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EPITAXIAL SILICON GROWTH FOR SOLAR CELLS

Quarterly Report No. 2

By
R. V. D'Aiello
B. W. Faughnan
P. H. Robinson
D. Richman

April 1978

Work Performed Under Contract No. NAS-7-100-954817

RCA Laboratories
Princeton, New Jersey

MASTER

U.S. Department of Energy

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SECTION I

SUMMARY

The objective of this program is to develop and apply epitaxial growth techniques to the fabrication of efficient solar cells on low-cost forms of silicon.

During this period, progress was made in the following areas:

A. SINGLE-CRYSTAL BASELINE STRUCTURES

1. The efficiency of baseline epitaxial solar-cell structures of about 1 mil thickness grown on single-crystal substrates and processed with diffused junctions has been reproducibly established at ~13% (AM-1).

2. Experiments were conducted in the growth of the entire cell structure including the junction layer. For baseline cells fabricated on these layers, efficiencies of ~10% have been obtained.

These structures were grown with junction depths of 0.8-1.0 μm which resulted in short-circuit current densities of ~24 mA/cm. Techniques for the reproducible growth of thinner surface layers are being pursued, in order to increase the short-wavelength response of these structures.

B. LOW-COST SILICON SUBSTRATES

Epitaxial techniques were applied in the growth of diagnostic layers and solar-cell structures on two potentially, low-cost, polycrystalline silicon substrates, namely Wacker (SILSO)* and a Refined Metallurgical Grade** (RMS) silicon. X-ray topographic studies have shown improved crystallographic quality in the epitaxial layers grown on both substrate forms. The best solar cells were fabricated on the RMS substrates where an AM-1 efficiency of 10.6% was obtained with a 16- μm thick epitaxial layer. Epitaxial structures on the Wacker substrates yielded efficiencies in the 5.6-9.5% range.

*Wacker Chemical Corporation, Richardson, Texas.

**Supplied by Dr. P. Kotval, Union Carbide Research Laboratory, Tarrytown, New York.

SECTION II

EXPERIMENTAL RESULTS

A. EPITAXIAL CELLS ON SINGLE-CRYSTAL SUBSTRATES

1. Diffused Junctions

These cells are grown and fabricated on conventional single-crystal substrates in order to monitor the epitaxial layer quality and to establish baselines for comparison with low-cost substrates. Last quarter, we reported [1] the attainment of AM-1 efficiencies in the 11-12% range for the basic structures shown in Fig. 1. In those structures, the n^+/p junction was formed by diffusion into the grown epitaxial layer.

Figure 1. Parameters for epitaxial baseline structures.

1. R. V. D'Aiello, P. H. Robinson, D. Richman, *Epitaxial Silicon Growth for Solar Cells*, Quarterly Report No. 1, Prepared for Jet Propulsion Laboratory, by RCA, Jan. 1978.

During this quarter the efficiency of these structures has been improved to the 12-13% level. This improvement was achieved by: (1) cleaner epitaxial techniques which resulted in somewhat longer diffusion lengths, and (2) by increasing the doping level in the base layer by a factor of two to three which resulted in higher open-circuit voltages. A summary of the typical improved cell performance for the three structures is given in Table 1.

TABLE 1. SUMMARY OF SOLAR-CELL PARAMETERS BASELINE
DIFFUSED/EPITAXIAL STRUCTURES

Structure	W_{epi} μm	J_{sc} mA/cm^2	AM-1 PARAMETERS		
			V_{oc} mv	F.F. -	η %
I	14	28.2	578	0.790	13.2
II	22	27.3	563	0.772	12.1
III	47	28.6	562	0.782	13.0

2. Epitaxially Grown Junction Layers

One of our overall objectives is to evaluate cells with grown base and junction layers so that the entire cell structure can be grown without the need for a separate junction formation process. For that purpose, we have prepared sets of samples having epitaxially grown p-type base layers of structures I, II and III (see Fig. 1) and grown n^+ junction layers. In our initial experiments, for purposes of control and reproducibility, the n^+ layers were grown $\sim 1\text{-}\mu m$ thick and arsenic doped at $\sim 2 \times 10^{18} \text{ A/cm}^3$. $\sim 2 \times 10^{18} \text{ A/cm}^3$.

