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# THIN-FILM GaAs PHOTOVOLTAIC SOLAR ENERGY CELLS

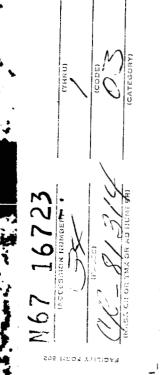
by

P. A. CROSSLEY (Project Scientist)
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Prepared for NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-8510

ASTRO ELECTRONICS APPLIED RESEARCH LABORATORY DAVID SARNOFF RESEARCH CENTER PRINCETON, NEW JERSEY



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#### MIDPOINT REPORT

## THIN-FILM GOAS PHOTOVOLTAIC SOLAR ENERGY CELLS

Ьу

P. A. Crossley (Project Scientist)
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**Prepared** for

#### NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

November 17, 1966

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Technical Management NASA Lewis Research Center Cleveland, Ohio

Astro Electronics Applied Research Laboratory David Sarnoff Research Center Princeton, New Jersey

## THIN-FILM GaAs PHOTOVOLTAIC SOLAR ENERGY CELLS

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P. A. Crossley (Project Scientist), R. B. Gill, P. Vohl (part of reporting period), and M. Wolf (Project Supervisor)

### ABSTRACT

The reproducibility of the fabrication process for cells of Al/InAs/GaAs/Cu<sub>1.8</sub>Se structure has been improved so that high yields of operating cells have been obtained. This improvement has resulted from stabilization of the operation of the GaAs film growth equipment by greater control of the hydrogen supply to the furnace. A further contribution has been the use of optical transmission monitoring of the flash evaporation process for the Cu<sub>1.8</sub>Se film formation. Equipment has been developed for the growth of 10-cm<sup>2</sup>-area GaAs films, but problems of uniformity have been encountered with these films. Other work reported includes the investigation of two postfabrication etch treatments to improve cell stability, and an evaluation of platinum as a barrierforming material.

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## THIN-FILM GaAs PHOTOVOLTAIC SOLAR ENERGY CELLS

by

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### SUMMARY

The objective of the program is to develop an economical solar cell fabrication technique to produce cells with 5% sunlight efficiency, high power-to-weight ratio, and stability under storage and operating conditions.

The major emphasis during the reporting period has been on improvement of the reproducibility of the processes in use. The InAs and GaAs film growth techniques have been brought under control, and films suitable for the fabrication of cells can now be made with better than 90% yield. The flash evaporation equipment used for the formation of the  $Cu_{1.8}$ Se films has also been improved, and films with a sheet resistance of 60  $\Omega/\Box$  are now achieved with better than 80% yield.

The vapor-deposition technique has been applied to grow GaAs films of greater than  $10 \text{ cm}^2$ , but these have not been of sufficient uniformity to permit cells of corresponding area to be formed. To improve cell stability, post-fabrication etching has been examined; bromine in iso-propanol has been found to degrade cell performance, and results from the use of 2% HNO<sub>3</sub> are not yet conclusive. Platinum as a barrier layer has been found to give lower V<sub>oc</sub> values than Cu<sub>1.8</sub>Se.

### I. GALLIUM ARSENIDE FILMS

#### A. InAs ON Al

Near the end of the previous contract (NAS 3-6466), a quantity of  $5-\mu$ m-thick Al foil was obtained from Consolidated Aluminum Corporation. This foil was practically pinhole-free and easier to handle than the Al foil which had been prepared in this laboratory for use as substrates during the past work. For these reasons the commercially obtained foil has been substituted for the evaporated foil and has been used as substrate material throughout the present report period.

