}^{-3}$, or 50 percent of the added doping concentration. At 10^{19} cm^{-3} doping concentration the measured carrier concentration in the polycrystalline film is also 10^{19} cm^{-3} ; carrier concentrations in the polycrystalline films are essentially the same as those in the epitaxial films, although there are still significant differences in the carrier mobilities in the two cases in the 10^{19} cm^{-3} range.

These results appear to be independent of the specific polycrystalline alumina substrate used, that is, independent of the grain size in the polycrystalline film in the size range involved in these studies. However, as grain sizes approach $200 \mu\text{m}$ and larger, as occurs when substrates of refired Vistal alumina are used (Refs 1,4) for Si film growth, the relative importance of the properties of the individual crystal grains and those of the grain boundaries would be expected to change. Effects associated with such film structures are being examined as part of this study. In any case, the data given in Figure 2-15 are similar to those of Cowher and Sedgwick (Ref 10) and of Seto (Ref 9), although different in detail. Carrier mobility data (room temperature measurements) and film resistivity data are now being analyzed in terms of possible models of the conduction process in polycrystalline Si films in an attempt to evaluate the roles of impurity segregation, carrier trapping, and other possible effects associated with the grain boundaries. Further discussion will be given in subsequent reports.

X-ray diffraction analyses carried out during the quarter on B-doped polycrystalline Si films grown at $1025 - 1030^\circ\text{C}$ (observed temperature) on polycrystalline alumina substrates of MRC Superstrate, ASM805 (3M Co.), and Coors Vistal 3 and 4 (refired three and four times beyond normal processing) have given further confirmation of the tendency for very strong $\{110\}$ preferred orientation to occur in Si films grown on these materials. In two deposition experiments (146, 147) involving polished MRC Superstrate and Vistal 4, in which the SiH_4 flow rate was 25 ccpm and the H_2 carrier gas flow rate 4 lpm, the film growth rates were about the same (2.9 and $2.7 \mu\text{m}/\text{min}$, respectively) and the B_2H_6 flow rates used (0.1 and 2.0 ccpm, respectively) resulted in measured carrier concentrations of $< 3 \times 10^{14}$ and $2.5 \times 10^{15} \text{ cm}^{-3}$, respectively, in the epitaxial films grown simultaneously on sapphire. In both experiments the film on Superstrate exhibited a stronger $\{110\}$ orientation than did the film on Vistal 4. However, as noted in previous reports, there may still be some ambiguity in preferred orientation results obtained for films grown on polycrystalline substrates having many very large ($> 200 \mu\text{m}$ across) grains; this question is still not fully resolved.

In another pair of deposition experiments (150, 151) involving essentially the same CVD parameters but with much higher B_2H_6 flow rates (20 and 300 ccpm, respectively) that produced carrier concentrations of 1.8×10^{16} and $6.9 \times 10^{18} \text{ cm}^{-3}$, respectively, X-ray analysis again showed very strong $\{110\}$ preferred orientation on Superstrate and Vistal substrates (Vistal 4 in 150 and Vistal 3 in 151). However, in these experiments the preferred orientation was stronger in the films on Vistal than in those on Superstrate. Whether this apparent tendency for stronger $\{110\}$ orientation

on Superstrate in lightly doped Si films and stronger {110} orientation on Vistal in heavily doped Si films is a real effect or not requires further investigation. In general, such variations in film orientation with CVD parameters of film thickness and deposition temperature, for a given substrate material, should be determined because of their possible relationship to grain size and to barrier formation processes in films intended for photovoltaic application.

Si films grown in later experiments, in which SiH_4 flow rates of 10 ccpm and H_2 carrier gas flow rates of 1.5 lpm were used, exhibited similar characteristics. In one experiment (177) two substrates of large-grained ASM805 alumina (99.9 percent purity) that had been refired singly (that is, not stacked) one time beyond normal firing (see Table 2-1, Section 2.2.3.3, and Figure 2-7) were used - one with the "front," or more-reflective, side up and the other with the "back" side up. Very strong {110} preferred orientation was found in both doped films ($1 \times 10^{18} \text{ cm}^{-3}$ carrier concentration in epitaxial film on companion sapphire), more so in the film grown on the back, or less-reflective, side.

In an experiment (183) in which as-manufactured MRC Superstrate and single-crystal sapphire were used as substrates, but this time with the SiH_4 flow rate 25 ccpm and the H_2 carrier gas flow rate 1.5 lpm, Si films were grown at 1025°C with the B_2H_6 flow rate at 500 ccpm to produce heavy doping ($\sim 5 \times 10^{18} \text{ cm}^{-3}$) in the films, which were 18-20 μm thick. The polycrystalline film on the alumina was again very strongly {110} oriented, with other principal low-index planes present only to the extent expected for a randomly-oriented sample. There was evidence during the experiment that the portion of the film growing on the sapphire in the region nearest the alumina substrate was experiencing some perturbation in its orderly growth, which could have been some unidentified impurity emanating from the neighboring alumina.

A pair of polycrystalline Si films grown on polished and as-manufactured MRC Superstrate surfaces at 1025°C (experiment 184), with a SiH_4 flow rate of 10 ccpm and H_2 flow rate of 1.5 lpm, were in the 24-28 μm thickness range and had measured carrier concentrations of $\sim 3 \times 10^{17} \text{ cm}^{-3}$ produced by a B_2H_6 flow rate of 5 ccpm. X-ray analysis of these films also showed strong {110} preferred orientation, with the effect considerably more prominent in the film grown on the polished substrate, consistent with earlier comparisons of films grown on the two types of surface on this material.

Finally, a Si film grown with a very low B doping level ($\sim 10^{16} \text{ cm}^{-3}$ in the film on the companion sapphire substrate) on a polished MRC Superstrate substrate (experiment 186), with otherwise the same CVD parameters as in experiment 184, had even more pronounced {110} preferred orientation than the other samples described above. The other principal low-index planes were again in essentially random-orientation prominence in this film.

To verify that these preferred orientation observations for films on aluminas were not disproportionately influenced by any azimuthal anisotropy effects associated with the larger crystal grains in the Si films, the X-ray diffraction line intensities for the film on the as-manufactured MRC Superstrate of experiment 184 were examined for several rotational positions of the film (in its plane). Practically no difference in the line intensity ratios as a function of azimuthal rotation was observed for this sample. This experiment is being repeated for films grown on large-grained alumina substrates, such as Vistal 4, where the effect - if present at all - should be more pronounced.