Solar cells of 4.4 cm^2 area were fabricated and a comparison of their performance was made with similar structures having diffused junctions. This comparison is shown in Table 2. From this data, it can be seen that the lower efficiencies of the all-epitaxial cells are due to poor short-wavelength response, which is reflected in short-circuit current densities about 15% below those for the diffused junction cells. This result is not

TABLE 2. COMPARISON OF SOLAR-CELL PERFORMANCE FOR DIFFUSED AND EPI GROWN SURFACE LAYERS

Sample/ Structure	AM-1*Parameters								
	J _{sc} ^{**}	V _{oc}	F.F.	η	Quantum Efficiency at			Depth	Sheet Rh
	mA/cm ²	mV	--	%	0.4 μm	0.7 μm	0.9 μm x; μm	R _□ ⁵² /□	
GROUP A									
<u>EPI Grown Junction</u>									
240375-7/I	23.4	585	0.735	10.1	13.4	85.0	35.4	0.90	152
241311-8/II	23.9	570	0.730	10.3	10.0	81.1	37.1	0.86	170
242457-9III	23.3	555	0.734	9.8	10.5	73.1	44.0	0.90	150
GROUP B									
<u>Diffused Junction</u>									
229019/I	26.4	555	0.750	11.3	36.6	86.0	29.3	~0.2	187
230736/II	27.2	535	0.748	11.1	38.1	89.9	39.1	~0.2	240
232384/III	27.5	550	0.750	11.8	34.3	84.9	47.9	~0.2	180

*AM-1 Simulation at 97 mW/cm²**All cell areas = 4.4 cm².

surprising in view of the relatively thick junction layers employed in these structures. The growth parameters and control required for thinner surface layers are presently under study.

B. EPITAXIAL CELLS ON LOW-COST SUBSTRATES

The epitaxial techniques described above were applied to the growth of solar-cell structures of the same type on two potentially low-cost silicon substrates - Wacker (SILSO) polycrystalline silicon and Union Carbide Refined Metallurgical Grade (RMS) silicon.

1. Wacker (SILSO) Material

We used this material to gain experience in the growth of layers on defected polycrystalline substrates. We reported last quarter that epitaxial layers grown on these substrates showed a greatly reduced defect density and that solar cells fabricated in these layers exhibited efficiencies of 6.5-9.3%.

During this quarter, epitaxial structures including the junction layer were grown and processed into solar cells. Surface preparation included either polishing (P) or chemical etching (E). Structures I and II, containing nominally 15- and 20- μm thick base layers and $\sim 1\text{-}\mu\text{m}$ thick n^+ surface layers were grown simultaneously on both the Wacker materials and 10- $\Omega\text{-cm}$, p-type, single crystal, control wafers. A summary of the solar-cell performance for these structures is given in Table 3.

TABLE 3. SUMMARY OF CELL PERFORMANCE FOR ALL-EPITAXIALLY GROWN STRUCTURES ON POLYCRYSTALLINE WACKER SUBSTRATES

Sample/Structure	J_{sc} mA/cm ²	V_{oc} mv	AM-1 PARAMETERS		X_j μm	$R_{\square}$ 52/ $\square$	COMMENTS
			F.F. --	η %			
245090-P/I	22.1	525	0.620	7.4	1.1	194	Polycrystalline - surface polished
245366-E/I	22.2	550	0.626	7.8	0.8	242	Polycrystalline - surface etched
244870-Control	24.1	570	0.673	9.5	0.5	177	Single Crystal - 10 $\Omega\text{-cm}$ substrate
246386-P/II	22.0	520	0.570	6.8	0.8	119	Polycrystalline - surface polished
246874-E/II	22.8	540	0.570	7.3	0.8	150	Polycrystalline - surface etched
246176-Control	24.8	575	0.693	10.1	0.6	172	Single Crystal - 10 $\Omega\text{-cm}$ substrate

2. Epitaxial Solar Cells on RMS Silicon

(a) Material Characterization

The material used in these experiments was obtained from Union Carbide. They are in the form of round wafers (~ 2 -in. diam) and are large grained, randomly oriented, polycrystalline, p-type silicon of $\sim 0.06 \Omega\text{-cm}$ resistivity, having chem-mechanically polished surfaces. Projection x-ray topographs of two representative sections of this material with $150 \mu\text{m}$ of silicon growth are shown in Fig. 2. The dark areas are within 10° of the (100) direction, and the other areas are off the (100) axis by more than 10° . Figure 3 shows a series of section topographs taken at 1-mm intervals in the large grain at the lower right of Fig. 2. An enlargement of several sections of these topographs is shown in Fig. 4. In most areas of Fig. 2 it can be seen that the epitaxial layer (on the left) contains a much lower defect density than the substrate material. However, fractional areas [see Fig. 4(c)] still remain defected. The same observation of improved crystal quality in epitaxial layers was made and reported [1] for the Wacker polycrystalline substrates.

