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VACUUM DEPOSITED POLYCRYSTALLINE SILICON FILMS FOR
SOLAR CELL APPLICATIONS

Quarterly Report, September 15–December 31, 1979

MASTER

By
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March 1980

Work Performed Under Contract No. AC02-77CH00178

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U.S. Department of Energy

Solar Energy

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VACUUM DEPOSITED POLYCRYSTALLINE SILICON
FILMS FOR SOLAR CELL APPLICATIONS

QUARTERLY REPORT
FOR THE PERIOD SEPT. 15, 1979 - DEC. 31, 1979

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Norman A. Blum, and Frank G. Satkiewicz

MARCH 1980

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PREPARED FOR THE SOLAR ENERGY RESEARCH INSTITUTE
PHOTOVOLTAIC PROGRAM OFFICE
UNDER SUBCONTRACT XS-9-8278-1

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This First Quarterly Report covers the period September 15, 1979 to December 31, 1979, and describes work performed by the Johns Hopkins University, Applied Physics Laboratory for the Solar Energy Research Institute under Subcontract No. XS-9-8278-1. The Subcontract with SERI continues work previously supported for one year by DOE under Interagency Agreement No. ET-78-A-03-2208. C. Feldman is the Principal Investigator. Other professional staff members participating in this investigation are C. H. Arrington, N. A. Blum, H. K. Charles, Jr., and F. G. Satkiewicz. Technical assistance was provided by R. B. Givens, K. G. Hoggarth, E. W. Koldewey, and R. Neuwiller.

DESCRIPTION OF PROJECT

This study addresses the goal of fabricating low-cost, 10% efficient solar cells through the use of vacuum deposited, thin film, polycrystalline silicon. Work areas include methods of growing large grains, exploration and optimization of suitable substrate/bottom electrode material, improvement in photovoltaic efficiency, formation of n-layer by vacuum deposition rather than by diffusion, and analysis of film and junction properties. Emphasis is placed at each stage of the program on understanding and elucidating the pertinent physical and electrical phenomena through the judicious use of analytical tools such as secondary-ion mass spectrometry for impurity and compositional analysis and X-ray diffractometry and scanning electron microscopy for structure analysis.

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ABSTRACT

Polycrystalline silicon films 14-22 μm thick and with average grain diameters of 20-40 μm were deposited by vacuum deposition onto both ceramic and sapphire substrates which were previously coated with a thin (1-2 μm) TiB_2 conducting layer. The large grains are the result of an interaction in the initial growth stages between silicon and TiB_2 . SIMS studies of B/Ti/ Al_2O_3 , B/ Al_2O_3 , and Ti/ Al_2O_3 interactions are reported as part of a continuing investigation of TiB_2 formation and silicon interactions on the TiB_2 surface. The increase in grain size has lead to an improvement in the open-circuit voltage V_{oc} , but not to an increase in the short-circuit current J_{sc} . Capacitance-voltage measurements give results characteristic of an abrupt junction and a build-in voltage V_{D} consistent with the measured doping levels. A simple method for measuring the minority carrier diffusion length in the base region L_{n} is described. The measurements indicate that there is little change in L_{n} between large (20-40 μm) and small ($\sim 5 \mu\text{m}$) grained samples.

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1. INTRODUCTION

This is the First Quarterly Progress Report describing investigations on thin-film polycrystalline silicon solar cells performed under the Solar Energy Research Institute (SERI) Sub-contract XS-9-8278-1. The work is a continuation of research performed under Interagency Agreement ET-78-A-03-2208 with the Department of Energy.

The study addresses the DOE goal of fabricating low-cost, 10% efficient solar cells through the use of vacuum deposited, thin-film polycrystalline silicon. It is visualized that each step of the solar cell fabrication would be performed in a vacuum chamber and that the complete process would be carried out automatically in mass production. Investigations being carried out at present correspond to the separate fabrication steps in the formation of all-vacuum deposited solar cells. The cells are formed by successive depositions onto substrates of bottom electrodes, silicon layers, and top electrodes. Since the behavior of each successive layer depends upon what lies below, the entire film system is being examined concurrently.

Investigations during the prior year resulted in a structure consisting of a vacuum deposited silicon layer on a titanium boride coated Al_2O_3 substrate. An n-type layer was formed on the silicon film by diffusion of phosphorus into the surface forming the necessary p-n junction. In the present study, the n-layer is to be formed by vacuum deposition as well as by diffusion. Sets of masks which will allow junction formation by both diffusion and vacuum deposition were designed and fabricated this quarter (Section 5.1). The TiB_2 in the device structure serves as a bottom electrode and, in addition, appears to aid in the formation of large silicon crystallites. Since large crystallites are necessary in order to obtain high efficiency photovoltaic devices, an understanding of the Si- TiB_2 interaction is

essential. Through the use of low supersaturation ratios during deposition of silicon plus the under coating of the TiB_2 layer, Si crystallite size was increased from approximately 5 μm to 20 μm during the prior year. During the present quarter, a film with an average grain surface diameter of approximately 40 μm was formed; some crystallites in the layer appeared to be as large as 50 μm (Section 2). Due to the large crystallite growth at high temperatures on the TiB_2 surface, further effort must be spent in examining the TiB_2 surface with considerably more care than was done the preceeding year. The conclusions drawn last year, that the growth phenomenon was due to the formation of titanium silicide, needs to be confirmed. The role of SiB_6 which was observed in some samples needs to be examined. The kinetics of the TiB_2 formation must be fully understood. The studies on titanium boride are described in Section 3.

It will be shown in a discussion of the photovoltaic properties, in Sections 4 and 5, that increasing the grain size increases the open circuit voltage, but not necessarily the short-circuit current. The short circuit current is controlled by the minority carrier diffusion length which does not appear to have increased with grain size (Section 5.4).

A paper entitled "Vacuum Deposited Polycrystalline Silicon Solar Cells for Terrestrial Use" was presented at the 14th IEEE Photovoltaic Specialist Conference in San Diego, January 7-10, 1980. A copy of the paper is given in the Appendix and will be referred to in the main body of this report.

2. SILICON FILM FORMATION

2.1 Deposition Conditions

Vacuum depositions of silicon are being carried out in two entirely different vacuum systems. One is an oil-diffusion pumped, liquid nitrogen trapped system with a base pressure in the 10^{-9} Torr range. Silicon is deposited in the 10^{-7} Torr range. The rise in pressure is due to the high substrate temperature used as well as outgasing from the silicon source. During the deposition of silicon, the chamber is isolated from the oil diffusion pump and a titanium getter pump plus a small ion pump is used to maintain the vacuum. The second vacuum system uses oil-free pumping techniques and incorporates an ion-pump and an adsorption pump. The base pressure is in the low 10^{-10} Torr region. A small pin-hole leak in the inner jacket of the stainless steel, water-cooled bell-jar was recently discovered and this leak, plus a faulty isolation valve (which is still not working properly), has prevented the deposition until recently of silicon at the anticipated pressures in this second unit. The effect of vacuum pressure and type of vacuum system on the properties of the silicon films has not yet been determined. The silicon is deposited by electron-beam heating from water-cooled, molybdenum lined crucibles. A detailed description of the apparatus was given in the 1979 Final Report⁽¹⁾ and will not be repeated here.

Silicon samples deposited this quarter are listed in Table I. As in previous reports, the data listed in the Table refers to the particular sample measured and is assumed to be similar to the other samples in the run. Data for the other samples discussed in this report are given in the prior Final Report.⁽¹⁾ All of the depositions were done at high temperatures with the resulting large grain size on the TiB_2 -coated substrates. Boron doping was between about 5×10^{17} and 2×10^{18} atom/cm³. In some samples the initial deposition temperature was different from the final temperature.