Spreading resistance (SR) measurements made on some B-doped Si films grown on polycrystalline alumina substrates and their companion sapphire substrates have provided further information on the possibility of impurities from certain aluminas interfering with growth of films of desired properties. As an example, very lightly doped films grown simultaneously on single-crystal sapphire and as-manufactured MRC superstrate alumina at 1025°C (experiment 185), with SiH_4 flow rate 10 ccpm, H_2 flow rate 1.5 lpm, and B_2H_6 flow rate 0.5 ccpm, were found by van der Pauw and Hall bridge measurements to have average active carrier concentrations of $\sim 1 \times 10^{16}$ and $\sim 2 \times 10^{13} \text{ cm}^{-3}$, respectively, and resistivities of $\sim 6 \text{ ohm-cm}$ and $\sim 2 \times 10^4 \text{ ohm-cm}$, respectively.

The spreading resistance probe scan of the epitaxial film on sapphire as a function of depth into the film shows an average resistivity of about 10 ohm-cm (although there is considerable scatter in the data) from the surface to a depth of about 15 μm , below which a rapid increase in resistivity occurs through the final 3 or 4 μm , approaching a value in excess of 10^3 ohm-cm at the interface (Figure 2-16, lower curve). The resistivity throughout most of the thickness is fairly close to the value obtained by the four-terminal methods. When the SR probe values for ρ are converted to carrier densities, by means of the {111} bulk-crystal correction program, the value for the upper 15 μm of the film is $\sim 10^{15} \text{ cm}^{-3}$, an order of magnitude lower than the thickness-averaged value obtained by the Hall-effect methods.

There is also considerable scatter in the resistivity data obtained with the SR probe as a function of depth into the polycrystalline film grown on the alumina substrate in this experiment, as shown in the upper set of points in Figure 2-16. The resistivity begins increasing almost immediately from $\sim 4 \times 10^3 \text{ ohm-cm}$ at the surface to $\sim 2 \times 10^4 \text{ ohm-cm}$ at a depth

Figure 2-16. Resistivity as Function of Depth, Obtained from Spreading Resistance Probe Scans, for Lightly-doped Si Films Grown by SiH_4 Pyrolysis on Substrates of As-manufactured MRC Superstrate Alumina and Single-crystal sapphire at 1025°C in H_2 .

of $\sim 7.5 \mu\text{m}$ and finally to $2 \times 10^5 \text{ ohm-cm}$ or more in the interfacial region. This is consistent with the thickness-averaged value of $\sim 2 \times 10^4 \text{ ohm-cm}$ obtained by the other methods. These results are consistent with the presence of some impurity escaping from the alumina substrate and continuing to permeate the growing Si film on the alumina but in decreasing local density as the film thickness increases. Similarly, this same impurity may have access to the Si film on the sapphire in significant amounts only in the earlier stages of its growth, accounting partly for the differences in the two plots. Other possible explanations for the observed behavior exist, however, as was pointed out in Section 2.5.1.

The epitaxial Si films grown on single-crystal sapphire substrates simultaneously with the polycrystalline Si films on MRC Superstrate alumina substrates in experiments 183 and 184 (orientation characteristics of which were described earlier in this section) were also analyzed by spreading resistance measurements. The epitaxial film grown in experiment 183, CVD parameters for which were given previously, was found by the SR probe scan (Figure 2-17) to have a very uniform resistivity of $\sim 0.03 \text{ ohm-cm}$ throughout its thickness, with no indication of a significant increase in the interfacial region. The resistivity determined on another piece of the same sample by four-terminal measurements was 0.02 ohm-cm , in good agreement with the SR value.

The epitaxial Si film grown on sapphire in experiment 184, for which the CVD parameters were also given earlier, produced the SR probe scan also shown (upper set of data points) in Figure 2-17. Although the scatter of the data for this sample is somewhat greater than for the film of experiment 183, the resistivity is again very uniform with depth to a point $2\text{--}3 \mu\text{m}$ from the interface, averaging $\sim 0.09 \text{ ohm-cm}$ throughout, with the exception of the increase by about an order of magnitude near the interface. The average resistivity of this film as determined by the four-terminal method was also 0.09 ohm-cm .

Although the effect is not prominent in this sample, it appears that the resistivity plot is beginning to show the characteristics that are very prominent in the plot of resistivity vs depth for the lightly-doped epitaxial film on sapphire of experiment 185 (Figure 2-16). Additional investigations are necessary to determine if these effects are, in fact, caused by impurities entering the Si films during growth from the surface or the interior of the substrates being used. The evaluations may be extended to several aluminas (and possibly other polycrystalline ceramics) as well as to the glasses of primary interest, to provide further basis for substrate material selection.

Figure 2-17. Resistivity as Function of Depth, Obtained from Spreading Resistance Probe Scans, for Heavily-doped Epitaxial Si Films (Experiments 183, 184) Grown by SiH_4 Pyrolysis on Single-crystal Sapphire Substrates at 1025°C in H_2 .

2.6 TASK 6. FABRICATION AND EVALUATION OF SOLAR CELL STRUCTURES

The contract provides for the fabrication and evaluation of experimental solar cells in CVD Si sheet on various substrates. This part of the work is done by Optical Coating Laboratory, Inc., Photoelectronics Group, in City of Industry, CA, on a purchased-services basis.

The contract Statement of Work stipulates that the contractor shall "fabricate and evaluate solar cells with a minimum of 1 cm^2 area . . . " and that " techniques for producing solar cells from these films shall be, to the maximum extent possible, previously developed procedures." It is further stipulated that "one solar cell, on the average, shall be made per week during this program."

With the approval of the JPL Contract Technical Manager, an arrangement was developed with OCLI that provides the necessary solar cell processing and evaluation work yet still allows Rockwell personnel to concentrate on the Si CVD investigations involving low-cost substrate materials.

2.6.1 General Sample Processing Procedure at OCLI

Details of the handling processing, and measurement techniques applied to any one sample at OCLI are varied to accommodate the characteristics and/or limitations of the sample. There is a standard sequence of activities that is generally followed, to whatever extent possible. Standard and near-conventional solar cell processing methods are used, to allow correlation of results with those obtained with conventional bulk single-crystal Si cells. If such procedures exhibit limiting deficiencies when applied to the Si sheet material, then the procedures are modified and/or new processing methods are devised. It is intended that sufficiently rapid feedback of results will occur to permit timely influence of these results on subsequent CVD experiments at Rockwell.