(b) Solar-Cell Structures and Results

Six RMS wafers were used to grow two each of 15-, 20-, and 50- μm thick p/p⁺ graded cell structures I, II and III. Control samples were grown for each case on single crystal p-type substrates of about the same resistivity as the RMS material.

After the epitaxial growth, solar cells were fabricated by diffusing a phosphorus n⁺ junction layer $\sim 0.25 \mu\text{m}$ deep with a sheet resistance of $\sim 100 \Omega/\square$, metalizing (evaporated Ti/Ag) and mesa etching to define cells of 4.4 cm^2 . Spin-on titanium silica AR coatings were then applied.

A summary of the measured solar-cell and structural parameters is given in Table 4. An illuminated I-V curve for sample X-13 RMS is shown in Fig. 5. These preliminary results show the feasibility of attaining efficiencies of greater than 10% on refined metallurgical grade silicon.

Additional experimental results relating to diffusion length, lifetime and spectral response for these samples are described in the next section.

Figure 2. A projection topograph of Union Carbide Silicon: Grains 1 and 2.

Figure 3. A section topograph of Union Carbide Silicon, Grade 2. Topographs taken at 1.0 mm intervals across grain. Layer is at left edge of each topograph.

(a)

(b)

(c)

[0.1 mm]

Figure 4. A section topograph of Union Carbide Silicon: (a) and (b) - Grain 2; (c) - Grain 1. Layer is at upper left, of each topograph.

TABLE 4. MEASURED SOLAR-CELL AND STRUCTURAL PARAMETERS

<u>Sample-Substrate</u>	<u>AM-1 Parameters*</u>					<u>Diffused Junction</u>	
	W_{epi} μm	J_{sc} mA/cm^2	V_{oc} mV	F.F. --	η %	X_i μm	$R_{\square}$ $\Omega/\square$
X-13 - Single crystal	14	28.2	578	0.790	13.2	~ 0.25	72
X-13 - RMS (1 1/2")	16	25.4	535	0.660	9.3	~ 0.25	133
X-13 - RMS (2 1/4")	14	25.0	555	0.745	10.6	~ 0.25	71
X-14 - Single crystal	21	26.7	550	0.770	11.6	~ 0.25	132
X-14 - RMS (1 1/2")	20	25.9	538	0.726	10.4	~ 0.25	119
X-14 - RMS (2 1/4")	20	23.9	535	0.700	9.2	~ 0.25	121
X-15 - Single crystal	47	28.6	562	0.782	13.0	~ 0.25	111
X-15 - RMS (1 1/2")	50	25.9	538	0.720	10.3	~ 0.25	79
X-15 - RMS (2 1/4")	43	24.3	542	0.717	9.7	~ 0.25	117

*ELH lamp simulation at $97 \text{ mW}/\text{cm}^2$

Figure 5. Illuminated I-V curve for sample X-13 RMS.

C. DIAGNOSTIC MEASUREMENTS

1. Techniques

In addition to I-V curves, a variety of diagnostic measurements have been carried out. These include spectral response measurements, from which the diffusion length in the base region is computed, minority carrier lifetime measurement by the diode reverse recovery technique, and for a few cells, a laser scan technique which plots the short-circuit current as a function of position with a resolution of 10-20 μm .

The spectral response apparatus was set up in this quarter and will be used routinely for diagnostic measurements. It uses a tungsten light source and a filter wheel to select 1 of 12 narrow (50 to 100 $\text{\AA}$) wavelength regions from 0.4 to 1.1 μm . The light is chopped and detected by a phase-sensitive detector. Before reaching the test solar cell in the form of a narrow slit (1 μm X 8 μm), the light passes through a beam splitter. Approximately 50%

of the light is imaged on a reference diode whose quantum efficiency versus wavelength has been previously determined by measurement with a standard lamp traceable to NBS standards. The reference diode's response is first determined in both the test cell position and the reference position for each wavelength. Then, during a quantum efficiency measurement of a test cell, the ratio of I_{sc} of the test cell to I_{sc} of the reference diode is measured at each wavelength corresponding to the 12 filters. From this ratio and the known calibration of the reference diode, the quantum efficiency can be calculated. The system is found to give very reproducible results (<1%).

The laser scan apparatus has been developed on another project, and the scans were kindly taken for us by David Staebler of RCA Laboratories.