TABLE I
SILICON FILM PARAMETERS

Sample	Substrate	Sub. Temp. (°C)	Thickness (μm)	Deposit Rate ($\text{\AA}/\text{min}$)	Grain Size μm
Si 236A	Alumina	1250	14	470	5-35
B	Alumina				
C	Alumina/TiB ₂ 264B				
D	Alumina				
E	Sapphire/TiB ₂ 278E				
F	Sapphire				
G	Sapphire				
Si 237A	Alumina	1240	22	610	20
B	Alumina/TiB ₂ 279D				
C	Alumina				
D	Sapphire/TiB ₂ 272B				
E	Alumina/TiB ₂ 279F				
F	Alumina				
G	Sapphire				
Si 238A	Alumina	1280; 2 hrs 1160; 3 hrs	22	610	40
B	Alumina/TiB ₂ 282F				
C	Alumina				
D	Alumina/TiB ₂ 282D				
E	Sapphire/TiB ₂ 282E				
F	Alumina				
G	Sapphire				
Si 239A	Alumina	1210; 0.5 hrs 1060; 5.5 hrs	20	560	half 4, & half 10
B	Alumina				
C	Alumina/TiB ₂ 279C				
D	Alumina/TiB ₂ 282C				
E	Alumina/TiB ₂ 282B				
F	Alumina				
G	Sapphire

Fig. 1 SEM photomicrograph illustrating large silicon grains on Si 238E (800X).

The seeding or nucleation stage of deposition was carried out at a high substrate temperature* to produce large initial seed crystallites. The remaining deposition was carried out at somewhat lower temperatures resulting in perhaps a more pure film than if the entire deposition were done at the higher temperature. Unfortunately, time does not permit a separate research study in the use of two temperatures, but variations will be made and noted in the course of producing samples. Sample Si 238E, resulting from this two temperature technique, has uniformly distributed large grains. A SEM photomicrograph of the sample surface is shown in Figure 1. At the substrate temperatures being used, the silicon frequently adheres only to those areas covered by the titanium boride. The high temperature requirement to obtain large crystallite growth is achieved through the use of fused silica, iodine-filled, tungsten filament lamps. At high temperatures the lifetime of the lamps is very poor and some consideration may be given to a new heater design.

2.2 Silicon Nuclei Formation

In order to understand fully the reasons for the large silicon grain growth on TiB_2 -coated substrates, studies were carried out in the ion-pumped system using a substrate heater arrangement in which one of the 4-inch long, 3/8-inch diameter heating tubes was positioned in front of the face of the substrates so as to cause a shadowing effect of the edge of the deposit. This allows one to observe phenomena in very thin layers while forming thicker layers in the same sample. Some of this work was described previously.⁽¹⁾

The phenomena that occur during the initial stages of growth are illustrated in Figures 2 - 4. The nuclei, or seed crystals, shown in these figures do not necessarily represent the initial structure in the thicker portion of the sample, nor of the samples used in device formation. The arrival rate of atoms in the shadowed region is considerably less than in the unshadowed film, and the thin region is subjected to high temperature for a long period without being covered

(a)

(b) →

(c)

Fig. 2 SEM photomicrograph illustrating initial island formation of Si/on TiB_2 at different substrate temperatures: (a) 1160°C , (b) 1220°C , (c) 1270°C (1KX)

(a)

(b)

Fig. 3 SEM photomicrograph of SI*234D: (a) Si on boron, (b) Si on TiB_2 (1KX)

Fig. 4 SEM photomicrograph of SI*236E illustrating silicon islands before complete coverage (1.1KX)

over by a fresh silicon deposit. The figures do, however, illustrate the effects of temperature and substrate surface coating on nuclei formation and serve as a guide to understanding the phenomena involved.

The initial nuclei or seeds formed on the substrate depend on the surface diffusion distance χ_s of the atoms on the substrate. The diffusion distance is governed by the surface diffusion constant D_s and the lifetime of the arriving atom t_s . Thus:

$$\chi_s = (D_s t_s)^{1/2} \quad (1)$$

Here, $D_s \sim \exp(-E_d/kT_s)$ and $t_s \sim \exp(E_a/kT_s)$ where E_d and E_a are the activation energies for diffusion and desorption, respectively. This leads to an expression for the diffusion distance of

$$\chi_s = a \exp\left[(E_a - E_d)/2 kT_s\right], \quad (2)$$

where a is the distance between adsorption sites. It is generally assumed that new nuclei stop increasing as soon as the nuclei are one diffusion length apart. The nuclei then grow in two and three dimensions until they run into one another. The saturation number of nuclei is then given by the following expression:

$$N_s = \frac{1}{\chi_s^2} = \frac{1}{a^2} \exp\left[-(E_a - E_d)/kT_s\right] \quad (3)$$

From expression (3), since $E_a > E_d$, one sees that the higher the substrate temperature the greater the number of nuclei per unit area. Under the deposition conditions used here this is not the case. Figure 2 shows a series of SEM photomicrographs taken at the same magnification for three silicon films deposited at three different substrate temperatures on the TiB_2 -coated alumina substrates. The effect of temperature on these initial nuclei is clearly seen. The number of nuclei (islands) decreases as the substrate temperature

increases. Note that the SEM photomicrograph in Figure 2a was taken at a higher electron beam voltage than the other two photomicrographs. This accounts in part for the somewhat different appearance of the crystallites in that figure. The reason expression (3) gives the wrong temperature dependency lies in the desorption term. Account must also be taken of cluster size and capture rates which are affected in the case under study by compound formation. In more sophisticated theories, the saturation number of nuclei decreases with increasing temperature.⁽²⁾ The fact that expression (3) does not describe the observed behavior tends to indicate that silicon atoms may not be lost by desorption in spite of the low supersaturation ratio. This is in agreement with the measurements reported previously in which little difference in thickness was observed between cool and hot substrates.⁽³⁾

Figure 3 gives a side by side comparison of silicon nuclei formed on TiB_2 -coated alumina and boron-coated alumina at the same substrate temperature. The boron coating in this case was an exposed edge created during the formation of the titanium boride layer. As can be seen, the nuclei are far larger on the TiB_2 -coated substrate. It has been established from other experiments (see for example Figure 5 of the Final Report⁽¹⁾) that the nuclei are also smaller on the bare alumina substrate than on TiB_2 -coated substrate. The difference in the nuclei-cluster size deposited at the same rate and the same temperature is accounted for in expression (1) by the differences in atomic surface diffusion and lifetime.

The size of the crystal islands determines to some extent the size of the resulting crystallites. Thus, films deposited at higher substrate temperatures and on TiB_2 /alumina result in larger diameter crystallites. This can be seen by the curve in Figure 3 Appendix in which supersaturation ratio, which is directly related to substrate temperature is plotted against grain diameter for samples of essentially equal thickness.

Once complete coverage of the substrate is achieved, the subsequent deposits of silicon on silicon (homonucleation) should behave somewhat differently than in the heteronucleation case. The substrate temperature for best growth conditions, for example in the homonucleation case, may

be different (less) than that used in the initial seed formation. This is why the temperature was reduced during some of the depositions reported here.

Figure 4 shows the appearance of the silicon islands just before complete coverage. Figures 2 and 4 in this report can be compared with Figure 11 of the Final Report.⁽¹⁾ Sample Si*229E described in the 1979 Report was deposited at a lower substrate temperature than the recent sample described here.

2.3 SIMS Analysis of Large and Small Silicon Grains

A SIMS study was made of the impurity levels of a silicon film deposited on TiB₂-coated sapphire containing regions of both large and small grains. The sample, Si*236E, was deposited in the ion-pumped system and is not representative of the lower levels obtainable in the oil-pumped system. The results of the study presented in Table II show that there is little difference in impurity level between large (> 20 μm) and small grains (5 μm) regions. The sample was examined from the surface down to a depth of 1 μm and the similarity of composition of the large and small grained regions supports the view that the large grains are not the result of eutectic formation leading to a liquid-vapor type of growth. As stated in the Final Report,⁽¹⁾ the large grains are believed to be due to the formation of larger initial seed nuclei which are related to the formation of TiSi₂ and SiB₆.