The Si sheet samples received by OCLI are first routinely checked for surface characteristics, thickness, conductivity type, and resistivity by standard methods. In some cases a preferential etch is applied to delineate individual crystallites in selected areas; various surface treatments are used, if necessary, to prepare the sample for p-n junction formation. A small region of the sample is tested to determine if Schottky barriers of sufficiently good characteristics can be formed on the sheet surface to permit measurement of the minority carrier diffusion length in the as-received material.

A junction is formed by diffusion of phosphorus into the p-type sheet material. (In cases where conventional diffusion temperatures are too high for the sample involved, other barrier formation methods — such as ion implantation — may have to be introduced.) Diffusion oxides are removed and open-structure ohmic contacts are applied, using conventional deposition methods. The junctions are then isolated to reduce edge-leakage, and in some cases antireflection coatings are applied to permit more accurate measurement of photovoltaic conversion efficiency.

Because of the nature of the Si sheet samples it is occasionally found that conventional processing techniques cannot be successfully applied. The presence of excessive numbers of grain boundaries, a high concentration of carrier lifetime "killer" impurities, uneven sheet surface morphology, irregular or specially-shaped

sample configurations, temperature limitations associated with various substrate materials, and special contact configurations necessitated by the use of insulating substrate materials for the Si sheet growth may require development of alternative processing methods. These are established to meet the needs of the specific situation.

With illumination from a defined light source, such as the AMO or the AM1 spectrum from a solar simulator, the conventional photovoltaic parameters I_{sc} , V_{oc} , P_{max} , CFF, and power conversion efficiency are determined. The diffusion length of minority carriers in the completed cell structure is estimated or determined, if possible, by a photovoltaic method using a monochromatic light source. For samples in which the uniformity of photoresponse is of interest (for example, to examine effects of grain boundaries) a photocurrent scan of the surface of the sheet can be made using a small-diameter light spot to compare the output of various regions of the sample.

In most instances an array of small-diameter mesa diodes is formed on the junction structure by etching techniques. These diodes are evaluated separately to indicate the degree of homogeneity in the sample and correlate the electrical properties with any visible structural features (e.g., grain boundaries). Diode measurements include the photovoltaic parameters I_{sc} and V_{oc} , the dark forward diode characteristic, junction capacitance, and possibly an evaluation of trap properties.

Reports of all data and related observations concerning the sheet samples are supplied to Rockwell by OCLI. Technical consultation on the correlations between observed sheet properties and the details of the CVD sheet growth process takes place regularly as part of the working arrangement.

2.6.2 Si Sheet Sample Processing by OCLI

Several processed solar cell structures were returned by OCLI early in the fourth quarter, together with a written report on the procedures used and results obtained. Most of these results had been obtained earlier by personal communication and were included in the Annual Report (Ref 1). The only additional results not so included were those for samples OCLI-16, 22, 23, and 24; sample OCLI-15 has not been processed, as it was undoped. OCLI-16 was a polycrystalline film on ASM805 alumina (as fired), while OCLI-24 was a polycrystalline film on polished Superstrate; the other two were epitaxial films on sapphire (see Table 2-18, Annual Report, Ref 1).

The above samples were processed in the same way as samples OCLI-17, 20, and 21 -- as described in the Annual Report (Ref 1, pp. 134-135). Diffusion time of P from $POCl_3$ was 7 min. Separate n^+ islands (rather than connected n^+ islands as for OCLI-17, 20, and 21) were defined by acid-resistant tape masking and subsequent etching.

The results of the limited measurements made on these samples are summarized in Table 2-4. Reference should be made to Table 2-19 and the accompanying discussion in the Annual Report (Ref 1) for further details concerning the measurements. The new results given in Table 2-4 do not permit any further conclusions beyond those already discussed in the Annual Report.

Table 2-4. Results of Evaluation of Photovoltaic Properties of Solar Cell Structures in Si Sheet Samples OCLI-16, 22, 23, 24*

Measurement and/or Property	Control (2 ohm-cm s.c. Si)	Sample**			
		OCLI-16	OCLI-22	OCLI-23	OCLI-24
<u>Active cell area (cm²)</u>	~0.4	~0.4	~0.4	~0.4	~0.4
<u>W/o AR coating</u>					
AMO solar simulator					
V _{oc} (mV)	350	10	200	330	VLR
I _{sc} (ma/cm ²)	15.4	1	SR	5.0	VLR
Load power delivered (mw/cm ²)	SR	NM	SR	SR	VLR
W lamp (only)					
I _{sc} (ma/cm ²)	SR	NM	SR	SR	VLR
<u>After AR coating (SiO)</u>					
AMO solar simulator					
V _{oc} (mV)	NM	NM	290	NM	NM
I _{sc} (ma/cm ²)	NM	NM	7.5	NM	NM
Load power delivered (mw/cm ²)	NM	NM	NM	NM	NM

*See Table 2-18, p. 131, Annual Report (Ref 1), for properties of these samples.

**Symbols used: NM=not measured; VLR=extremely low reading--essentially zero; SR=suspect reading--too uncertain to report.

During the fourth quarter 11 additional Si sheet samples were delivered to OCLI for processing and evaluation. These are listed in Table 2-5 with their deposition parameters and relevant properties. Included were two polycrystalline films on Corning Code 1715 glass, two polycrystalline films on Owens-Illinois GS211 glass, two polycrystalline films on Owens-Illinois GS213 glass, one polycrystalline film on Owens-Illinois GS186 glass, one polycrystalline film on as-manufactured MRC Superstrate alumina, and two double-layer samples on single-crystal sapphire substrates, each consisting of a relatively thick p-type layer of medium B doping concentration ($\sim 5 \times 10^{17} \text{ cm}^{-3}$) on a thin ($4\text{--}7 \text{ }\mu\text{m}$) p^+ layer ($\sim 10^{19} \text{ cm}^{-3}$). Preparation of the latter samples was described in Section 2.4.

A spreading resistance probe scan was made on a small piece of the double-layer sample prepared in experiment 191, a portion of which was sent to OCLI as sample OCLI-35. The results of this scan, expressed both as resistivity and as carrier concentration as functions of depth into the composite film, are shown in Figure 2-18. The resistivity (and thus the calculated carrier density) is seen to be very uniform in the thicker upper layer; the calculated carrier concentration ($\sim 8 \times 10^{17} \text{ cm}^{-3}$) is somewhat higher than that estimated on the basis of deposition parameters (Table 2-5). In the heavily-doped bottom layer the measured resistivity averages 0.002 ohm-cm, while the calculated carrier density is $5\text{--}6 \times 10^{19} \text{ cm}^{-3}$ in this region. This doping concentration should be more than adequate for affecting the minority carrier lifetime properties of the upper p-type region through gettering action of the acceptor centers, the purpose for which this particular composite structure is intended.

