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**LASER-ZONE GROWTH IN A RIBBON-TO-RIBBON (RTR) PROCESS
SILICON SHEET GROWTH DEVELOPMENT FOR THE LARGE AREA
SILICON SHEET TASK OF THE LOW COST SOLAR ARRAY PROJECT**

Technical Quarterly Report No. 9, Motorola Report No. 2256/12
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Solar Energy

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THE JPL LOW-COST SOLAR ARRAY PROJECT IS SPONSORED BY THE U.S. DEPARTMENT OF ENERGY AND FORMS PART OF THE SOLAR PHOTOVOLTAIC CONVERSION PROGRAM TO INITIATE A MAJOR EFFORT TOWARD THE DEVELOPMENT OF LOW-COST SOLAR ARRAYS. THIS WORK WAS PERFORMED FOR THE JET PROPULSION LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY BY AGREEMENT BETWEEN NASA AND DOE.

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MOTOROLA PROJECT NO's 2319 - 25

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SUMMARY

We have achieved breakthroughs in two areas critical to the RTR process. A series of flat polycrystalline ribbons measuring 5 cm x 61 cm was grown and successfully separated from 24" long Mo substrates. Our first solar cells on gettered RTR silicon were grown from pre-etched ($\approx 1/2$ mil) CVD feedstock. The best cell had a conversion efficiency of 10.6%,* with $V_{oc} = 0.565$ volts, $I_{sc} = 29.8 \text{ ma/cm}^2$, and a fill factor of 63%. The low fill factor does indicate that still higher efficiencies can be attained on this material by improving the processing sequence.

The economic analysis for the overall RTR process has been updated in response to our technological progress. The total price for the overall process, including feedstock, was projected at \$19-\$23/m², assuming multiple ribbon growth.

* This efficiency occurred on a current run during the month of January and is reported here to show the most recent accomplishment.

Development of the semicontinuous polysilicon ribbon reactor continued. It was found necessary to increase the spacing between the fiberglass curtains at the exit and to increase the inert gas flow for the curtains to prevent backstreaming of air into the furnace. Several runs were made varying temperature profiles, process gas flow, and belt speed. It was found necessary to maintain the reaction zone at 1150°C for shearing of the ribbon from the substrate to reliably take place (as was predicted from results in a static induction heated reactor).

Flat ribbons 5 cm x 61 cm long were deposited on 0.040" x 2" x 24" Mo substrates carried through the furnace on a 0.015" thick Mo belt (Figure 1). Deposition directly on a thin Mo belt had resulted in "crowned" or curved ribbons which would not fit in the RTR apparatus, hence the use of thicker substrates on top of the belt. New belts 0.020" thick have been received, and initial experiments indicate that the silicon ribbon deposited on this thickness substrate/belt crowns very little and would be suitable for RTP growth. Belts 0.020" thick cannot be used on the present system since the feed and takeup reels are too small in diameter and the belt would break after a heat treatment. Design of a new system, with large diameter reels and utilizing four Mo belts to completely cover the four sides of the reactor chamber, is underway.

Although Si_3N_4 coatings on the Mo substrates proved to be ineffective as a diffusion barrier, they have proved to be beneficial in promoting smooth, uniform silicide formation which is essential to obtain successful shearing.

Figure 1: SILICON RIBBONS GROWN IN SEMICONTINUOUS BELT FURNACE

SiO₂ coatings appear to be effective barriers. Metallographic sections show no silicide formation (Figure 2) and the silicon films are strongly adherent and do not shear off.

Experiments were made using 304 stainless steel (18.5% Cr, 9.5% Ni, 0.08% C max, balance Fe) and 410 stainless steel (12% Cr, 0.15% C max, balance Fe) as substrates at temperatures of 950° C and 1050° C, respectively. The films visually appeared not to be silicon and were strongly adherent in spite of much higher expansion coefficients of the substrates. It is known that Fe and Ni form silicides at low temperatures and it may be conjectured that they diffuse as rapidly above 900° C and that the films consist entirely of silicide. They are presently being analyzed.