The Al foil substrate is precoated with a polycrystalline film of n-type InAs before the growth of the GaAs film. The InAs film is grown by vapor transport from n-type polycrystalline source wafers at a substrate temperature of approximately 650°C. The InAs source temperature is estimated to be approximately 725°C. Typically, films averaging between 3.5 and 4.5  $\mu$ m in thickness were obtained from a 20-hour growth. Since the vapor transport is believed to utilize the oxide reaction<sup>1</sup>

$$2 \ln As_{(s)} + H_2O_{(V)} - \ln_2O_{(V)} + As_{2(V)} + H_{2(V)}$$
(1)

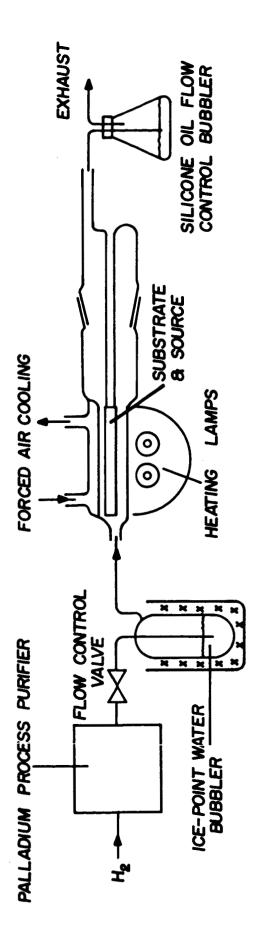
it was thought that increased transport rates could be obtained by the introduction of controlled amounts of water vapor into the furnace. Consequently, the "dry" hydrogen gas flow line was modified as shown in Figure 1. Commercial hydrogen is passed from the gas cylinder through a palladium purifier to a water trap at 0°C through which it is bubbled prior to entry into the furnace. In this manner, a controlled amount of water vapor is permitted to enter the furnace. Using this modified system it is now possible to prepare InAs films approximately 4  $\mu$ m thick in two hours. The distribution of average InAs thickness currently being obtained for a 120 ± 15 minute growth period is shown in Figure 2. The InAs films prepared by the modified process also appear to be much more uniform than the films obtained in the past.

#### B. GaAs GROWTH PROCESS (SMALL AREA)

#### 1. Initial Growth Process

The GaAs growth process which was developed earlier<sup>2</sup> employed the closed-space technique in an ambient of ''dry'' ultra-pure hydrogen gas. Single-crystal n-type GaAs wafers were utilized as the source, the substrate being aluminum foil coated with an InAs film. It was established that to produce GaAs films suitable for solar cell fabrication, a 16-hour overnight growth followed by a 5-hour growth from a freshly etched source wafer was necessary.

During the first three months of this report period, this process continued to be characterized by a low yield and lack of reproducibility of GaAs films suitable for use in solar cells. In addition to the furnace instabilities which resulted in nonreproducible electrical properties it was found that large variations of average GaAs film thickness could occur for films prepared under what were apparently the same growth conditions. Table I lists the average thickness of





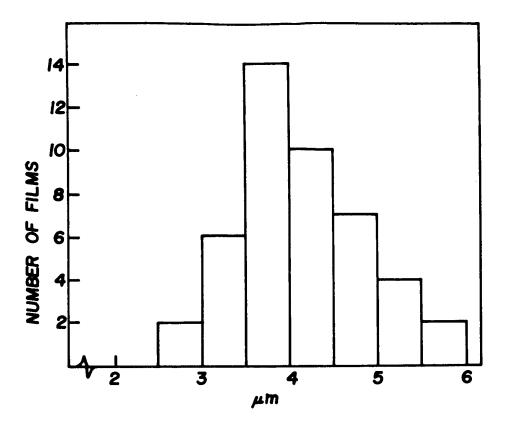


Figure 2. Thickness distribution for InAs films.

### TABLE I

PROPERTIES OF GAAS FILMS GROWN BY "DRY HYDROGEN" PROCESS

Film No.	Length of Growth (Hours)	H <sub>2</sub> Flow (cm <sup>3</sup> min <sup>-1</sup> )	< t > (µm)
R 38	B 16 5		8.3
R 40	16	5	4.3
R42	16	4	9.3
R43	16	5	8.2
R44	16	5	4.4
R45	16	. 5	9.3
R40a	4 3/4	5	2.5
	1	1	
R41a	4	5	3.5
	1	1	
R42a	4	4	3.1
	1	1	
R43a	4	5	2.1
	1	1	
R44a	4	4	2.8
	1	1	1

some of the GaAs films prepared by the above-described process. The average film thickness is computed from the difference in weight of the film structure before and after the GaAs growth. Any weight loss due to transport of InAs from the substrate is neglected.