2. Results

The spectral response (quantum efficiency) curves were measured for most of the cells fabricated this quarter, and the results are shown in Figs. 6 to 11. The diffusion length in the base region can be extracted from a suitable plot of the long wavelength region of the quantum efficiency (QE) curve. The results of this are shown in Table 5. This number will only be a true diffusion length if: (1) The base region is approximately four times longer than the diffusion length; (2) The reflectivity of the solar cell versus wavelength is known and corrected for in the QE plots. Neither of these requirements are usually met in the case of epitaxially grown cells on polycrystalline substrates. The measured diffusion lengths (see Table 5) are usually comparable to the base width. In fact, if the true diffusion length is greater than the base width, the measurement should yield just the base width. This appears to be the case in many of the cells of Table 5. Properly interpreted, this is still a useful measurement. However, since the measurement tells us that for those cells, efficiency is not limited by diffusion length in the base region, in one case, 13-C (epi layer on single crystal silicon), the apparent diffusion length is three times the width of the base region! One interpretation is that electrons created by light absorbed in the Si substrate are also collected at the epi junction, thereby increasing the effective base region.

The unknown reflectivity also introduces an error in the QE curves. This could also have a substantial effect on the overall efficiency of the cell.

Figure 6. Quantum efficiency of Epi solar cells: 6-diff, 6-C, 6-P.

Figure 7. Quantum efficiency of Epi solar cells: 10-C, 10-E, 10-P.

Figure 8. Quantum efficiency of Epi solar cells: 11-E, 12-C, 12-E.

Figure 9. Quantum efficiency of Epi solar cells: X-13.

Figure 10. Quantum efficiency of Epi solar cells: X-14 Union Carbide EPI layers on polysilicon.

Figure 11. Quantum efficiency of Epi solar cells: X-15 Union Carbide layers on polysilicon.

TABLE 5. BASE DIFFUSION LENGTH, LIFETIME, AND EFFICIENCY MEASUREMENTS OF EPITAXIAL STRUCTURES ON POLYCRYSTALLINE SUBSTRATES.

Substrate Source	Sample No.	τ_{RR} μm	$L_e^a(\tau_{RR})$ μm	L_e^b μm	Epi Base Thickness (μm)	η %
Wacker	6 diff. ^c	2.4	85	61	300	-
	6-C	0.6	42	42	70	13.0
	6-P	*	-	28	65	8.7
Wacker #244870 ^d	10-C	*	-	16	20	9.5
Wacker #245366	10-E	*	-	14	20	7.8
Wacker #245090	10-P	*	-	14	20	7.4
Wacker #246874	11-E	*	-	17	22	
Wacker #247663	12-C	*	-	32	50	9.1
Wacker #247863	12-E	*	-	30	52	7.1
Union Carbide	13-C			45	16	13.2
Union Carbide	13-a (1 1/2")			22	16	9.3
Union Carbide	13-b (2 1/2")			14	16	10.6
Union Carbide	14-c	*		23	21	11.6
Union Carbide	14-a (1 1/2")	*		21	20	10.4
Union Carbide	14-b (2 1/2")	*		20	20	9.2
Union Carbide	15-c	0.3	30	62	47	13.0
Union Carbide	15-a (1 1/2")			41	50	10.3
Union Carbide	15-b (2 1/2")			37	43	9.7

* τ_{RR} not measurable

a Diffusion length obtained from $L = \sqrt{D_e \tau_{RR}}$ assuming $D_e = 30 \text{ cm}^2/\text{s}$.

b Minority carrier diffusion length in base obtained from spectral response curve.

c Diffused cell directly on Wacker Substrates, no epi layer.

d Number used in previous reports to identify cell.

For example; if we compare cells 11-E and 12-E, from Table 5, we see that cell 12-E has a substantially higher effective diffusion length than 11-E, i.e., 30 μm versus 17 μm , and a correspondingly higher QE in the long wavelength region. However cell 12-E has a considerably lower peak efficiency, i.e., 63% versus 78%. Both cells have AR coatings. However, visual inspection of the cells show that the quality of cell 12-E is much poorer and, hence, the AR coating is probably much less effective. Our spectral response apparatus could be modified to measure the light reflected from the cell at each wavelength so that this factor could be quantitatively evaluated.