Processing of the samples listed in Table 2-5 was still in progress at the time of preparation of this report. However, some preliminary results have been obtained and are outlined below.

The procedure used in fabricating cell structures in samples OCLI-25, 26, 28, 29, 32, 33, and 35, as well as in a single-crystal 2 ohm-cm Si control wafer, was as follows. All traces of previously applied metal contact pads or other surface debris were removed, followed by a standard degreasing (trichloroethane and blow-dry); no surface etch was used. All samples were then P-diffused simultaneously at 840°C for 15 min, using a POCl_3 source. All surface glasses were removed after diffusion by immersion in a $1\text{HF}:10\text{H}_2\text{O}$ etch for 30 sec, followed by a thorough wash and blow-dry. All samples probed n type at that stage.

A grid contact pattern of Ti-Ag was then deposited by vacuum evaporation through an aperture mask onto all samples. Etch-resistant tape was then used to cover a "picture-frame" around the edge of each sample. By means of wax masking, small areas about 1 mm in diameter were defined within the picture frame, and mesas were formed by etching in $1\text{HF}:10\text{HNO}_3$ long to remove $4\text{--}5 \text{ }\mu\text{m}$ of the Si film in the exposed regions. Approximately half of these mesa regions were crossed by a contact stripe of the deposited grid pattern. The tape frame was then removed, the mesas were masked, and the frame region was etched for ~ 20 sec. The region among the mesas was probed to confirm that it was uniformly p type, as was the contact frame. Ti-Ag was then vacuum deposited onto the picture frame region, with the mesa area masked. The Ti-Ag contact was not sintered at this stage, however.

Table 2-5. B-doped CVD Si Sheet Samples Submitted to OCLI during Fourth Quarter for Solar Cell Processing and Measurement

SAMPLE NO.	SUBSTRATE MATERIAL AND THICKNESS (μm)	OBSERV. DEPOS. TEMP. ($^{\circ}\text{C}$)	CARRIER GAS AND FLOW RATE (ℓpm)	SiH_4 FLOW RATE (ccpm)	DOPANT GAS* FLOW RATE (ccpm)	FILM THICKNESS (μm)	AVE. GROWTH RATE ($\mu\text{m}/\text{min}$)	FILM RESISTIVITY (ohm-cm)	HOLE CONCENTRATION (cm^{-3})	HALL MOBILITY ($\text{cm}^2/\text{V-sec}$)	SAMPLE DIMENSIONS (cm) AND APPROX AREA (cm^2)	FILM STRUCTURE AND/OR SURFACE TEXTURE
OCLI-25	Corning Code 1715 glass 800	850	He 1.5	10	50	30	~ 0.6	8†	$3.0 \times 10^{17}\dagger$	2.6†	1.1x0.9 0.99	Poly; {100} preferred orientation
OCLI-26	Corning Code 1715 glass 800	865	He 1.5	10	500	~ 11	0.24	0.20**	$2.6 \times 10^{18}\text{**}$	12**	1.5x1.0 1.5	Poly; {100} preferred orientation
OCLI-27	Owens-Illinois GS211 glass 1050	851	He 1.5	10	50	~ 19	0.38	0.37**	$1.2 \times 10^{18}\text{**}$	14**	1.2x1.3 1.6	Poly; {100} preferred orientation
OCLI-28	Owens-Illinois GS213 glass 1025	858	He 1.5	10	500	~ 16	0.36	0.37**	$1.6 \times 10^{18}\text{**}$	10**	1.2x1.2 1.4	Poly; {100} preferred orientation
OCLI-29	Owens-Illinois GS213 glass 1025	856	He 1.5	10	50	29	0.32	6.3**	$2.5 \times 10^{16}\text{**}$	40**	1.3x1.1 1.4	Poly; {100} preferred Orientation
OCLI-30	Owens-Illinois GS185 glass 1025	839	He 1.5	10	50	38	0.42	14**	$1.2 \times 10^{17}\text{**}$	3.8**	1.2x1.2 1.4	Poly; {100} preferred orientation
OCLI-31	Owens-Illinois GS211 glass 1050	861	He 1.5	10	300	27***	0.3***	0.5***	10^{18}***	10***	1.2x1.1 1.3	Poly; {100} preferred Orientation
OCLI-32	(0112) Al_2O_3 (Polished) 750	1025	H_2 1.5	10	5	25	1.4	0.12***	$6 \times 10^{17}\text{**}$	88**	1.2x0.8 0.96	Epitaxial
OCLI-33	MRC Superstrate Alumina (as mfd) 875	1025	H_2 1.5	10	5	25	1.4	2.3†	$2.6 \times 10^{17}\dagger$	11†	1.2x0.8 0.96	Poly; {110} preferred orientation
OCLI-34	(0112) Al_2O_3 (Polished) 750	1025	H_2 1.5	10	1) 300†† 2) 6††	1) 4*** 2) 17***	1) 1.3*** 2) 1.3***	1) 0.005*** 2) 0.1***	1) 10^{19}*** 2) $5 \times 10^{17}\text{***}$	1) 35*** 2) 90***	2.3x1.2 2.8	Epitaxial (both layers)
OCLI-35	(0112) Al_2O_3 (Polished) 750	1031	H_2 1.5	10	1) 295†† 2) 6††	1) 6*** 2) 21***	1) 1.1*** 2) 1.5***	1) 0.005*** 2) 0.1***	1) $2 \times 10^{19}\text{***}$ 2) $5 \times 10^{17}\text{***}$	1) 35*** 2) 90***	2.3x1.3 3.0	Epitaxial (both layers)

* Films B-doped from B_2H_6 -in-He (46 ppm)

† Measured by Hall bridge method

** Measured by van der Pauw method

†† Double Layer: No. 1 Deposited First, then No. 2

*** Estimate, based on CVD parameters and other factors.

Figure 2-18. Spreading Resistance Probe Scan Showing Resistivity (and Calculated Carrier Concentration) as Function of Depth in Composite P/P⁺ CVD Si Sample OCLI-35 (Table 2-5), Grown on Sapphire Substrate by SiH₄ Pyrolysis at 1031°C in H₂.