The GaAs transport process utilizes the oxide reaction

$$2 \text{ GaAs}_{(s)} + H_2 O_{(V)} \neq Ga_2 O_{(V)} + As_{2(V)} + H_{2(V)}$$
(2)

and the transport rate is extremely sensitive to the water vapor (oxygen) concentration present in the furnace. Since "dry" ultra-pure hydrogen, passed directly from the gas cylinder to the furnace without further purification, was employed as the ambient, the sources of water vapor (oxygen) which would in fact control the transport process are believed to have been determined by:

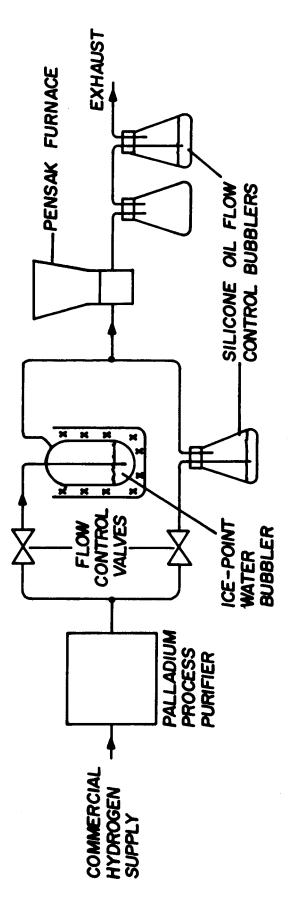
- (a) impurities in the ultra-pure hydrogen,
- (b) water and oxygen absorbed on the furnace walls during the time that the furnace is open to air,
- (c) water vapor absorbed by the graphite heater, and
- (d) microscopic leaks to air in the furnace system.

It is believed that (c) and (d) were predominant. Stable operation of the furnace under these conditions was extremely difficult to achieve since both the microscopic leaks and the external furnace environment could not be readily controlled.

It was also established that the GaAs growth rate dropped rapidly from about 1  $\mu$ m per hour in the first hour of growth to approximately 0.2  $\mu$ m per hour in the 16th hour of growth. Assuming a leak-free system, it is seen that the decreased growth rate would be a result of the reduction in water vapor concentration from the initial value, brought about by the flow of hydrogen during furnace operation. It is believed that variations in the water vapor concentration were also the predominant cause of the difficulties encountered in attempting to obtain reproducible electrical characteristics in the GaAs films.

#### 2. Modified Growth Process

For the reasons outlined above the hydrogen flow system has been modified as shown in Figure 3. Commercial tank hydrogen is passed through a palladium purifier to a tee from which it can be either bubbled through a water trap which is maintained at 0°C by an ice bath or passed directly to the furnace. Using this scheme, the mixing of various amounts of 'wet'' and 'dry'' hydrogen prior to entry into the furnace is possible. The flow rate through either arm of the tee can be controlled by needle valves located in each arm and monitored by noting the number of bubbles per unit time as hydrogen passes through an oil trap which is located on the exhaust side of the furnace. Care is taken to ensure minimization of leakage effects. As a result, it is possible to vary the growth environment in a controlled, reproducible manner.





#### 3. GaAs Film Properties

Besides the large variations in GaAs film thickness just described, it has also been established that when using the initially described transport process, small variations in the hydrogen flow rate would produce large changes in the electrical characteristics observed when the GaAs films were tested with a pressed Au dot contact (Figure 4). Since past experience has indicated that solar cells must be fabricated from films having a breakdown voltage greater than 3 V, it is seen that it is necessary to operate under conditions in which a slight variation in