TABLE II
LARGE GRAIN vs SMALLER GRAIN MAXIMUM IMPURITY
CONTENT Si*236E (ION-PUMPED SYSTEM)

SPECIES	Concentration ($\times 10^{18}/\text{cm}^3$)	
	LG	SG
B	1.0 ± 0.51	0.88 ± 0.23
Na	0.10 ± 0.06	0.042 ± 0.024
Al	0.49 ± 0.25	0.24 ± 0.15
Ti	0.071 ± 0.026	0.058 ± 0.023
Cr	0.10 ± 0.01	0.14 ± 0.05
Fe	ND	$< 2.7 \pm 1.8$
Ni	ND	$< 0.82 \pm 0.53$
Cu	ND	$< 0.46 \pm 0.57$ (decrease w/depth)
Mo	0.29 ± 0.12	0.18 ± 0.09

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3. THE BOTTOM ELECTRODE - SUBSTRATE

3.1 TiB₂ Deposition

The TiB₂ samples used in the formation of silicon devices shown in Table I are listed in Table III. The samples were formed by deposition of Ti and B in separate vacuum chambers. The TiB₂ reactions were carried out in the system used for the deposition of boron. The procedures for the TiB₂ formation are described in the prior Final Report.⁽¹⁾ In addition to forming samples for photovoltaic devices, special thin samples were deposited to allow detailed SIMS analysis. As stated previously,⁽⁴⁾ excess boron is removed slowly by reaction with water vapor or oxygen in the vacuum.

Since the titanium diboride used as a bottom electrode also appears to partially react with silicon at elevated temperatures to provide nuclei for large grains, it has become important to characterize the surface in greater detail. This includes an examination of the reaction kinetics of TiB₂ formation as well as the loss of excess boron. In addition, a knowledge of the surface composition of the TiB₂ just prior to silicon deposition is required. There is some evidence that carbon or carbon compounds occasionally form on the TiB₂ which may then affect the silicon adhesion or grain size.⁽³⁾

3.2 SIMS Studies on the Boron-Titanium Interactions

Several unreacted films of B/Ti/sapphire (TiB₂ 285) were prepared. These were made thinner than those for practical applications in order to simplify the SIMS studies. The thicknesses of the B and Ti layers were measured by optical interference using one sample and assuming the same value for the rest of the six samples. One unreacted sample was examined by SIMS to obtain the relative ion yields of the B and Ti and to provide reference profiles for depth resolution corrections. Unfortunately, pinholes often present on such thin films ($\sim 2000 \text{ \AA}$)

TABLE III
BOTTOM ELECTRODE (TiB₂) PARAMETERS

Sample	Ti Thickness (μm)	B Thickness (μm)	TiB ₂ Thickness (μm)	Calculated Excess (μm)	Formation Temp (°C)	Time - Hrs in Vacuum	Resistivity (μΩ-cm)
TiB ₂ 264	0.77	0.89	1.11	0.23 B	945	3.0	60
TiB ₂ 272	0.74	0.71	1.07	0.07 B	950	4.5	82
TiB ₂ 278	2.47	2.21	3.59	0.09 B	950	4.0	-
TiB ₂ 279	0.29	0.30	0.42	0.05 B	950	4	160
TiB ₂ 282	1.77	1.33	2.24	0.23 Ti	980	10	70
TiB ₂ 285	0.118	0.150	0.17	0.05 B	950	0.5*	74

* Special thin sample - see SIMS discussion - heated in He.

Fig. 5 Intensity-time profiles from the sputtering of sample TiB_2 285D (unheated B/Ti/sapphire).

complicated profile calculations, especially in relation to the film/substrate interactions. The neutral sputtering rates of B and Ti were obtained by sputtering separate films deposited on sapphire.

In addition to studying the interaction in B/Ti/Al₂O₃, B/Al₂O₃, and Ti/Al₂O₃ this quarter, the O₂-TiB₂ interaction results from a previous study of TiB₂ are used here to provide an understanding of the total phenomenon.

The samples were heated at 950°C for various times in either a He atmosphere tube furnace and in vacuo in the commercial NRC deposition system (oil-pumped). The work is still in progress. However, one set of results will be described in detail to illustrate the way in which interpretation of the intensity vs time data is made.

Sample TiB₂ 285D was sputtered with a defocused beam of 10 keV Ar⁺. The ¹¹B⁺, ¹⁶O⁺, ²⁷Al⁺, and ⁴⁶Ti⁺ or ⁴⁸Ti⁺ intensity profiles were obtained in repetitive succession. These are plotted in Figure 5 against sputtering time. The energy window was 250 eV. When the beam sputtered through to the substrate, chargeup occurred resulting in an abrupt loss of signal. This phenomenon was used as an indicator for the removal of the film. Subsequent crater depth measurements gave the thicknesses of the composite films. The profiles start after the removal of 90 Å of boron since four area elements would have been needed to reconstruct the initial profiles of all four species. Within two minutes it is possible to "sit on" all four peaks. (In this run, the oxygen profile starts somewhat later; in the subsequent calculations a background oxygen intensity level was assumed.) The boron profile shows a rise up to the point where the Ti profile becomes prominent, plunges, and then levels out. The Ti profile shows a plateau in the boron region followed by a maximum, a small plateau, and second maximum at the substrate. The oxygen profile has features similar to the Ti profile. The Al signal rises gradually and then very

Fig. 6 The effect of oxygen on the Ti^+ yield from sputtering a titanium film with 10 keV Ar^+ ; $E_w = 250$ eV.

steeply at the substrate. The interpretation of the curves is not trivial. How does one convert intensity to concentration and time into depth from the surface? The case of one pure material on another separated by a mathematical plane is straightforward and involves only the relative ion yield of B and Ti as well as their respective total sputtering yields. The plateau then represents a pure phase and is the intensity that results when sputtering pure boron under the fixed primary beam conditions. This intensity corresponds to a surface or phase fraction of boron of value unity. (See Quarterly Report #3, p. 27,⁽³⁾ for a discussion of these terms.) When the time for the signal to drop to zero is divided into the film thickness, the total sputtering rate is obtained (constant density and beam conditions assumed). The same applies to the titanium plateau.

In practice, the intensity profiles are more complicated and require additional treatment. The greatest difficulty is the effect of oxygen on the ion yield. In this sample, the oxygen signal is derived not only from the bulk but from background sources. Furthermore, the presence of TiO_x between the B and Ti is indicated by the similar Ti and O profiles. The effect of another oxygen source also shows up as the substrate is approached where the enhanced Ti signal comes from the oxygen due to co-sputtering of the Al_2O_3 . The use of an oxygen beam or sputtering in a high oxygen background to diminish yield problems leads to either loss of information or another set of complications. However, studying the effect of O_2 on pure Ti or B (and TiB_2 in the case of the heated couple) provides profile correction factors. The responses of the Ti^+ peak from Ti to O_2 and for B^+ and Ti^+ from TiB_2 to O_2 are shown in Figures 6 and 7.

The oxygen intensity was decoupled by using the following expression derived from the sputtering of single films or bulk samples.

Fig. 7 The effect of oxygen on the B^+ and Ti^+ yields from sputtering a TiB_2 film with 10 keV Ar^+ ; $E_w = 250$ eV.

$$I_{O^+})_{B, \text{ Bkgd}} = 0.00079 I_{111B^+} \quad (4)$$

$$I_{O^+})_{Ti, \text{ Bkgd}} = 0.0114 I_{48Ti^+} \quad (5)$$

$$I_{O^+})_{Al_2O_3} = 0.01 I_{Al^+} \quad (6)$$

The use of (4) - (6) gives a more realistic estimate of the oxygen distribution than the total O^+ profile alone.

The first plateau in the Ti profile can be attributed to one of the following:

- a. memory from previous sputtering;
- b. presence of pinholes in the boron;
- c. presence of Ti in the boron starting material;
- d. diffusion of Ti in boron;
- e. "push out" effect or displacement of incoherent Ti or TiO_x by the deposition of boron atoms; and
- f. beam inhomogeneity.