Silicon

Quartz

Molybdenum

FIGURE 2: SILICON-QUARTZ-MOLYBDENUM INTERFACE

2.0 RIBBON CONTAMINATION

Recently, solar cells fabricated on RTR ribbons have exhibited low efficiencies. Because of suspected Mo contamination, these results were not considered surprising in the case of CVD substrates. However, we have also observed low efficiencies for ribbons grown from single crystal feedstock, which is contrary to earlier results. In attempting to determine the cause of the abnormally low cell efficiencies, it was found that diffusion lengths on as-grown ribbons had dropped to very low values. While typical diffusion lengths for as-grown single crystal feedstock have previously been reported in the 5 μm to 10 μm range, recent measurements on ribbons grown from both CVD and single crystal feedstock showed diffusion lengths that were essentially zero. Even in finished solar cells which have undergone a process sequence which was earlier shown to produce considerable "gettering," diffusion lengths have been usually much lower than expected. This is in contrast to previous results which have shown average diffusion lengths in excess of 50 μm .

This is obviously a serious problem and major efforts were initiated to isolate the difficulty. We have studied our records and it appears that the drop in diffusion length coincided with changes made in post-heaters and the incorporation of a pre-heater. These changes were made to allow growth of wider ribbons and to improve the thermal profile sufficiently to handle CVD ribbons. Close scrutiny of the present furnaces has brought to light several possible problems.

- 1) Possible platinum contamination. Platinum heater elements are being used and, because of the particular geometries involved, platinum could be transported to the melt by means of gaseous diffusion. This possibility was much less likely in the previous furnace design. Neutron Activation Analysis (NAA) has been performed on several samples. Samples which had not been passed through the furnace exhibited Pt levels below about 70 ppbw (the detection

limit. However, one sample which has been regrown with our present furnace was shown to have 1.2 ppma of Pt, a clear case of contamination.

2) Vaporization of furnace parts. Because of the high reflectivity of liquid silicon to the CO_2 laser beam, a great deal of power is contained in the reflected beam. This beam may strike parts of the furnace, which can then vaporize. These contaminants can be transported to unmelted and melted regions of the ribbon, again by diffusion and convection processes. Materials of concern are quartz, stainless steel, high-alumina insulation, and ceramic parts, all of which can have trace metallic impurities.

3) Long-distance convective transport of contaminants. The present growth chamber is quite large with numerous mechanical, optical and electronic components within the enclosure. While these parts are normally cool, stray laser beams could cause emission of volatile components. An example would be the plastic shields used in front of the TV cameras. Furthermore, normal convective air currents could bring general contaminants to the melt.

2.1 EXPERIMENTS

In an attempt to clarify the nature of the problem, several experiments were performed, all with single-crystal feedstock. First, in an effort to duplicate earlier runs which had resulted in good material, the original small furnace was set up. Numerous growth runs were made but all resulted in unmeasurably short diffusion lengths. Next, growth runs were made without any furnace at all. To perform these experiments, very small growth rates ($\sim 0.2''/\text{min}$) were necessary, and a combination of focused and defocused beams was used to produce some stress relief in the ribbon. Again, "zero" diffusion lengths resulted, indicating that general contamination was prevalent. During these experiments, various feedstock sources (sawn ingots, scribed wafers, Czochralski, float-zone, etc.) and various pre-cleaning/etching steps were

utilized in an attempt to eliminate possible contamination from the material itself, or from pre-cleaning residues.

In order to verify that a pervasive atmospheric contaminant is indeed to blame, a special chamber was constructed. This chamber, illustrated in Figure 3, utilized a copper tube with narrow slots cut into the top and bottom for ribbon transport, and slots in the sides for laser beam access and viewing. Pure nitrogen (and other gas ambients) entered at the ends of the tube, exiting at the slots. Copper was used because of its high reflectivity at $10.6\ \mu\text{m}$ (to avoid vaporization of the tube) and because copper is not a serious lifetime killer when present in silicon. The interior surface of the copper was roughened so that radiation reflected from the silicon onto the walls of the tube would be diffusely reflected back onto the sample, i.e. it would not act like a cylindrical reflector. (It is interesting to note the similarity of this configuration with the hemispherical reflector concept. In fact, one experiment with smooth inner walls did show a significantly increased coupling. Unfortunately, it also resulted in an unstable molten zone, so we had to sand-blast the inner walls of the copper tube to reduce this effect.)