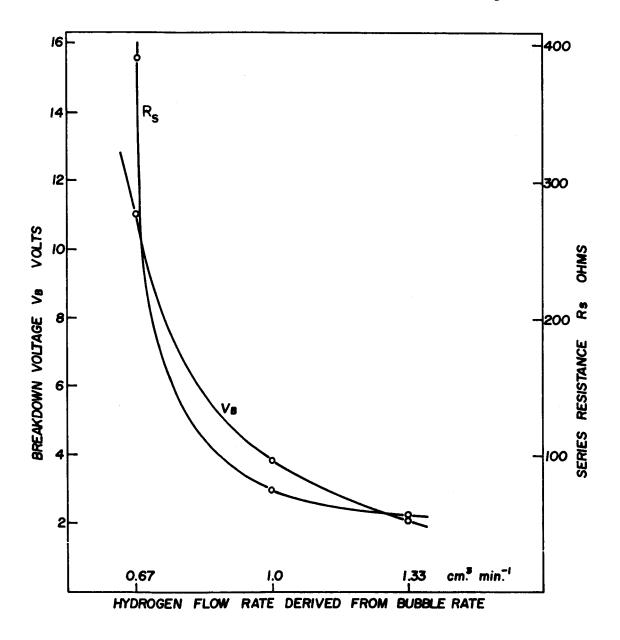


Figure 4. Electrical properties of gold dot contact to GaAs films as a function of hydrogen flow rate.

hydrogen flow rate would result in either a film whose series resistance is too high or a film with a low breakdown voltage. It has also been established that the relationships shown in Figure 4 apply only to a particular furnace operating under uncontrolled initial conditions. Thus, variations in the growth environment produce unpredictable shifts to the right or left of the curves shown in Figure 4. While a similar behavior has been observed in a furnace which was a duplicate of the one used in the above test, it was found that the actual operating conditions required to obtain comparable electrical properties of the films were quite different.

From the above results one can postulate compensation as the mechanism that ultimately determines the electrical characteristics of the GaAs films. Further, it is known that:

- (a) oxygen behaves as a compensator in n-type GaAs, and
- (b) oxygen partakes in the transport process.

It is believed that oxygen is entering the films as a compensator and ultimately determines the electrical properties of the GaAs films. Since the degree of compensation is governed by the concentration of water vapor in the furnace, the shifts of the curves of Figure 4 to the right or left in an unpredictable manner would be a result of the variations of water vapor concentration caused by the furnace instabilities described earlier. Thus, for a given initial concentration and leak rate, higher flow rates would lower the net water vapor concentration at any given time since the hydrogen flow would tend to sweep the water vapor out of the furnace. This would result in a dependence of electrical properties on flow rate similar to that shown in Figure 4.

From the above discussion, the experienced low yield (~ 20%) of GaAs films possessing acceptable electrical characteristics is easily understood. Furthermore, it was found that the results of the pressed gold dot electrical measurement were independent of thickness. It was observed that only about 20% of the films grown had an average thickness greater than 12  $\mu$ m, which had earlier been established as the minimum thickness requirement. Consequently, one could not expect a yield of solar cells greater than 4% from the original process, assuming a 100% yield of cells from acceptable films and 0% yield from films which did not meet minimum requirements. The yield in practice was between 5 and 7% for solar cells having power output greater than zero.

Using the modified GaAs growth process described earlier it has been found that:

- (a) GaAs films of satisfactory thickness (> 12  $\mu$ m) can be readily produced.
- (b) The GaAs crystallite size at the surface of the film has been significantly increased.
- (c) The instabilities in the small-area furnace have been reduced to secondorder effects.
- (d) The electrical properties of the GaAs films as exhibited when tested with a pressed gold dot contact can be readily reproduced.