Preliminary evaluation of open-circuit photovoltages was then made using a tungsten-lamp source having a total intensity somewhat greater than 1 sun, although its output is largely in the wavelength region longer than 0.6 μm . Table 2-6 summarizes the results of measuring photovoltages on several mesas on each of the samples under these conditions; included are the highest and the lowest values obtained for those mesas tested in this preliminary examination. The contact to the top of the mesa for each entry in the table was made by a mechanical probe only, in direct contact with the Si (i. e., not on a Ti-Ag contact stripe).

It is evident from these data that the cell structure made in the composite p/p⁺ Si film sample (OCLI-35) compares favorably, in this very limited test, with the two single-crystal Si control wafers (each of which has a minority carrier diffusion length of $\sim 100 \mu\text{m}$). It also appears that the more lightly doped films of the pairs of polycrystalline films on glasses are more satisfactory. However, the results of further tests now in progress must be obtained before any major conclusions can be proposed. These results will be described in subsequent reports.

Table 2-6. Preliminary Measurements of Open-circuit Photovoltages
Obtained with Tungsten Lamp Source and Mesa Diodes Formed
in Samples OCLI-25, 26, 28, 29, 32, 33, and 35.

SAMPLE	OPEN-CIRCUIT PHOTOVOLTAGE V_{oc} (mV)	
	LOWEST	HIGHEST
Control No. 1 (s.c. Si) (Full backside contact)	525	550
Control No. 2 (s.c. Si) (Picture frame front contact)	375	398
OCLI-25 (Polycrystalline Si on 1715 glass; $3 \times 10^{17} \text{ cm}^{-3}$ in base region)	71	145
OCLI-26 (Polycrystalline Si on 1715 glass; $3 \times 10^{18} \text{ cm}^{-3}$ in base region)	4	12
OCLI-28 (Polycrystalline Si on GS213 glass; $2 \times 10^{18} \text{ cm}^{-3}$ in base region)	14	30
OCLI-29 (Polycrystalline Si on GS213 glass; $2 \times 10^{16} \text{ cm}^{-3}$ in base region)	156	200
OCLI-32 (s.c. Si on s.c. sapphire; $6 \times 10^{-17} \text{ cm}^{-3}$ in base region)	304	330
OCLI-33 (Polycrystalline Si on Superstrate alumina; $3 \times 10^{17} \text{ cm}^{-3}$ in base region)	52	80
OCLI-35 (s.c. Si double layer on s.c. sapphire; $5 \times 10^{19} / 8 \times 10^{17} \text{ cm}^{-3}$ in base region)	426	475

3. CONCLUSIONS AND RECOMMENDATIONS

Over 20 different suppliers have now submitted a variety of substrate materials for consideration and/or evaluation in this program. The latest are two high-temperature glazes formed on high-purity alumina wafers by the Ferro Corporation, to be tested by Si deposition experiments early in the coming quarter. Surfaces of several other possible substrate materials have been characterized--primarily by surface profilometry and SEM examination. In general, the lower the purity of the polycrystalline ceramic the poorer the surface quality (pits, voids), even after polishing. Some of the ceramics, such as mullite and zircon, appear to consist of crystallites of the primary material embedded in a glasslike matrix of some other material. It has also been found that refiring of polycrystalline aluminas, to produce enlarged grains, generally results in only limited grain enlargement unless the individual wafer surfaces are kept out of contact with other surfaces during the firing process.

The needed shift in emphasis from substrates of polycrystalline aluminas and other ceramics to substrates of lower-cost glasses has occurred during the fourth quarter. Efforts are continuing in the search for additional special glasses with properties closely matched to the requirements for Si film growth by CVD, and it is still hoped that suitable glass-ceramics can be obtained for evaluation in the near future.

Repeated evidence of some type of impurity contamination of Si films deposited on various glass substrates examined to date, as well as on the companion sapphire monitor substrates, has required that attention be given to identifying possible causes--such as instability of the substrate material in the CVD growth atmosphere, surface contamination caused by various processes used on the substrate during its manufacture, or residual impurities left by cleaning procedures employed prior to deposition experiments. It was determined that exposure to flowing He gas alone at typical Si deposition temperatures (850-900°C) does not produce detectable changes in the surfaces of four different substrate glasses of major interest (Corning Code 1715, Owens-Illinois GS213, GS211, GS186), while the surface of Owens-Illinois GS210 glass may actually be improved by the He "annealing" due to its low softening temperature. In the limited tests conducted to date, no detectable differences have been found in either full- or partial-coverage films of Si deposited by SiH_4 pyrolysis in He onto glass substrates cleaned by three different controlled procedures.

Deposition experiments during the past quarter have been concentrated on (1) production of p-type polycrystalline Si films in a range of B doping concentrations on glasses and polycrystalline aluminas, and (2) early-stage island-growth experiments on these same substrate materials. It was found that more uniform Si film growth rates can be achieved by reducing both He and H_2 carrier gas flow rates to 1.5 lpm at typical SiH_4 flow rates of 10 ccpm. It was also found necessary to establish preliminary data for available carrier concentrations in polycrystalline Si films vs added B concentration (in the form of 46 ppm B_2H_6 in He) for growth in He in the 850°C range, and some information of this type has been obtained.

Several unexpected phenomena have been observed for growth on various glasses under the above conditions. Growth rates, both on the glass and the companion sapphire, have been significantly depressed relative to the expected values for the parameters used, and are generally larger on the glass than on the sapphire. Evidence of some discoloration of the sample pedestal (susceptor) in regions surrounding the glass substrates was noted after some deposition runs, and in several instances there was clearly an interference with the orderly growth of the (polycrystalline) Si layer on the companion sapphire.

Electrical measurements have indicated a higher carrier concentration in the film on glass than in that on the sapphire in most cases, although the resistivity was generally higher in the film on glass. Spreading resistance measurements as a function of distance into the film have provided data consistent with the possibility of a compensating donor impurity entering the film from the substrate, at least for the case of Corning Code 1715 glass. Films grown to date on Owens-Illinois GS211 glass, on the other hand, have not shown such an indication of some compensating donor centers present in increasing density toward the interface. Similar measurements in doped films on other glasses are in progress.

Analysis of X-ray diffraction line intensities for Si films 15 μ m or more in thickness, grown under the standard conditions on various glass substrates, has shown that very strong {100} preferred orientation occurs in polycrystalline films deposited on Corning Code 1715 glass at ~850°C, and strong (but less dominant) preferred orientation of the same planes occurs in films on Owens-Illinois glasses GS211, GS210, and GS186. Investigation of possible variations in this orientation habit as a function of film thickness as well as of deposition temperature is in progress.