Most likely of the above are b and f. The presence of pinholes was observed in the Ti and B calibration films. The extent of the plateau almost corresponds to the Ti plateau upon reaching the bulk of the Ti layer. Pinholes in the Ti layer may also account for the initial portion of the Al^+ profile. The humps in the Ti^+ profile and O^+ profile coincide, suggesting the presence of an oxide or oxygen rich interface. The sputtering of Ti alone showed a spike in the initial Ti^+ and O^+ intensities which could be attributed to a surface oxide. Although not necessarily proved, the initial rise of the Ti^+ profile was considered to be associated with the sputtering of an oxide. The relative ion yield of Ti out of this matrix was taken to be $12.8 Y_{Ti} \text{ (element)}$.

Beyond the maximum was assumed to be essentially elemental Ti. The relative ion yields (E_w of 250 eV) used in calculating the concentration of atoms is shown in Table IV.

TABLE IV
Relation Ion Yield Factors

Species	Y ($Y_{Ti (TiB_2)} = 1$)
B (element)	1.4
B (TiB_2)	0.064
Ti (element)	0.29
Ti ($Ti-O_2$)	3.7
Ti (TiB_2)	1
O (Al_2O_3)	0.2
Al (Al_2O_3)	28.5

These were applied to the decoupled intensities. The concentration (surface fraction of atoms, f) was calculated from

$$f_X^+ = \frac{\frac{I_X^+}{Y_X^+}}{\frac{I_X^+}{Y_X^+} + \frac{I_Z^+}{Y_Z^+} + \dots + \frac{I_N^+}{Y_N^+}} \quad (7)$$

where the I's are intensities of all the major species and the Y's their corresponding relative ion yields.

The relation of time to depth for an unreacted sandwich of two films is readily obtained by applying the respective total sputtering yields to the times demarcating the intensity plateaus of the layers. For mixtures of phases the problem is more complicated. The region between B and Ti contains another compound with its own sputtering rate. Due to imperfect depth resolution (or diffusion) various phases overlap. In this region it appears reasonable to obtain a combination sputtering rate.

Fig. 8 Concentration-depth profiles from the sputtering of sample TiB₂ 285D (unheated B/Ti/sapphire).

Thus at the interface:

$$R_C = f_B R_B + f_{Ti} R_{Ti} + f_{Al_2O_3} R_{Al_2O_3} \quad (8)$$

where the f 's are phase or surface atom fractions and the R 's total sputtering rates for the phases.

The following expression also holds:

$$f_B + f_{Ti} + f_{Al_2O_3} = 1 \quad (9)$$

Applying Eq.(4)-(9) with Y 's from Table IV, the concentration profiles vs. depth for the unreacted film is shown in Figure 8. Graphical integration of the $Ti(TiO_x)$ profile gave an oxide or oxygen rich region of 60 Å. The values of R for B and Ti used in expression (8) were 45 Å/m and 125 Å/m respectively.

The depth resolution of the beam can be determined from either the time or depth in which the plateau intensity or concentration decays by a factor of 10. Using those for B, we obtain a resolution of 29 ± 1.5 min and 1500 ± 60 Å.

Sample TiB_2 285E, another one of the same series described above was placed in a He atmosphere for 30 minutes at 950°C. Using Thebault et al. kinetics⁽⁵⁾, complete reaction between Ti and B should take place in 1.9 seconds @ 950°C. Boron excess would be 757 Å according to:

The extra long heating was simply to determine the effectiveness of excess boron removal in the tube furnace and to obtain some idea of TiB_2 -substrate reaction. Applying decoupling procedures described above and in Quarterly Report #3, p. 29,⁽³⁾ and using a set of yield factors similar to those in Table IV the concentration profiles shown in Figure 9 were obtained.

Fig. 9 Concentration-depth profiles from the sputtering of sample TiB₂ 285E (B/Ti/sapphire heated in a He atmosphere for 30 m at 950°C).

The sputtering rate used for TiB_2 was $67 \text{ \AA}/\text{m}$. The volume change on reaction can be seen in formation of the TiB_2 layer (here seen as a plateau). The large excess of boron is not evident indicating that even with higher purity He, enough O_2 or H_2O is getting on the sample surface to partially volatilize the boron. Graphical integration of the remaining unreacted boron (into a coherent and homogeneous layer) shows $82 \text{ \AA}$ in excess. Thus $680 \text{ \AA}$ were removed in this heating cycle.

It is also evident that the surface is rich in oxygen. It is not certain that some of the TiB_2 reacted with residual O_2 or H_2O . This question may have to be answered since a clean TiB_2 layer is assumed to be necessary for proper silicon coupling and growth.

The Al profile now shows a step not present in the unreacted sample. The possibility of reaction with Ti or TiB_2 cannot be conclusively established from just this result. Further analyses are in progress involving heating cycles of different times.

3.3 Estimated Composition of a Mullite Substrate

A candidate for relatively inexpensive substrate material for solar cells is mullite. A sample (3M Company #847) was recently examined by SIMS to determine its impurity levels and thus its suitability for use in fabricating solar cells by vacuum deposition. Particular attention was paid to alkali metals since these are volatile at high temperature and also might diffuse into the silicon during deposition; however, the presence of an intermediate layer of TiB_2 might serve as a barrier. Both polyatomic and atomic spectra were used to obtain the results shown in Table V. Since a calibration sample was not available, ion yield factors from glasses of known composition were used to convert ion intensities to atomic concentrations. The analysis must be only considered an estimate.

TABLE V

ESTIMATED COMPOSITION OF MULLITE 847
SPUTTERED WITH 10 keV Ar⁺ (DEFOCUSED); E_w = 0eV

Species X ⁺	Intensity I (X 10 ¹⁰ amp)	Yield * (Y _{Si} =1)	Atom fraction, f
Li	12	0.44	0.00066
B	9.8	0.35 §	0.00068
O	48	0.0017	0.68
Na	650	4	0.004
Mg	525	3.3	0.0038
Al	27200	2.6	0.25
Si	2090	1	0.051
K	540	21**	0.00063
Ca	300	12.3	0.00058
Ti	28	3.6 §	0.00019
Fe	‡	0.71	0.00066
Cu	‡	1.1 §	1.4 X 10 ⁻⁵
Sr	2.4	10**	5.8 X 10 ⁻⁶
Ba	4.6	9.1**	1.2 X 10 ⁻⁵

* Factors from sputtering a soda lime glass of known composition.

** Factors from sputtering a lead glass of known composition.

§ Smith and Christie factors (ref 6)

‡ Values for Fe and Cu were obtained from an atomic spectrum to avoid interferences from Si₂⁺ and CaNa⁺

4. ELECTRICAL MEASUREMENTS

The dark current-voltage and capacitance-voltage characteristics were measured for a number of samples. Figure 10 shows a semi-log plot of the I-V curve for Si 237D. A similar curve for Si 209E is shown in Figure 7 of the Appendix. The current in diodes formed from polycrystalline silicon films appears to be dominated by recombination so that the straight line portion of the I-V curves fits the expression:⁽⁷⁾

$$J = J_{02} \left(\exp \left(\frac{qV}{nkT} \right) - 1 \right) \quad (11)$$

where J_{02} is the recombination current density within the space charge region, n is a constant > 1 , k , q , V , and T have their usual meanings. The open circuit voltage V_{oc} is then obtained from:

$$V_{oc} = \frac{nkT}{q} \ln \left(\frac{J_{sc}}{J_{02}} + 1 \right) \quad (12)$$

Thus, using the values of J_{02} and n determined from the dark I-V curves (Eq. 1) and the short circuit current J_{sc} from Table XIII Appendix and the photocurrent - photovoltage curve in Figure 8 Appendix, V_{oc} can be determined and compared with the measured value. Table VI shows a comparison of two samples described here plus two described in previous reports⁽¹⁾ (kT/q is taken as 0.025V).