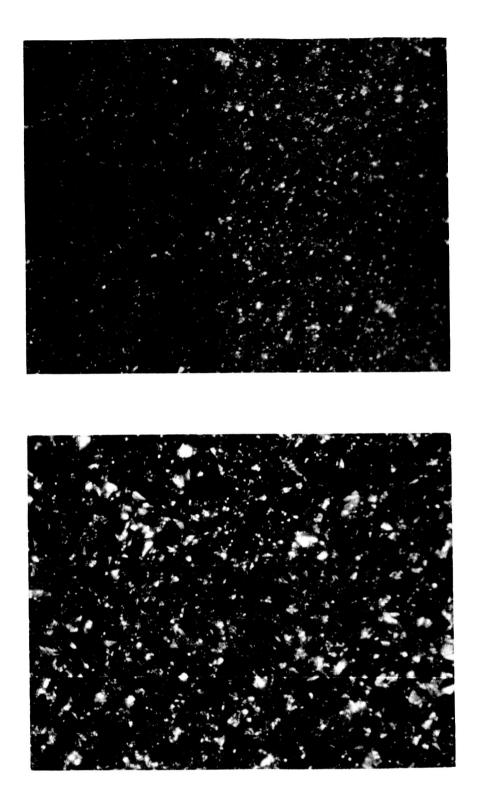
The initial results utilizing the modified GaAs growth process indicated that films of approximately 15  $\mu$ m in average thickness could be reproducibly grown during a single 22-hour growth cycle. Recent modifications in the substrate mounting have since increased the average thickness to approximately 20  $\mu$ m as shown in Table II. It seems then that the problems of thickness control and reproducibility have been virtually eliminated.

Film No.	Length of Growth (Hours)	H <sub>2</sub> Flow (cm <sup>3</sup> min <sup>-1</sup> )	< t > (µm)		
	^				
R-66	22	10	16.6		
B-4	22	10	14.2		
<b>R-</b> 67	22	10	17.6		
B-5	22	10	15.4		
<b>R-6</b> 9	22	-10	14.5		
B-7	22	10	15.8		
$\langle t \rangle = (15.7 \pm 1.0) \ \mu m$ (FINAL MODIFICATION)					
<b>R-</b> 71	22	10	19.2		
B-9	22	10	19.5		
<b>R-</b> 72	22	10	18.8		
B-10	22	10	20.0		
<b>R-73</b>	22	10	21.2		
B-11	22	10	19.3		
<b>R-74</b>	22	10	18.7		
B-12	22	10	18.7		
$< t > = (19.5 \pm 0.6) \mu m$					

TABLE IIPROPERTIES OF GaAs FILMS GROWTH BY MODIFIED PROCESS

A by-product of the increased GaAs film thickness currently being obtained has been a pronounced increase in the GaAs crystallite size at the film surface as shown in the photomicrographs of Figure 5. Film R-40a is one of the last films prepared using the original double growth process while film R-74 is one of the most recently grown films using the modified growth technique. The difference in crystallite size at the surface is readily observed. While no large crystallities can be found on the surface of film R-40a, it is apparent that the surface of film R-74 is composed mainly of 15- to  $20-\mu m$  GaAs crystallites. The dark portion of R-40a has a surface film of Cu<sub>1.8</sub>Se that is approximately 200 Å thick.

Although sufficient data are not yet available to permit choice of an optimum GaAs growth environment, it has been tentatively decided to operate in an environment obtained by mixing one part 'dry' hydrogen and one part 'wet' hydrogen at a total flow rate of approximately 10 cm<sup>3</sup> per minute. The electrical characteristics of two recently grown films are shown in Figure 6. Film R-77 was grown in the original small-area furnace while film B-15 was prepared in a furnace that was recently assembled. These films were prepared under the same environmental and operating conditions. To date no difficulty has been encountered in reproducing electrical characteristics of the type shown in Figure 6. It should also be noted that no breaking-in period was required for the new furnace.