Post-nucleation island growth experiments with normal CVD parameters have indicated that essentially complete Si coverage of single-crystal sapphire or large-grained polycrystalline alumina substrates is achieved in ~0.1 sec for growth in H₂ at ~1025°C. Shorter exposure to the reactants results in partial coverage, and wide differences in the area density of Si islands on individual grains of polycrystalline alumina substrates have been observed, indicating a possible dependence of initial nucleation density on crystallographic orientation. Islands tend to congregate at grain boundaries and--to a smaller degree--at steps in the surfaces of individual grains in regions removed from the grain boundaries.

Similar experiments on various glass substrates, but involving Si deposition at ~850°C in He, have provided evidence that to date is somewhat conflicting. Some experiments tend to indicate that deposition for times the order of 0.1 sec results in complete coverage of the substrate by a layer of extremely fine-grained or perhaps even amorphous Si, while other experiments have raised doubts as to the integrity of a Si film grown for as long as 6 sec. Investigation of these nucleation and island-growth phenomena is continuing.

The study of the relationship between added B impurity concentrations and the available carrier concentrations in polycrystalline Si CVD films doped during growth at 1025°C in H₂ has been continued. Measured carrier concentrations in epitaxial films grown simultaneously on single-crystal sapphire substrates have been used as a measure of the B concentrations added to the polycrystalline films grown on alumina substrates. For B concentrations of ~5x10¹⁴ cm⁻³ the available carrier concentrations in the polycrystalline films are in the low- to mid-10¹² cm⁻³ range. Above the mid-10¹⁶ cm⁻³ B concentration range a very rapid increase in measured carrier concentration occurs as the added impurity concentration is further increased. For a B concentration of 10¹⁸ cm⁻³ the carrier concentration in the film is approximately 50 percent of that value, and at 10¹⁹ cm⁻³ the B impurity density and the carrier concentration are essentially the same. These and related data are being used to establish the impurity additions required for obtaining polycrystalline Si films of proper carrier concentrations for solar cell fabrication, and for identifying a satisfactory model for the conduction process in polycrystalline Si sheet material.

Additional B-doped polycrystalline Si films on four different glasses and one polycrystalline alumina, as well as epitaxial films on sapphire, have been prepared and submitted to OCLI for solar-cell fabrication and evaluation during the past quarter. Included were two double-layer p/p⁺ Si films, the p⁺ layer in each case doped to $\sim 10^{19}$ cm⁻³ to evaluate the possible improvement in photovoltaic performance that might accrue from minority-carrier lifetime enhancement caused by the presence of a gettering sublayer. Initial results indicate an improvement has occurred, so the composite structure will now be tested with polycrystalline films on other substrates. Si sheet solar cell structures now being processed are in the form of individual mesas approximately 1mm in diameter, with contact made to the top of the mesa by a Ti-Ag contact stripe and the base layer contacted by a single bus contact around the periphery of the sample. Other design variations are being developed while fabrication and evaluation of cell structures in this group of samples is being completed.

The results obtained with glass substrates to date are encouraging in that several glasses have been found that appear to be compatible with the Si CVD process atmosphere and - at least to some degree - with the Si film itself. However, these are two problem areas that require considerable further attention. First, it is necessary to identify and determine how to minimize the apparent impurity contamination which has been in evidence much of the time when the low-cost materials (especially glasses) have been used as substrates. Such contamination can be expected to influence the film nucleation and early growth process; grain sizes may be strongly affected and available carrier concentrations for given added doping densities may also be influenced. It is thus important to examine the effects of various substrate cleaning procedures on film nucleation and growth. The contamination usually reveals itself during thick film growth but, as indicated above, will probably also influence nucleation processes. Therefore, a successful cleaning procedure will also be indicated in more than one way.

The major source of contamination, on the other hand, may be the instability of the substrate in the growth atmosphere and/or the volatility of the impurities that are present in the substrate. It might be assumed that once the substrate is covered with Si then contamination would cease, but unfortunately the growing film does not coat the hot bottom of the substrate, which is in contact with the heated pedestal. This could be a relatively constant source of impurity contamination that would be alleviated only by sealing the substrate bottom, or perhaps removing the volatiles at a temperature higher than the growth temperature. Several procedures for minimizing contamination of this nature will be explored.

The second major problem area involved in use of low-cost glass substrates is that the Si films that have been grown on the glasses have not possessed grains with sizes that can be expected to result in high efficiency cells. Special large-grained alumina, such as Vistal, is not considered cost-effective as a substrate, and even though grains as large as 200 μ m are present in the refired Vistals the grain sizes are variable. Straightforward CVD growth procedures for Si do not seem to lead to orders-of-magnitude changes in grain size on the low-cost substrate materials. It seems necessary, at least with the substrates already tested, to deviate further from standard growth procedures in order to obtain large grains. This will be done by use of special procedures proposed prior to the start of the program, such as two-step growth processes using HCl and/or dichlorosilane and those involving annealing of partially-covered surfaces. This will first require continuing the experiments relating to nucleation and early growth on the most promising substrates and using

various techniques and/or growth parameters to produce larger grains on the substrate prior to complete film coverage. In particular, in situ annealing at various stages of the early post-nucleation growth of a film - when island coalescence is playing a dominant role in development of the layer - may cause significant effects.

The planned studies will also examine Si film orientation as a function of growth temperature, film thickness, and cleaning procedure. Reflection electron diffraction (RED) will be used to determine the thickness range at which major changes in film crystallinity occur for different film growth temperatures. This information will be helpful in determining the conditions most useful for effecting major changes in grain size and for selecting the most satisfactory glass substrate.

The results obtained to date in fabricating solar cell structures in both epitaxial Si films on sapphire and polycrystalline films on low-cost substrates continue to indicate that additional measures should be taken in preparing the films for such processing. In particular, the use of a heavily doped gettering layer beneath the principal base region should improve the minority carrier properties (esp. diffusion length) in the epitaxial layers processed into baseline reference cells, and might also produce distinct improvements in cells fabricated in polycrystalline films. First tests of this approach applied to epitaxial material are in progress, and it will be extended to polycrystalline Si films in the coming quarter.

Also, it has been pointed out before (Ref 1) that, because of impurity diffusion characteristics peculiar to polycrystalline Si films, it may not be possible to obtain an accurate measure of the best photovoltaic performance of solar cell structures in the CVD Si sheet material unless processing methods other than diffusion--such as in situ growth of the p-n junctions in the CVD reactor--are applied. This possibility should be explored experimentally as soon as possible.