This experiment was successful, and diffusion lengths of $6\ \mu\text{m}$ to $17\ \mu\text{m}$ were obtained on ribbons grown in the copper tube. Since this experimental arrangement was primarily a protective cover against the atmosphere in the growth chamber, it confirmed the existence of a pervasive atmospheric contaminant. We then disassembled the growth chamber and cleaned it thoroughly, removing all unprotected plastic surfaces (and covering those that could not be removed with aluminum foil). The first sample regrown from Cz feedstock in the clean growth chamber had an SPV-measured diffusion length of $18\ \mu\text{m}$. In parallel with our efforts to clean up the growth chamber, we carried out some gettering experiments. These experiments were spectacularly successful, and are fully discussed in sections 4.0 and 4.1.

FIGURE 3. CONTROLLED ATMOSPHERE EXPERIMENT

Furnace designs to date have catered primarily to achievement of wide ribbon growth at high velocities. Because of this emphasis, possible contamination mechanisms have not received the attention they warrant. Recent NAA analyses have shown that, at least occasionally, platinum is making its way into the grown ribbons; this platinum is coming from the platinum heater elements. An additional problem is caused by reflection of the laser beam onto furnace parts that can vaporize. These mechanisms are shown in Figure 4, which also illustrates the type of structure now in use.

To alleviate these problems, an alternative furnace configuration is being investigated. This modified structure is conceptually indicated in Figure 5. Purging gas is introduced at the top and bottom of the furnace, exiting at the central region where the melt occurs. By adjusting each of the heater elements, the proper temperature profile may be achieved (with the gas flow). By proper choice of flow rates, the exit gas velocity should effectively reduce the possibility of contaminant counter-diffusion. Platinum shields protect the quartz and other components of the furnace from the reflected beam. Since the platinum shields are at a relatively low temperature ($\geq 1200^{\circ}\text{C}$) and are bathed by the purging gas stream, no contamination problems were anticipated.

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FIGURE 4: POSSIBLE SOURCES OF CONTAMINATION IN FURNACE

FIGURE 5: PURGED FURNACE DESIGN

4.0 GETTERING STUDIES - CZ FEEDSTOCK

Since we did not know the actual element (or elements) responsible for the pervasive atmospheric contamination in our growth chamber, we speculated that it might be a fast diffuser which could be effectively gettered. A number of 5/8" wide ribbons* were grown from Cz feedstock without using a pre-heater, post-heater or the copper tube. The diffusion lengths in some of these ribbons were measured immediately after growth; four ribbons went through the gettering sequence. The as-grown ribbons all had unmeasurably short diffusion lengths. After gettering, the average of eight diffusion lengths measured on the four ribbons was 124 μm .

The gettering sequence needed to achieve these diffusion lengths is very simple. The ribbons were subjected to a standard PH_3 diffusion process at 900°C . However, the backs of the ribbons were not protected (as they normally are during this step). Thus an $n^+ - p - n^+$ structure was formed. The back junction was then etched off, and the diffusion lengths measured by OCPV using the front $n^+ - p$ junctions as a barrier.

Two diffusion lengths were measured in different areas of each ribbon. The diffusion lengths range from 88 μm to 210 μm , with an average of 124 μm . This average diffusion length matches the maximum we have ever reported on RTR silicon. In our previous work, the deposition of the Si_3N_4 AR coating was found to provide an additional measure of gettering. This seems to be the case with the long diffusion length ribbons as well. After Si_3N_4 deposition, the diffusion lengths for two such ribbons (from Czochralski feedstock) increased from 88-120 to 275 μm and 80-130 to 130-328 μm .

* This growth was done before the growth apparatus was disassembled and cleaned.

4.1 GETTERING STUDIES - CVD FEEDSTOCK

The improved gettering sequence described above has also been used to increase the diffusion length in PTR silicon grown from recrystallized CVD polyribbon.

Diffusion lengths from 25-50 μm have been obtained after the two-sided PH_3 diffusion. The average value for 14 CVD ribbons is 24 μm , with one sample as high as 130 μm . The Si_3N_4 deposition can result in a further increase in diffusion length, although the results are less spectacular and the data more scattered than in the case of Czochralski feedstock. These results represent an increase by more than an order of magnitude over diffusion lengths previously reported for this material.