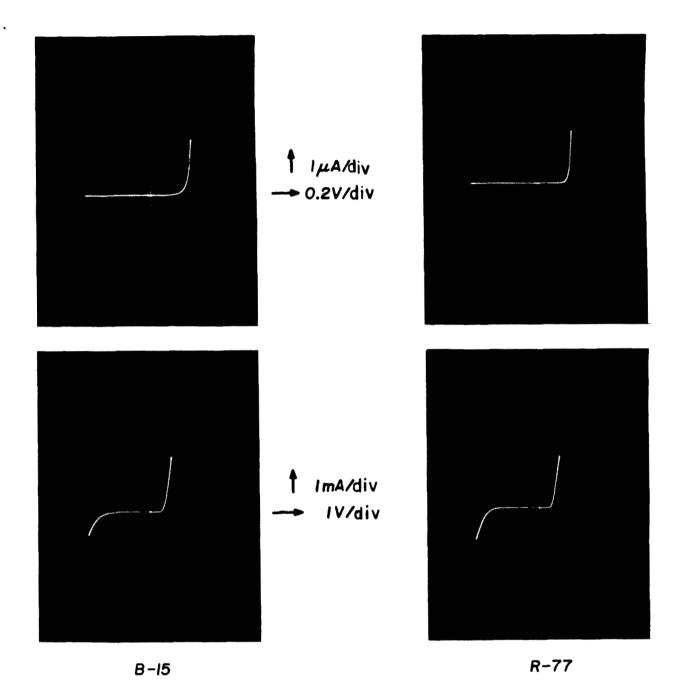


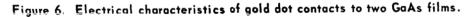
R-40a



## \_\_\_\_\_ IO MICRON DIVISIONS

Figure 5. Photomicrographs of GaAs film surfaces.





In summary, using the modified growth techniques it is now possible to operate two furnaces under similar environmental conditions and obtain from both of them a high yield (> 90%) and reproducibility of GaAs films suitable for solar cell fabrication.

#### C. GaAs GROWTH PROCESS (LARGE AREA)

#### 1. Equipment

The design of equipment for the growth of large-area films of GaAs  $(10 \text{ cm}^2)$  was based on that used in the work on  $1-\text{cm}^2$  films. A diagram showing the major features of the furnace is given in Figure 7.

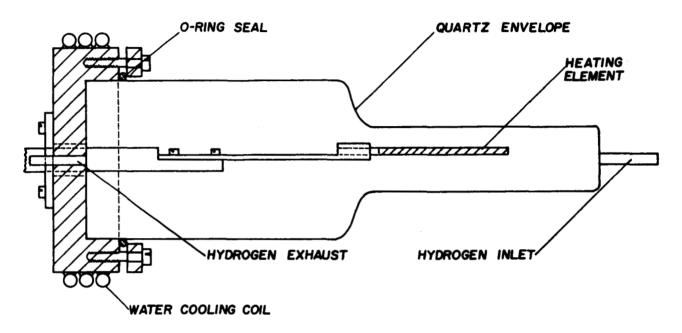


Figure 7(a). Vertical section of large-area GaAs film furnace.

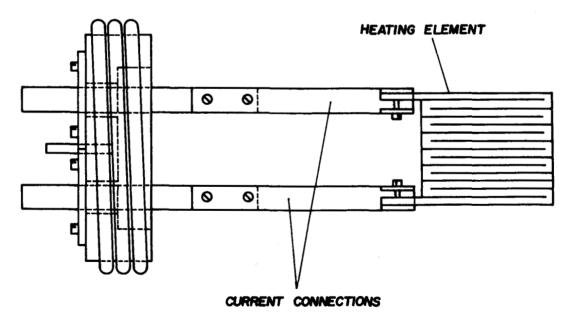


Figure 7(b). Plan view of large-area GaAs film furnace, quartz envelope removed.

The GaAs source wafers are separated from the substrate by alumina spacing pieces around the periphery of the growth area. The source wafers rest on the heating element, which is of graphite heated directly by the passage of an electric current. The heating element is mounted between the two arms shown in the figure, these providing both mechanical support and electrical connections.

These two arms pass through a metal plate which forms the end piece of the furnace envelope. This plate is water-cooled by means of the coil shown, and electrical isolation from the two arms is provided by annular ceramic seals. The remainder of the outer envelope is of quartz, the seal to the end-plate being made by means of an 0-ring. Tubulation for the hydrogen ambient used in the furnace is provided at the ends of the furnace envelope. The hydrogen supply has been ultra-high-purity cylinder gas, used without further treatment.