The methods being used for film characterization in Task 5 - optical microscopy, scanning electron microscopy, x-ray diffractometry, surface profilometry, spreading resistance measurements, Hall coefficient (and resistivity) measurements, minority-carrier lifetime measurements by the pulse-MOS (C-V-t) method - will be continued. The complex nature of the mechanisms of charge transport in polycrystalline Si films requires that careful consideration be given both to the types of measurements made and the interpretation of these measurements. Attention should also be given to developing an improved model of conduction in polycrystalline films to fit the data being obtained. When the properties of the Si films have improved sufficiently, additional techniques--such as Schottky-barrier methods for determination of impurity distributions, EBIC-mode analyses with the SEM to investigate properties of individual crystal grains and the intervening grain boundaries, and surface photovoltage measurements to obtain effective minority-carrier diffusion lengths--will be applied to give more complete understanding of the Si sheet properties.

4. PLANS FOR NEXT QUARTER

The planned work for the next three months will follow the Updated Technical Program Plan given in Appendix B of this report. The planned work, summarized by task, is as follows:

TASK 1

The work of this task was completed during the second quarter.

TASK 2

1. Continue to screen new candidate substrate materials as they are received from various vendors, with major emphasis on glasses and related materials
2. Continue to examine effects of various controlled substrate processing steps on quality of deposited Si sheet material
3. Plan and carry out experimental evaluation of various configurations (e.g., single-component substrates, composite-layer substrates, substrate materials deposited in situ) of most promising substrate materials, to identify preferred configurations

TASK 3

1. Investigate in further detail the effects of various annealing cycles and procedures on grain size in Si films grown on low-cost substrate materials
2. Determine compatibility of glass and ceramic substrates in atmospheres containing dichlorosilane as source of Si for CVD
3. Complete experimental evaluation of two-step deposition process involving HCl and make decision regarding its further use in program.

TASK 4

1. Prepare samples of appropriately doped CVD Si films on selected glass and polycrystalline ceramic substrates for fabrication of experimental solar cell structures
2. Prepare p/p⁺ composite Si films on selected substrates for fabrication of solar cell structures with enhanced properties
3. Prepare samples of doped epitaxial Si on single-crystal sapphire substrates, at regular intervals, for processing into baseline solar cell structures
4. Prepare various CVD Si samples for evaluation and demonstration and for delivery to JPL.

TASK 5

1. Continue analyses of Si film and substrate structural properties by surface profilometry, x-ray diffraction, metallographic sectioning, reflection electron diffraction, and scanning electron microscopy techniques
2. Continue application of x-ray diffraction methods for determination of preferred orientation and grain size in polycrystalline CVD Si films on various substrates
3. Continue determination of film electrical properties by van der Pauw and Hall bridge measurements, and compare results at various doping levels
4. Continue measurements of electrical properties of doped polycrystalline Si films at various known impurity doping concentrations to provide data for model of conduction mechanisms in polycrystalline Si
5. Continue use of spreading resistance measurements to determine carrier concentration profiles and locate possible impurity contamination in polycrystalline Si films on glass substrates
6. Investigate and apply methods for measurement of minority carrier diffusion lengths/lifetimes in CVD Si films - including pulsed C-V method in MOS structures, EBIC-mode analysis of barriers in SEM, and surface photovoltage measurements.

TASK 6

1. Prepare and submit samples of CVD Si sheet to OCLI for solar cell processing and evaluation, emphasizing doped films on glass, glass-ceramic, and low-cost polycrystalline alumina and/or other ceramic substrates.

5. NEW TECHNOLOGY

No reportable items of new technology have been identified during the conduct of the fourth quarter of work on this contract, which is the period covered by this report.

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APPENDIX A. MANPOWER AND FUNDING EXPENDITURES

This report covers the fourth quarter of the contract, through the twelfth month. Through the eleventh month of the contract (that is, through November 27, 1976) a cumulative total of 5307 engineering and support manhours and a cumulative total of \$175,303 (excluding fee and commitments) were expected.

For the twelfth month of the contract (November 28 through December 31, 1976) a total of 341 engineering and support manhours and a total of \$12,564 (excluding fee and commitments) were expended.

The cumulative manpower expenditure total through December 31, 1976, is thus 5648 manhours, and the cumulative cost total (excluding fee and commitments) through that date is \$187,867.

APPENDIX B. UPDATED TECHNICAL PROGRAM PLAN

The Initial Technical Program Plan was approved by the JPL Technical Manager on February 4, 1976.

An Updated Technical Program Plan, revised to show changes in the date of completion of reactor modifications and the date of the design review for Task 1, was included in the Monthly Technical Progress Report for April, 1976. That revised plan was approved by the JPL Technical Manager on May 17, 1976.

A further updating of the plan, including a suggested change in schedule for Technical Goal No. 4 of Task 5, was shown in Quarterly Report No. 2 and in the Monthly Technical Progress Report for July, 1976.

Additional changes in the Technical Program Plan, involving changes in several technical goals, were discussed with and tentatively approved by the JPL Technical Manager at the Bimonthly Program Review Meeting at the Rockwell Anaheim facility on August 12, 1976. These changes were approved by the JPL Technical Manager on September 2 and September 21, 1976. The Updated Technical Program Plan shown here includes those approved changes.

Additional changes in several technical goals of the Technical Program Plan were discussed and agreed upon with the JPL Technical Manager at the Bimonthly Program Review Meeting held at the Rockwell facility on December 7, 1976. Formal approval of these changes, however, has not been received so the Updated Technical Program Plan that follows does not include them. The plan is updated to show the achieved technical goals (filled-in triangles) through December 31, 1976, and the actual manpower and funding expenditures through that same date.