Experiments are also being done to further improve the gettering. One promising approach is to do the normal two-sided PH_3 diffusion, strip both sides of $\approx 10 \mu\text{m}$ of silicon, which removes the $\sim 0.5 \mu\text{m}$ deep junction, and then process the ribbon as usual. The first attempt resulted in a CVD ribbon with a diffusion length as high as 190 μm before Si_3N_4 deposition.

Three major changes in our experimental procedures are responsible for this improvement:

1. All our CVD feedstock is now etched prior to laser recrystallization. Roughly 1/2 mil of Si is removed from each side of the ribbon.
2. These ribbons were grown without a pre- or post-heater. Previous ribbons grown with the heaters might have been contaminated by platinum and other vaporized furnace components.
3. Two-sided phosphorus diffusion is now used to getter the silicon ribbon. Experiments to further optimize the gettering sequence are underway.

5.0 SOLAR CELLS - CVD FEEDSTOCK

The first solar cells have been fabricated on the gettered CVD material. The best overall efficiency was 10.6%,* with $V_{oc} = 0.565$, $I_{sc} = 29.8 \text{ ma/cm}^2$ and a 63% fill factor for simulated AM1 illumination (see Figure 6). The diffusion length was measured after complete cell fabrication to range from 27 to 40 μm . Note that the voltage is the highest we have ever attained; on single crystal feedstock RTR ribbon, $V_{oc} \sim 0.50$. The short circuit current is also very encouraging. The low fill factor shows that we have room for improvement. For example, with a 76% fill factor (which has been observed on CVD RTR samples), the efficiency would increase to 12.8%.

The metallization used for this cell used an experimental electroplated Ni-Ag contact, which may be responsible for the poor fill factor. A short, 5-minute sinter at $\sim 300^\circ \text{C}$ was used. The open circuit voltage did not degrade during metallization.

* These numbers were updated in proof--the best cell was completed in January 1979 and included in this report to show the most recent accomplishment.

CELL NO.: 9E7A-2
AREA: 1.32 cm²
V_{OC}: 0.565 VOLTS
I_{SC}: 29.8 mA/cm²

FIGURE 6. I-V DATA ON RTR SAMPLE GROWN FROM CVD FEEDSTOCK

6.0 ECONOMIC ANALYSIS: UPDATE

In our most recent price projection (1), we reported a $\$16.9/\text{m}^2$ price for polycrystalline ribbon grown by CVD and an RTR add-on price ranging from approximately $\$20/\text{m}^2$ at $100 \text{ cm}^2/\text{min}$ to $\$11/\text{m}^2$ at $200 \text{ cm}^2/\text{min}$ (multiple ribbons). These results are being updated in response to changes in three factors with significant cost impact:

1. Deposition Geometry: This is the most important factor. We had assumed a two-belt deposition system, mainly because it appeared that a two-belt system would be simpler to design than a four-belt system. Recent experiments with silicon ribbon deposition systems (2), however, have shown that a four-wall system, since it eliminates the need for masking, would not be a particularly difficult design problem.
2. Capital Cost-Laser: The cost of a multi-kilowatt CO_2 laser was $\$30/\text{watt}$ in 1977. However, the production of high-power CW CO_2 lasers suitable for heat-treating, surface hardening, etc., applications is predicted to increase by 25% per year through 1985 (3). Thus the total production of these lasers will more than triple over the next five years. Assuming a 20% learning curve, the cost of high-power CO_2 lasers could drop to $\$21/\text{watt}$ by 1984 (in constant dollars). This price was used for this analysis.
3. Quartz Furnace Liner: Since the four-belt system protects the quartz from being attacked by SiHCl_3 , HCl and B_2H_6 , the quartz furnace liner will need to be replaced only on a yearly basis.