TABLE VI
PARAMETERS IN DIODE EQUATION

Sample	n	J_{02} (mA/cm ²)	J_{sc} (mA/cm ²)	V_{oc} Calc, (Volts)	V_{oc} Meas., (Volts.)	$\bar{d}$ (μm)
Si 187C	1.6	4.7×10^{-2}	10.1	0.22	0.21	4.7
Si 200D	2.0	5.0×10^{-3}	10.6	0.38	0.38	26
Si 209E	2.2	9×10^{-2}	13.5	0.28	0.28	5.2
Si 237D	1.7	3.2×10^{-3}	10.0	0.36	0.35	15

Fig. 10 Dark current-voltage characteristic of Si 237D.

As can be seen, there is excellent agreement between the calculated and measured values of V_{oc} . The increase in V_{oc} with grain size appears to be due to the decrease in J_{O_2} rather than to an increase in J_{gc} .

The capacitance per unit area of an abrupt junction is given by⁽⁸⁾

$$\frac{1}{C^2} = \frac{2}{q\epsilon N_B} (V_D - V), \quad (13)$$

where ϵ is the permittivity, V_D is the built-in diffusion potential, and N_B is the impurity concentration of the lightly-doped base region. Figure 10 shows a plot of $1/C^2$ versus V for the same device, Si 237D, shown in Figure 11. From this curve, V_D is determined to be 0.95V and $N_B = 1.0 \times 10^{17}$ atoms/cm³. N_B by SIMS measurements gives a value of 2.9×10^{17} atoms/cm³. Thus it may be, in this case, that some boron atoms are not active in producing free carriers. Hall measurements discussed in the Final Report,⁽¹⁾ however, indicate a better agreement between the number of free carriers and the concentration of boron atoms determined by SIMS. Using the value of $N_B = 1 \times 10^{17}$ atoms/cm³ and $N_A \approx 2 \times 10^{19}$ atoms/cm³ as estimated by SIMS for similar n-type phosphorus diffusions, V_D can be estimated from

$$V_D = \frac{kT}{q} \ln \frac{N_A N_B}{N_i^2} = 0.92V \quad (14)$$

where N_i is the intrinsic concentration of carriers in silicon. Eq. 14 is reasonably close to the measured value.

Fig. 11 Plot of $1/C^2$ vs V of Si 237D.

5. PHOTOVOLTAIC DEVICES

5.1 Processing Samples into Photovoltaic Devices

The silicon/TiB₂/alumina sandwiches were processed in the microelectronics facility according to the description in the 1979 Final Report.⁽¹⁾ Minor deviations from the procedures described in the Report generally worsened device performance.

A new series of masks has been fabricated for n-region vacuum deposition. Masks have also been made to allow the same new pattern to be processed by diffusion of the n-region, if desired. The n-region evaporation/diffusion mask is depicted in Figure 12. The corresponding electrode configuration is shown in Figure 13. Table VII lists the sizes of the various regions on the pattern. This pattern is designed "Pattern F." The largest device has a total (n-diffused/deposited) area of 1 cm². These masks will be used for device fabrication in the next quarter.

TABLE VII
DEVICE AREAS IN PATTERN "F"

Device*	n-Region (cm ²)	Electrode (cm ²)	Effective Area (cm ²)
A	1.006	0.226	0.780
B	0.184	0.045	0.139
D1, D5	2.32 X 10 ⁻²	0.65 X 10 ⁻²	1.68 X 10 ⁻²
D2, D3	5.81 X 10 ⁻³	0.65 X 10 ⁻³	5.16 X 10 ⁻³
C4, D4	2.58 X 10 ⁻³	0.32 X 10 ⁻³	2.26 X 10 ⁻³
C2, C3	1.45 X 10 ⁻³	0.16 X 10 ⁻³	1.29 X 10 ⁻³

* C3 is a MOS capacitor, A = 2.58 cm²

Fig. 12 n-Region delineation mask for "Pattern F".

Fig. 13 Electrode mask for "Pattern F".

5.2 Photovoltaic Device Properties

During this reporting period sixteen samples were processed into photovoltaic devices. Several of these were subjected to various experimental treatments which, one way or another, destroyed the samples for all practical purposes. Five samples processed using standard procedures with minor variations together with pertinent parameters for the best device on the sample substrate are listed in Table VIII.

Several attempts were made to improve photovoltaic performance by heating in air at 500°C for 30 minutes and/or heating in a flowing hydrogen ac-discharge at 400°C for several hours. Results are inconclusive: heating in air for up to an hour slightly improved V_{oc} for a few devices, further heating degraded performance; heating in the hydrogen discharge was generally unsatisfactory - although a few devices showed slight improvement in voltage.

Photovoltaic performance has not improved in devices made during this reporting period. Sample Si 237D has an average silicon grain diameter of $\sim 20 \mu\text{m}$. The open circuit voltage of half the devices on this substrate is greater than 300 mV under AM1 light, the fill factor (.63) of one device (C2) is one of the highest ever measured in this program, and the efficiency is 2.2%. The poor efficiency is due to the low value of J_{sc} ($\sim 10 \text{ mA/cm}^2$), which is in the same range as samples with $5 \mu\text{m}$ grains. Sample Si 238E has $40 \mu\text{m}$ grains and also exhibits $J_{sc} \sim 10 \text{ mA/cm}^2$. This sample appears to suffer from processing problems, possibly relating to etching of the electrodes, which is reflected in a low V_{oc} . A point contact measurement on several devices after n-type diffusion but prior to electroding showed a V_{oc} of 350 mV. The spectral response of both of these large-grained samples (Si 237D and Si 238E) indicates that the increased grain size does not result in an increase in the minority carrier diffusion length. This is discussed in more detail below.

TABLE VIII
THIN FILM PHOTOVOLTAIC DEVICES

Sample (Device)	$\eta_{\max}$ (%)	V_{oc} (mV)	J_{sc} (mA/cm ²)	Fill Factor (fraction)	Comments
227D (C3)	1.6	232	15.4	.45	some improvement noted after several heatings in air and hydrogen discharge
230E (C3)	2.3	280	15.1	.55	underwent several heating and etching treatments - some improvement and some degradation noted
231D (C2)	1.6	250	11.6	.56	after heating
237D (C2)	2.2	346	10.1	.63	unchanged by heating
238E (E1)	-	(< 100)	10.6	-	V_{oc} low on all devices after electroding, point of contact before elec- troding gave $V_{oc} \sim 350$ mV. J_{sc} similar to others.

5.3 Spectral Response Measurements

Spectral response measurements were made on devices with different silicon grain sizes. All devices exhibited maximum spectral quantum efficiency at wavelengths at or below 0.5 μm , the response falling rapidly with increasing wavelengths. Representative results for four different samples are shown in Figure 14 and important parameters are summarized in Table IX.

The quantum efficiency was determined by comparing device response with the response of a spectrally calibrated standard silicon solar cell (NASA/Lewis Research Center Standard Cell No. Z-21, calibrated on 7/13/76). Light from an AM1 Simulator (ELH lamp) was passed through a series of thirteen narrow-band-pass filters in the range 0.41 to 1.05 μm . The short-circuit current density J_{sc} of the standard cell is proportional to the incident (monochromatic) power density in mW/cm^2 . The value of J_{sc} (mA/cm^2) for the test device divided by the power density for each of the nominally monochromatic wavelengths then equals the spectral response for the test device at each wavelength in mA/mW . This response value multiplied by the photon energy (eV/photon) yields the quantum efficiency η (electrons/photon). The data in Figure 14 have been normalized so that the maxima are all adjusted to a relative quantum efficiency of unity.