CHEMICAL VAPOR DEPOSITION GROWTH
SILICON SHEET GROWTH DEVELOPMENT

JPL CONTRACT NO. 954372

TASK 2: LARGE AREA SILICON SHEET
JPL/ERDA LOW COST SILICON SOLAR ARRAY PROJECT

UPDATED TECHNICAL PROGRAM PLAN

(Note: Numbered technical goals are listed at end of each task)

TASK/ACTIVITY	1976												1977					
	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J
1. MODIFICATION AND TEST OF EXISTING CVD REACTOR SYSTEM A. PREPARE REACTOR SYSTEM FOR INITIAL CVD EXPERIMENTS B. DESIGN REACTOR SYSTEM MODIFICATIONS C. INSTALL NEW REACTOR SYSTEM COMPONENTS AND CONTROLS D. TEST MODIFIED CVD REACTOR SYSTEM E. DEFINE AND DOCUMENT STANDARD OPERATING PROCEDURE FOR REACTOR SYSTEM 1. Complete required modification of CVD reactor system 2. Conduct required Design and Performance Review																		
2. IDENTIFICATION/DEVELOPMENT OF SUITABLE SUBSTRATE MATERIALS A. IDENTIFY AVAILABLE CANDIDATE MATERIALS B. CONDUCT CVD EXPERIMENTS TO SCREEN AVAILABLE CANDIDATE MATERIALS C. VISIT SUBSTRATE SUPPLIERS TO ARRANGE PREPARATION OF SPECIAL MATERIALS D. CONDUCT CVD EXPERIMENTS ON SPECIAL SUBSTRATE MATERIALS E. EVALUATE COMPOSITE SUBSTRATE STRUCTURES F. INVESTIGATE EFFECTS OF SUBSTRATE SURFACE TREATMENTS ON Si PROPERTIES 1. Identify most promising available material(s) using conventional Si CVD growth techniques 2. Initiate experiments on deposition of metals for Si nucleation 3. Identify most promising special substrate material(s) 4. Specify preferred substrate surface treatment 5. Identify preferred configuration(s) of most promising substrate material(s)																		
3. EXPERIMENTAL INVESTIGATION OF Si CVD PROCESS PARAMETERS A. CONDUCT EXPERIMENTS TO IDENTIFY PREFERRED PARAMETERS FOR CANDIDATE SUBSTRATE MATERIALS B. INVESTIGATE 2-STEP DEPOSITION PROCESS FOR CANDIDATE SUBSTRATE MATERIALS C. STUDY EFFECTS OF <u>IN SITU</u> AND POST-GROWTH ANNEALING ON Si PROPERTIES D. ESTABLISH DOPING PARAMETERS FOR Si ON VARIOUS SUBSTRATES E. DETERMINE EFFECTS OF DOPANTS ON Si GROWTH PHENOMENA 1. Decision regarding application of 2-step process using HCl 2. Identify preferred parameters for p-type doping of CVD Si sheet 3. Select acceptor doping impurity most favorable to Si sheet growth 4. Identify preferred carrier gas for Si CVD growth process 5. Identify preferred <u>in situ</u> annealing procedure 6. Specify details of 2-step process for improved Si sheet growth 7. Define preferred CVD growth parameters for candidate substrate materials 8. Identify preferred parameters for n-type doping of CVD Si sheet 9. Determine/characterize effects of annealing procedures																		
4. PREPARATION OF Si SHEET SAMPLES A. PREPARE SAMPLES FOR MATERIAL CHARACTERIZATION STUDIES B. PREPARE SAMPLES FOR POST-GROWTH PROCESSING C. PREPARE SAMPLES FOR SOLAR-CELL FABRICATION																		

UPDATED TECHNICAL PROGRAM PLAN (Cont)

TASK/ACTIVITY	1976												1977					
	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J
5. EVALUATION OF SI SHEET MATERIAL PROPERTIES																		
A. APPLY X-RAY, SEM & OPTICAL TECH. FOR GRAIN SIZE DETERMIN. B. USE X-RAY AND ELECTRON MICROSCOPE METHODS FOR ORIENTATION DETERMINATION C. DEVELOP/ADAPT MODEL FOR INTERPRETING CHARGE TRANSPORT MEASUREMENTS D. MEASURE ELECTRICAL PROPERTIES USING CHARGE TRANSPORT AND STORAGE, SEM, AND OPTICAL METHODS E. DETERMINE IMPURITY CONTENT AND OTHER PROPERTIES BY SUITABLE METHODS																		
1. Obtain x-ray linewidth standards for grain size in polycrystalline Si 2. Establish detailed procedures for determining preferred orientations by x-ray methods 3. Establish details of x-ray methods to be used for grain size determination 4. Determine suitability/reliability of van der Pauw method for electrical properties 5. Complete apparatus (or vendor arrangements) for spreading resistance measurements 6. Determine applicability of dark-field transmission and-reflection electron microscopy methods for orientation determination in selected samples 7. Complete apparatus/procedure for determining minority carrier diffusion lengths by SEM and/or barrier photocurrent methods 8. Determine suitability of SEM techniques for grain size determination 9. Establish suitability of C-V-t measurements for determining minority carrier lifetimes 10. Determine suitability of SEM electron channeling method for grain-orientation determination 11. Complete definition of model • Correlate experimental data for electrical properties of polycrystalline CVD Si films with existing conduction model(s). 12. Establish correlation between electrical properties of polycrystalline Si films measured by van der Pauw and Hall bridge methods 13. Define improved model for electrical properties of polycrystalline Si films																		
6. FABRICATION AND EVALUATION OF SOLAR CELL STRUCTURES																		
A. ESTABLISH DETAILS OF OCLI SAMPLE PROCESSING AND EVALUATION MEASUREMENTS B. SUBMIT EPITAXIAL Si-ON-Al ₂ O ₃ SAMPLES FOR PROCESS AND MATERIAL BASELINE DATA C. SUBMIT SELECTED SAMPLES FOR CELL FABRICATION AND EVALUATION AND CORRELATE RESULTS WITH CVD EXPERIMENTS																		
1. Issue purchase order to OCLI for solar cell processing using CVD Si sheet samples																		
TECHNICAL DOCUMENTATION																		
A. PROGRAM PLAN AND UPDATE B. MONTHLY TECHNICAL PROGRESS REPORT C. QUARTERLY REPORT D. INTERIM SUMMARY REPORT E. ANNUAL REPORT F. DRAFT FINAL REPORT G. FINAL TECHNICAL REPORT H. LABORATORY OPERATIONS NOTEBOOK																		
TECHNICAL MEETINGS																		
A. TASK INTEGRATION SESSIONS B. PROGRAM REVIEW MEETINGS C. WORKSHOP																		

CHEMICAL VAPOR DEPOSITION GROWTH
SILICON SHEET GROWTH DEVELOPMENT

JPL CONTRACT NO. 954372

TASK 2: LARGE AREA SILICON SHEET
JPL/ERDA LOW COST SILICON SOLAR ARRAY PROJECT

PROGRAM LABOR SUMMARY

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PROGRAM COST SUMMARY

*excluding fee

JPL CONTRACT NO. 954372
CHEMICAL VAPOR DEPOSITION GROWTH
SILICON SHEET GROWTH DEVELOPMENT