The SAMICS equation was used to calculate the price of ribbons: $\text{SAMICS} = 0.49 (\text{EQFT}) + 96.9 (\text{SQFT}) + 2.1 (\text{LABOR}) + 1.3 (\text{UTILITY}) + 1.3 (\text{MATERIAL})$. All results are expressed in 1975 dollars. As requested by JPL, the cost of the

source gas was not burdened. The deposited ribbon thickness was 220 μm . Twenty microns are then etched off the back surface to remove the Mo contamination. The ribbon is then stretched to a 100 μm thickness during the RTR recrystallization. The price of the polyribbon is expressed in $\$/\text{m}^2$ of recrystallized ribbon.

The results of these calculations are shown in Tables I and II. Table I shows the price dependence for the polyribbon on deposition rate, molybdenum belt thickness and Mo belt cycles. Choosing a fairly modest set of parameters--100 cycles/belt, 600 μm deposition rate--the polyribbon can be grown for $\$12.6/\text{m}^2$. Table II shows the add-on price for the RTR recrystallization, as well as the total price assuming $\$12.6/\text{m}^2$ polyribbon.

TABLE I

POLYCRYSTALLINE SILICON RIBBON BY CVD

Source Gas: SiHCl_3 at \$5/Kg-Si

Utilization Factor: 80%

Plant Capacity: 500 MW

Mo Belt Utilization (cycles)	Mo Belt Thickness (μm)	Silicon Deposition efficiency (per pass)	Deposition Rate ($\mu\text{m}/\text{min}$)	Growth Rate (cm^2/min)	SAMICS Price (\$/ M^2)
100	400	0.20	4	40	14.1
			5	50	12.5
			6	60	11.4
			8	80	10.1
100	400	0.20	6	6	11.4
	500				12.0
	600				12.6
	800				13.7
50	500	0.20	6	60	14.8
100					12.0
200					10.6

TABLE II

ADD-ON AND TOTAL PRICE FOR RECRYSTALLIZED (RTR)
SILICON RIBBON - 100 μm THICK

GROWTH RATE	ADD-ON PRICE (\$/M ²)	POLYRIBBON PRICE (\$/M ²)	TOTAL PRICE (\$/M ²)
100 cm ² /min	17.7	12.6	30.3
150* cm ² /min	12.2	12.6	24.8
200* cm ² /min	10.3	12.6	22.9
250* cm ² /min	7.9	12.6	19.5

*These growth rates could readily be achieved with multiple ribbon growth.

7.0 PLANS

Pinpointing the source of contamination in RTP growth will be the number one priority. Experiments involving highly controlled purged atmospheres and a variety of pre-cleaning techniques will be conducted. Gettering studies will also be emphasized together with other effects to maintain diffusion lengths through completion of cell fabrication.

8.0 PROBLEMS

The short diffusion lengths appearing in as-grown and gettered ribbons is a major concern. While long diffusion lengths have been obtained, this has not been on a regular basis. The extra effort necessary to solve this problem has necessarily slowed progress in other areas.

9.0 NEW TECHNOLOGY

The following New Technology items have been developed on this program:

1. Description - Polygan Scanner System
Innovator - Dr. Richard Gurtler
Progress Reports - Technical Progress Report No. 14, October 1977
Pages - 1, 10, 11A and 11
2. Description - Hemispherical Reflector to Improve Effective Absorption Coefficient of Liquid Silicon
Innovator - Dr. Richard Gurtler
Progress Reports - Technical Quarterly Report No. 7, Motorola Report 2256/9, January 1, 1978 - March 31, 1978
Pages - Appendix Pages 11 to 13
3. Description - Dendritic Growth on RTR Silicon
Innovators - Dr. A. Baghdadi, R.J. Ellis, Dr. R.W. Gurtler
Progress Reports - Technical Quarterly Report No. 6, Motorola Report No. 2256/8, October 10, 1977 - December 31, 1977
Pages - 14-23
4. Description - Controlled Dendritic Growth
Innovators: Dr. A. Baghdadi and Mr. R.J. Ellis
Progress Reports - Monthly Report No. 21, August 1978, JPL/DOE No. 954376
Page - 1
5. Description - Coated Substrates for Silicon Deposition
Innovator - Dr. R. Legge
Progress Reports - Monthly Report No. 20, July 1978, JPL/DOE No. 95476
Page - 20

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- (1) Special Report to R. Kachare, JPL.
- (2) K. R. Sarma, Personal communication.
- (3) Optical Spectra, October 1978, p. 28.