5.4 Minority Carrier Diffusion Length

A very useful parameter for understanding the performance of a solar cell is the minority carrier diffusion length L_D . A long diffusion length is desirable because longer wavelength light which is absorbed at a greater depth in the base region of the cell generates carriers which can be collected by the junction and converted into electrical energy along with the carriers generated at shallower depths. The effective value of L_D can be directly related to the reciprocal of the optical absorption constant in the base material and to the wavelength dependence

TABLE IX
ESTIMATED MINORITY CARRIER DIFFUSION LENGTHS

(Device)	Thickness (μm)	Grain Size (μm)	η_{max}	$\lambda(\eta_{\text{max}})$ (μm)	L_D (μm)
208A (E4)	3.4	4.7	.51	.502	3.1
209E (C3)	14	5.2	.50	.502	2.8
237D (C2)	22	20	.58	.455	2.1
238E (E1)	22	-	.47	.502	2.7

Fig. 14 Spectral response curves for four devices listed in Table IX.

of V_{oc} or J_{sc} , as in the surface photovoltage (SPV) or short-circuit current (J_{sc}) methods of measuring L_D . In earlier reports⁽¹⁾ the J_{sc} method was used. In most instances, assumptions are made concerning the wavelength dependence of the optical absorption constant $\alpha(\lambda)$: values are taken from the literature for single crystal or polycrystalline silicon, as appropriate. In polycrystalline silicon there is undoubtedly some variation in $\alpha(\lambda)$ from sample to sample depending on grain size, surface roughness, preparation conditions, etc. In the absence of accurate values of $\alpha(\lambda)$ for each polycrystalline specimen, measurements of L_D using SPV or J_{sc} techniques must be considered approximate.

One may obtain estimates of L_D which are consistent with those obtained by the SPV or J_{sc} methods directly from the spectral response curves, provided the optical absorption $\alpha(\lambda)$ is known. Assume that the peak of the spectral response curve (set equal to unity) reflects the intrinsic collection capability of the device (electrode efficiency, junction figure of merit, etc.). The (relative) quantum efficiency represents the fraction of carriers collected per incident photon at each wavelength. Comparison with J_{sc} measurements on single crystal samples indicates that $\alpha^{-1}(\lambda_D)$, where λ_D is the wavelength at which the spectral response falls to approximately 50% of its maximum value, corresponds to a reasonable estimate of the effective L_D .

The use of the 50% value of the maximum spectra response is exactly correct for the simple solar cell model in which the cell thickness $d \gg L_D$. This is usually a reasonable assumption for single crystal cells, but may not be valid for polycrystalline cells. Assumptions concerning effects of the surface and depletion region are the same as for the SPV method.⁽⁸⁾ The wavelength dependence of the reflection coefficient at the front surface of the device is neglected.

Let N_0 be the number of photons (per unit area and time) incident at the effective top surface of the base layer. At a distance x below this surface the photon intensity is

$$N(x) = N_0 e^{-\alpha x} \quad (15)$$

where α is the optical absorption constant. In an increment of thickness Δx at a depth x the number of photons absorbed is

$$\Delta N(x) = -N_0 \alpha e^{-\alpha x} \Delta x \quad (16)$$

From the definition of diffusion length L_D , the incremented fraction of carriers collected from the layer Δx at a depth x is

$$\Delta f(x) = \Delta N(x) e^{-x/L_D} \quad (17)$$

assuming that each absorbed photon generates a minority carrier. The fraction of incident photons (of wavelength λ) returned to the junction as current carriers (the quantum efficiency) is

$$f(d) = -N_0 \alpha \int_0^d \exp -(\alpha + L_D^{-1}) x \, dx \quad (18)$$

Assuming $L_D \ll d$, this becomes

$$f(\infty) = -N_0 \alpha \int_0^\infty \exp -(\alpha + L_D^{-1}) x \, dx = \frac{N_0 \alpha}{\alpha + L_D^{-1}} \quad (19)$$

To take account of processes other than optical absorption and minority carrier diffusion length, assume that at some wavelength nearly all the carriers generated at the top surface of the base layer are collected and normalize the quantum efficiency to this wavelength. Experimentally, this is the wavelength of maximum efficiency. At some longer wavelength λ_D the quantum efficiency will fall to half the maximum value. From Eq. 19 this occurs when $\alpha(\lambda_D) = L_D^{-1}$:

$$f(\infty) = \frac{N_o \alpha(\lambda_D)}{\alpha(\lambda_D) + \alpha(\lambda_D)} = \frac{N_o}{2} \quad (20)$$

Therefore $L_D = \alpha^{-1}(\lambda_D)$ for the value of λ_D where the quantum efficiency is 50% of its greatest value. Knowledge of $\alpha^{-1}(\lambda)$ for the material being studied is required.

Values of $\alpha^{-1}(\lambda)$ were obtained from the literature for "polycrystalline silicon."⁽⁹⁾ The values of L_D obtained in this manner are given in Table IV. As can be seen from this Table, the effective minority carrier diffusion length does not appear to increase as the grain size of the sample increases.

6. DISCUSSIONS

Studies this quarter confirm the conclusions of the last quarter discussed in the 1979 Final Report⁽¹⁾. Large grains, 40 μm in diameter as measured on the surface, are obtainable in silicon films. These large grains are the result of an interaction in the initial stages of growth of the silicon and the TiB_2 . Because of the importance of this interaction a more detailed study of the TiB_2 formation and the silicon interaction on the TiB_2 surface is being undertaken. A better understanding of the growth phenomenon will lead to perhaps even larger grains and more important, more perfect grains.

The increase in grain size has lead to an improvement in the open-circuit voltage. This increase in open-circuit voltage appears to be due, however, entirely to the reduction of J_{02} , the reverse bias recombination current. This is confirmed in several samples through measurement of dark and light electrical characteristics. This reduction in reverse bias current is probably due to the reduction in surface leakage at the grain boundaries which tends to shunt the p-n junction. The results of heating samples in a hydrogen discharge, resulting in a slight improvement in V_{oc} but no improvement in J_{sc} ,⁽¹⁾ is also explained by the reduction of the shunting resistance due to intergranular leakage.

The p-n junctions in the films appear to be reasonably well behaved. The large grained samples follow a V vs $1/C^2$ dependency characteristic of an abrupt junction. The built-in voltage determined from the V vs $1/C^2$ curve agrees within the accuracy of the measurement to the voltage expected from the measured doping levels.

The achievement of large grained samples has, however, not led to an improvement in short circuit current density. This is seen in Table VIII as well as in the measurements of the spectral response. The spectral efficiency of small and large grained samples is essentially the same.

The determination of L_n from the spectral response is based on a simple solar cell model which neglects surface effects and absorption down

through the depletion layer and which also assumes that the base region is much thicker than L_n . These approximations are essentially identical with those used in the more conventional SPV or J_{sc} methods of measuring L_n . All these methods require a knowledge of the optical absorption coefficient α in the silicon base material. A lack of accurate values for α appears to be the greatest source of uncertainty in these measurements. While the absolute accuracy of L_n may be in doubt, the relative measurements among various devices indicates that there is little, if any, change in L_n between large (20-40 μm) and small ($\sim 5 \mu m$) grained samples.

The observation that the minority carrier diffusion length, spectral response, and short-circuit current have not improved with the increase in grain size, indicates that something other than grain size alone is limiting the photovoltaic efficiency of the devices.

Thus, it appears that one must carefully examine the defects and impurities within the grains. The series resistance in the system due to the TiB_2 -silicon interface and the rather inefficient collection electrode must also be evaluated. The series resistance is, of course, not the total cause of the low collection current since the minority carrier diffusion length measurements are independent of this resistance.