#### 2. Operation

The flow rate of hydrogen through the furnace during operation has been monitored by observing the bubble rate in an oil trap on the exhaust side of the furnace, the flow rates used being too low for the use of flowmeters.

The furnace temperature is limited by the melting point of the aluminum substrates, the furnace being operated as near to this point as possible. The temperature has been set during operation by monitoring the heater current, and to obtain adequate stability in this way, the power to the heater has been obtained from a regulated supply. Currents in the region of 20 A have been employed, the exact value depending on the heating element in use.

Typical furnace growth periods have been around 16 hours.

#### 3. Results

Large-area films have been grown in the furnace, and portions of these have been suitable for solar cell fabrication. However, films suitable for the fabrication of 10-cm<sup>2</sup> cells have not been obtained, and the factors which are believed to have contributed to this result are discussed below.

The major factor is thought to have been nonuniformities in temperature over the growth area, caused by nonuniformities in the heating element temperature. Several designs of heating element have been evaluated, the most successful form being the "picket-fence" type shown in Figure 7, although this also exhibits some low-temperature areas around its edges.

The films which have been obtained show surface features which appear to have been caused by gas flow nonuniformities in the growth region. These are possibly due in part to the temperature nonuniformities discussed above, and possibly due in part to small gaps between the alumina spacers used in mounting the substrates. Work in the small-area furnace also encountered difficulties due to nonuniformities, and, for this reason, the operation of the large-area furnace was suspended until the problems in the small-area furnace were overcome. The stabilization of the growth process in the small-area furnace, by the introduction of controlled amounts of water vapor, indicates that this also may be a possible approach to the solution of the difficulties with the large-area furnace.

### II. CUPROUS SELENIDE

#### A. MODIFICATIONS TO EQUIPMENT

#### 1. Flash Evaporator

Evaporations conducted using the original flash evaporation feed equipment resulted in a low yield of Cu<sub>2</sub>Se films with adequately low resistance (40 to 70  $\Omega/\Box$ ) and high transmission of 1.5-eV radiation (60 to 70%). For this reason, the flash evaporation particle feeder was redesigned. The new particle feed scheme is outlined in Figure 8.

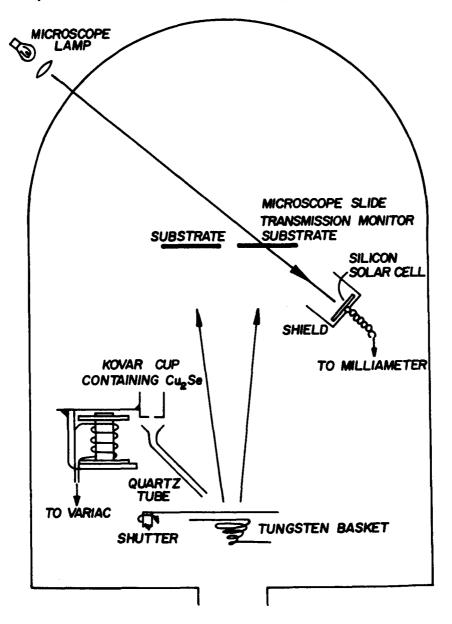


Figure 8. Modified cuprous selenide flash evaporator.

A 60-Hz current is passed through the coil, which by induction causes the 20-mil magnetic spring steel plate to vibrate. A Kovar cup is spot-welded to one end of the steel plate. The cup contains cuprous selenide particles and has in its center a hole approximately 3X the average particle size. During operation, the cuprous selenide particles fall through this hole into a quartz tube which directs them into a tungsten heater maintained at 1400°C. If the number of particles in the can is large compared with the number required for the evaporation, a uniform feed results from the random scattering of the particles by the vibrating steel plate. The rate of feed can be easily controlled by varying the current passing through the coil which in turn directly determines the amplitude of vibration of the steel plate.