The minority carrier lifetimes were also measured, whenever possible, by the diode reverse recovery method. The data is shown in Table 5. This technique is very simple to use but the measurement cannot be made if the lifetime is too short. From Table 5 the smallest lifetime we could measure was 0.3 μsec . The minority carrier diffusion length in the base can be estimated from the equation $L = \sqrt{D\tau}$. We have assumed $D_e = 30 \text{ cm}^2/\text{sec}$ for electrons in the p-type base region. For two of the measurements the agreement is reasonable (less than 30% difference) but for the shortest lifetime measured, the estimates of L are off by a factor of two. Our experience with a large number of wide base (>200 μm) single crystal solar cells is that the two methods usually agree to within 30%. The laser scans of an epi cell grown on single crystal silicon and one grown on polysilicon are shown in Fig. 12 and Fig. 13. I_{sc} of the cell grown on the single crystal substrate is seen to be very uniform with position, as might be expected. On the other hand, I_{sc} of the cell grown on polysilicon shows large variation in certain regions which can probably be associated with the grown boundaries. This interesting technique could be of potential benefit in our attempts to improve the quality of epi solar cells grown on polycrystalline silicon, and will be used during the contract whenever it is deemed appropriate.

D. EPITAXIAL GROWTH OF SILICON USING ADVANCED REACTOR DESIGN

A series of epitaxial layers, p/p⁺ were grown to a specific thickness and resistivity on single crystal silicon substrates using a reactor similar to the one described in U.S Patent No. 4,062,318. Thicknesses and doping levels were chosen to include the range of anticipated use in solar-cell structures

Figure 12. Laser scan showing short-circuit current as a function of position for epitaxial solar cell on single crystal substrate.

Figure 13. Laser scan showing short-circuit current as a function of position for all-epitaxial solar cell on polycrystalline substrate.

(i.e) 10- to 80- μ m thick and p-type doping levels of 2×10^{15} to 2×10^{17} A/cm². Trichlorosilane (a cheaper silicon source than either silicon tetrachloride or dichlorosilane) was used as the silicon source material. Diode structures were fabricated and minority carrier lifetimes were measured using both open-circuit voltage decay and the reverse recovery techniques. These results are presented in Table 6 and should be adequate for thin film solar-cell operation.

TABLE 6. RESULTS OF MINORITY CARRIER LIFETIME MEASUREMENTS
FOR DIODE STRUCTURES GROWN IN THE ROTARY DISC REACTOR

<u>Doping Level A/cm²</u>	<u>Minority Carrier Lifetime (μsec)</u>
2×10^{15}	3.7
2×10^{16}	2.4
1×10^{17}	1.3

SECTION III

CONCLUSIONS AND RECOMMENDATIONS

This quarter, the epitaxial growth of thin solar-cell structures was extended to include a potentially low-cost form of silicon, namely polycrystalline refined metallurgical grade silicon substrates. An AM-1 efficiency of 10.6% was achieved with a cell structure having only 14 μm of silicon grown on the RMS silicon substrate. An average efficiency of 10% was obtained for six samples prepared with three epitaxial layer configurations. This, and other sources of suitably defined metallurgical grade silicon, will be evaluated as they become available to us.

Studies by x-ray topography have shown significantly lower defect density in epitaxial layers grown on both RMS and Wacker polysilicon substrates.

Diagnostic measurements were conducted to include spectral response and the determination of diffusion length in the solar-cell structures. For the epitaxial layers on RMS silicon, it was found that the diffusion length in all cases was at least as long as the thickness of the epitaxial layer. Evaluation of the implications of this data will be pursued.

We have also conducted studies of all epitaxial solar cell structures including the junction layer grown on single crystal substrates. The results show that an efficiency of 10% is obtainable with 1- μm thick surface layers. Spectral response measurements show that significant improvement in efficiency is possible with reduced surface layer thickness, and work in that direction is planned for next quarter.

Growth studies were conducted in a laboratory model of RCA's rotary disc epitaxial reactor. Initial growths showed good control of concentration profiles and minority carrier lifetime adequate for thin solar cells.

SECTION IV

PROGRAM PLAN AND ACTIVITIES FOR NEXT QUARTER

Our overall program plan is tabulated below and a milestone chart for this plan is given in Fig. 14. The work for the second quarter has been accomplished on schedule.

Plans for the next quarter include:

1. Submicron surface layers, advanced and standard reactor - reproducibility.
2. Evaluate all-epi structures on RMS.
3. Evaluate electrical properties of layers grown on Ti doped single crystal silicon.
4. Another form of metallurgical grade silicon will be evaluated.
5. Preliminary cost analysis (SAMICS) of advanced epi reactor.

Figure 14. Milestone for overall program plan.