7. REFERENCES

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8. APPENDIX

VACUUM DEPOSITED POLYCRYSTALLINE SILICON
SOLAR CELLS FOR TERRESTRIAL USE

Presented at the
14th IEEE Photovoltaic Specialist Conference
(Jan. 7-10, 1980)

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14th IEEE Photovoltaic Specialist Conference, San Diego, Calif.
(Jan. 7-10, 1980)

VACUUM DEPOSITED POLYCRYSTALLINE SILICON SOLAR CELLS FOR TERRESTRIAL USE*

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ABSTRACT

The DOE goal of obtaining low-cost, 10% efficient solar cells is being approached through the development of a potentially all-vacuum fabrication process incorporating vacuum deposited, thin-film, polycrystalline silicon. Experimental devices were constructed in layers as follows: alumina substrate/TiB₂ bottom electrode/p-type polycrystalline silicon film/diffused silicon n-region/Ti-Ag electrode. An essential feature of this design is the TiB₂ bottom electrode which remains conducting after the silicon deposition and subsequent processing. Grain growth, film composition, interfacial analyses and photovoltaic characteristics were investigated using SIMS, SEM, X-ray diffraction and conventional electrical measurements. Under certain conditions 20-40 μ m Si grains were formed on TiB₂-coated alumina, raising the possibility of greatly improved photovoltaic efficiency in vacuum deposited polycrystalline silicon solar cells.

INTRODUCTION

At the 12th IEEE Photovoltaic Conference devices with double-diffused junctions were described which had been fabricated from vacuum deposited polycrystalline silicon films (1). These early samples were deposited directly on sapphire substrates and used a planar configuration. The efficiency of these devices was approximately 2% (AM-2). The average silicon grain diameter in the samples was 5 μ m. In this paper, sandwich type devices using only one diffusion and yielding up to 3% (AM-1) efficiency will be described. In addition, successful experimental efforts to increase the grain size from 5 μ m to about 40 μ m will be discussed.

Construction of the experimental devices is illustrated in Fig. 1. The samples consist of the following layers on an alumina or sapphire substrate: TiB₂ bottom electrode/p-type polycrystalline silicon film/diffused silicon n-region/Ti-Ag electrode. The bottom electrode, in the present configuration, is buried beneath the silicon layer for protection during subsequent diffusion and oxidation steps in the fabrication process. The TiB₂ layer is formed by reacting deposited layers

of Ti and B in a vacuum prior to the silicon deposition. The boron layer is slightly larger than the titanium layer to prevent direct contact between silicon and titanium. The boron doped silicon film is formed by co-deposition of boron and silicon. Phosphorus is diffused into the silicon film using standard techniques to create a n-p junction. Top electrodes of titanium coated with silver are used in place of the aluminum electrodes described previously (2). Details for forming each layer will be given in this paper. Parameters of the particular samples described here are given in Table I.

Table I

Deposition parameters of photovoltaic devices

Sample	Si 200D	Si 237D	Si 209E
TiB ₂ thickness	1.6 μ m	1.0 μ m	1.1 μ m
TiB ₂ resistivity	62 $\mu\Omega$ -cm	48 $\mu\Omega$ -cm	38 $\mu\Omega$ -cm
Si thickness	11 μ m	22 μ m	14 μ m
Si substrate temp.	>1200°C	1240°C	1160°C
Si deposition rate	344 Å/min	611 Å/min	433 Å/min
Substrate	Alumina	Sapphire	Alumina
Si grain diameter	~20 μ m*	20 μ m	5.2 μ m

*20 μ m grains in limited regions only.

Composition, orientation, and grain structure were studied by secondary-ion mass spectrometry (SIMS), X-ray diffraction and scanning electron microscopy (SEM). SIMS was used in the examination of interactions at each interface. There are interactions between titanium and boron in forming the bottom TiB₂ electrode, between TiB₂ and the alumina substrate, between TiB₂+B and the residual gas in the vacuum, between TiB₂ and the silicon film, and between Si and SiO₂ at the surface. The system illustrated in Fig. 1 is thus rather complicated in detail. With the exception of the TiB₂-Si interaction, interfacial phenomena will not be discussed here. At high substrate temperatures (~1200°C) silicon crystallite growth on the TiB₂ electrode proceeds differently than it does on alumina alone. Unusually large (20-40 μ m) grains were observed on TiB₂ under conditions which will be described below.

*Work supported by the U. S. Department of Energy, Division of Solar Technology, under Interagency Agreement No. ET-78-A-03-2208.

In this approach to forming solar cells, a vacuum deposited electrode is required between the substrate and the silicon film. The electrode must meet the following criteria:

- a. It must be able to withstand deposition and processing temperatures without melting or deteriorating;
- b. Any reaction products between Si and the electrode must be stable and conducting;
- c. Detrimental impurities must not be introduced into the silicon layer;
- d. The electrode must not adversely effect nuclei formation and subsequent grain growth in the silicon film;
- e. The expansion coefficient of the electrode and/or reaction products must be similar to that of both the substrate and the silicon film.

Various materials were considered and tried, and TiB_2 has emerged as most nearly satisfying the above criteria (3),(4). Titanium diboride is a very refractory material (melting point $\sim 3000^\circ\text{C}$) which exhibits high electrical bulk conductivity. Furthermore, it is extremely stable and has excellent resistance to corrosion and chemical attack. TiB_2 was formed by depositing a layer of titanium followed by a layer of boron and diffusing the two together in vacuum. Titanium (99.7% purity) was vacuum deposited onto the alumina substrates from a tungsten boat at a rate of about $1000 \text{ \AA}/\text{min}$ to $2000 \text{ \AA}/\text{min}$. Samples were then transferred to another vacuum system in which boron was deposited by means of electron beam heating from water-cooled, molybdenum-lined crucibles. The boron deposition rate was from $700 \text{ \AA}/\text{min}$ to $800 \text{ \AA}/\text{min}$. The substrates were maintained at approximately 500°C by radiation from iodine-filled, tungsten filament lamps.

In the earlier paper, preliminary studies of TiB_2 were reported in which excess boron remained on top of the TiB_2 layer (1). In this present work TiB_2 was reacted completely prior to the silicon deposition. Thus silicon was deposited on essentially a stoichiometric surface of TiB_2 . The diffusion was generally at $950\text{--}975^\circ\text{C}$ for 3-5 hours, depending on thickness. The Ti-B reaction was studied by Thebault et al and is probably rapid(5); however, excess boron (when it exists) appears to be removed by a $\text{B-H}_2\text{O}$ reaction which may be rather slow (6). Extensive use of SIMS and X-ray analysis assured that stoichiometric TiB_2 was formed. The grain size in the TiB_2 layer was approximately $0.1 \mu\text{m} - 0.5 \mu\text{m}$. During the vacuum heatings, Al from the substrate was found to penetrate the TiB_2 layer and this penetration or interaction probably aids in the excellent adhesion between TiB_2 and the Al_2O_3 substrates.

Silicon and its dopant boron were thermally evaporated from separate water-cooled crucibles by electron beam heating in a 12" stainless steel, bell-jar vacuum system. Vacuum pressure was in the 10^{-7} Torr range during deposition. Fixture and support materials which became hot were made of tantalum to avoid contamination of the film during deposition. Tantalum was found to be superior to molybdenum in this respect. Substrates were heated by fused silica, iodine-filled, tungsten filament lamps. Substrate temperatures were between 1000°C and 1250°C . The temperature of the substrate was measured with thermocouples resting on top (back) of the substrates. In an effort to avoid contamination, there were no rate monitors or thickness monitors in the system. The deposition rate was determined by measuring the thickness and deposition time. A calibration curve relating electron-beam power to the deposition rate was used to obtain desired thickness and doping. The source-substrate distance was approximately $5 \frac{1}{2}$ ". Both sapphire and alumina substrates were employed. At the high substrate temperatures ($\sim 1200^\circ\text{C}$) used to achieve larger grain growth, the silicon film only adhered to the TiB_2 -coated regions of the Al_2O_3 substrates. Non-adherence to the alumina is probably due to the reaction between Si and Al_2O_3 (8).

Recently, it has been found possible to grow grains far larger than expected under normal growth conditions. The grains are columnar shaped and are several times longer than their surface diameters. Cross-sectional examination shows that single grains often extend from the bottom electrode to the surface. A SEM photomicrograph illustrating the surface appearance of the grains in sample Si 737D is shown in Fig. 2. Fig. 3 shows a plot of supersaturation ratio v/v_0 versus the average surface grain diameter d . Here v is the rate per unit area of the atoms leaving the substrate and v_0 is their arrival rate. The curve represents the linear least-square fit to the data points for silicon on alumina. The triangular points represent regions in films or entire films where growth of large grains has taken place on TiB_2 . Data on samples indicated in Fig. 3 are given in Table I and Table II. It is obvious that something additional has occurred to produce data points which lie well outside the growth curve. The large grain formation appears to be due both to an increased surface diffusion of Si on TiB_2 and to an interaction between TiB_2 and Si. SIMS, X-ray and SEM analysis reveal that the initial islands (or seeds) which were being formed directly on the TiB_2 surface were many times larger than those formed on alumina alone. TiSi_2 and SiB_6 have been identified in these islands.

The total impurity level detected by SIMS for a typical film deposited in the oil-diffusion pumped system was 30 ppma. This included O, C, Na, Mg, Al, Tr, Cr, and Ni but not the added B. SIMS analysis on a sample which contained large regions of both large and small grains did not show a significant difference in impurity content between the two regions.

The silicon/TiB₂/alumina sandwiches were processed by standard microelectronic techniques to form a number of diode devices of different sizes on 1" X 0.33" substrates; a conducting "pad," which provides contact to the back electrode was also incorporated into the sample structure. The n on p junction was formed by high-temperature diffusion. This included the following steps: cleaning, oxidation, photolithography, etching, diffusion, and drive-in. The diffusion and oxidation were done at 975°C. Phosphorus was deposited from phosphine for 6.5 minutes at a flow rate of 16.5 ml/min. Drive-in was one hour in oxygen. Details of the typical processing steps have been reported elsewhere (2) (4). Ti or Ti/Ag top electrodes are deposited by vacuum evaporation and delineated photolithographically. Samples were generally heated in air following electrode formation at 500°C for 30 minutes. A photograph illustrating a device pattern on a substrate is shown in Fig. 4. The rather large pad on the p-doped silicon used to provide contact to the TiB₂ layer is clearly visible in Fig. 4.

Oscilloscope traces illustrating the diode characteristics of sample Si 237D are shown in Figs. 5 and 6. The thin film diodes exhibit characteristics which make them potentially useful for microelectronic applications. The dark current-voltage curves of sample Si 209E is shown in Fig. 7. The straight line portion of the forward direction shows a slope of $n = 2.2$ which is characteristic of a recombination current [i.e. $J = J_0 \exp (qV/nkT) - J_0$]. A capacitance (C) versus voltage (V) analysis for the sample Si 237D shown in Figs. 5 and 6 produced a good fit to a $1/C^2$ versus V curve indicating an abrupt junction with a built-in voltage of about 0.9 V.

An illuminated (AM-1) current-voltage behavior of the three devices described in this paper is shown in Fig. 8. The simulated AM-1 light source consists of a GE type ELH tungsten-iodine lamp filtered by a KG2 infrared filter and adjusted for 100 mW/cm². In prior work, the xenon source was stronger in violet end of the spectrum than the present ELH lamp simulator (1). The photovoltaic responses from these devices without antireflection coating or electrode geometry optimization is presented in Table II.

Table II

Parameters of thin film photovoltaic devices

Sample	Si 200D	Si 237D	Si 209E
V _{oc}	364 mv	345 mv	276 mv
J _{sc}	15 ma	10 ma	13.5 ma
ff	0.57	0.62	0.56
Effective area	1.3 X 10 ⁻³ cm ²	5.2 X 10 ⁻³ cm ²	5.2 X 10 ⁻³ cm ²
Efficiency (AM1)	3.1%	2.2%	2.1%

Note that the area used in estimating the efficiency is the n-diffused region less the electrode area. A spectral response for Si 237D is shown in Fig. 9. The maximum at 0.5 μm rather than 0.8 μm for single crystal cells is probably due to the small minority carrier diffusion length (5 μm) in the polycrystalline device.

Carrier concentrations in the base region were obtained in a companion sample to Si 200D but without the TiB₂ layer by both Hall effect and SIMS measurements and were $4.5 \times 10^{17} \text{cm}^{-3}$ by Hall measurements, and $7.6 \times 10^{17} \text{cm}^{-3}$ by SIMS; resistivity of the sample was 0.7 Ω-cm.

CONCLUSION

The vacuum deposited polycrystalline silicon photovoltaic devices described here represent an improvement in efficiency and geometry over those described in the 12th Photovoltaic Conference. Titanium diboride appears to be a suitable bottom electrode material for silicon layers. It can be formed by vacuum deposition, is conducting, and remains stable throughout the silicon deposition and device processing. Diffusions were used to create n-type junctions in the p-type deposited material. Formation of the n-layer by diffusion is, however, regarded as an interim technique in order to proceed one step at a time and to compare the polysilicon device with those made conventionally on single crystal silicon. As the evaporated polysilicon technology evolves, it is anticipated that the n-layer will be vacuum deposited. Thus, the entire fabrication process would take place using vacuum deposition techniques. Eliminating the microelectronic processes of oxidation and diffusion will allow direct contact to the back electrode and thereby improve somewhat the forward diode current. Vacuum deposition of the n-type silicon layer will provide more abrupt junctions. Further improvement in grain size can also be expected as more is learned about the Si-TiB₂ interaction.

It is well recognized that photovoltaic response increases with increasing grain size. The data presented here (Table II) is generally consistent with the theoretical predictions of Ghosh et al whose curves indicate V_{oc} = 0.38V, J_{sc} = 17 ma/cm², ff = .62 and efficiency = 3.8% for samples with 20 μm grains having a density of surface states of $1.6 \times 10^{13} \text{cm}^{-2}$ (9). A reduction in the density of intergranular surface states would lead to higher efficiencies. Techniques such as annealing in hydrogen may aid in this reduction. Attention must also be paid to the internal defect structure and impurity content of the grains. Under the high temperature conditions used to form the larger grains additional impurities from the TiB₂ and from the vacuum system may be introduced into the film.

It is anticipated that improvement in device formation, grain size, purity, thermal treatments, etc. will lead to further increases in the photovoltaic efficiency of the thin polycrystalline silicon devices.

ACKNOWLEDGEMENTS

The author acknowledges, with pleasure, the efforts of R. B. Givens in SEM examination, K. G. Hoggarth, in vacuum depositions, E. W. Koldey, in crystallite examinations and R. D. Neuwiller in device processing.

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Fig. 2 SEM photomicrograph of crystallite surfaces in silicon film on TiB_2 -coated sapphire substrate after complete processing into devices (Si 237D) (1000X)

Fig. 1 Schematic of cross-section of thin film vacuum deposited silicon photovoltaic device.

Fig. 3 Ratio of v/v_0 versus average surface grain diameter $\bar{d}/d_0$. $d_0 = 1 \mu\text{m}$.
 $v = 5 \times 10^{14} R_d$ where R_d is the deposition rate, $v_0 = 6.6 \times 10^{21} P_{T_S}/T_S^{1/2}$
 where P is the silicon vapor pressure at substrate temperature T_S .
 • = Si film on Al_2O_3 , Δ = Si film on $\text{TiB}_2/\text{Al}_2\text{O}_3$, (A) Si 200D,
 (B) Si 237D, (C) Si 209E

Fig. 4 Photograph of thin film silicon sample on 1" X 1/3" alumina substrate illustrating photovoltaic device configuration.

Fig. 5 Oscilloscope traces of I-V curves in dark and AM-1 conditions for Si 237D.
 Horz: 0.1 V/div Vert: 0.02 mA/div

Fig. 6 Oscilloscope traces of I-V curves in sample Si 237D illustrating reverse breakdown.
 Horz: 2V/div Vert: 0.02 mA/div

Fig. 7 Dark forward and reverse I-V curves for sample S1 209E.

Fig. 8 Photovoltaic I-V curves - AM-1.
(A) S1 200D, (B) S1 237D, (C) S1 209E

Fig. 9 Spectral response of photovoltaic device S1 237D.