#### 2. Film Thickness Monitor

The complex nature of the cuprous selenide evaporation process, which had been previously established, clearly indicated that simple monitoring of the cuprous selenide film resistance did not permit accurate prediction of the film transmission. Since

- (a) effects in solar cell performance due to small variations in the sheet resistance of the cuprous selenide film can be minimized by a suitable grid structure, and
- (b) any variation in cuprous selenide film transmission would produce a firstorder effect in solar cell performance,

a means of monitoring the transmission of the cuprous selenide film during formation was clearly required. A simple film transmission monitor, as outlined in Figure 8, has been installed in the vacuum system.

Light from an external source is passed to a silicon solar cell through a microscope slide that is positioned in the evaporant stream. The current of the solar cell, which is directly proportional to the transmission of the cuprous selenide film formed on the glass, is monitored during the evaporation. In this manner it is possible to obtain cuprous selenide films of predetermined transmission with good reproducibility.

#### B. RESULTS OBTAINED WITH MODIFIED EQUIPMENT

Some recent results using this monitor are shown in Table III. Evaporation S-14 is not considered typical since during evaporation difficulties were encountered in maintaining a uniform particle feed rate.

As found in the previous work, the cuprous selenide films are unstable in air, the films being characterized by a drop in both sheet resistance and transmission after several weeks of shelf life. The cause of the instability is not yet fully understood.

## TABLE III

Evaporation Number	Transmission Percent (1.5 eV)	Resistance (Ω∕□)
S-14	67	300
S-15	71	52
S-16	69	50
S-17	70	52
S-18	74	56
C-1	70	40
C-2	73	37

## CUPROUS SELENIDE FILM CHARACTERISTICS ON GLASS

#### A. CELLS ON GOAS FILMS GROWN BY INITIAL PROCESS

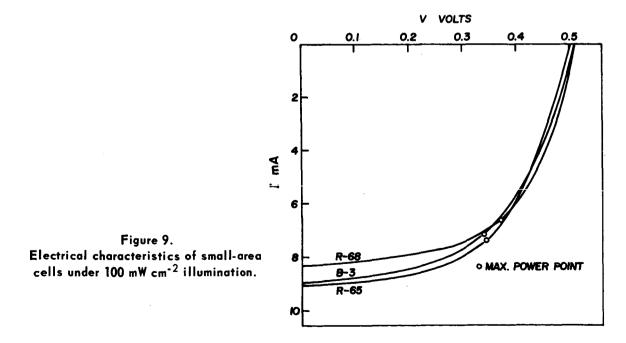
During the early part of this work, 12 cells were fabricated from GaAs films which had been grown by the initially described transport process. These cells varied in area from 0.1 to  $0.7 \text{ cm}^2$ . When probed with a pressed gold dot contact immediately following the cuprous selenide evaporation, all of them were characterized by low shunt resistance and nonuniform photovoltaic response. In several instances the low shunt resistance could be eliminated, and this resulted in a significant improvement in both the photovoltaic and diode properties of the cells. However, in all cases in which efficiencies in the 2 to 3% range were indicated by testing the ungridded cell with a 3-mW light, evaporation of a gold comb grid structure resulted in a gridto-InAs short circuit which rendered the cell useless for further measurements.

The lack of control and nonreproducibility of the GaAs film properties during this portion of the work led to a very low yield of working cells.

#### B. CELLS ON GaAs FILMS GROWN BY MODIFIED PROCESS

Recently, fabrication of cells from GaAs films grown by the modified process was initiated. Of the 20 cells attempted to date, 15 working cells, each approximately  $0.7 \text{ cm}^2$  in area, have been fabricated. Of the five failures, four were due to a poorly controlled cuprous selenide evaporation and one was due to cell breakage during post-fabrication handling. All cells had an evaporated gold comb grid structure but no antireflection coating.

These cells were evaluated under 100-mW cm<sup>-2</sup> tungsten illumination immediately after fabrication. The characteristics of several cells under test conditions are shown in Figure 9.



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The photovoltaic response of the small-area cells to  $100\text{-mW} \text{ cm}^{-2}$  tungsten illumination has been summarized in Table IV. None of the cells except B-7, B-9, R-69, and R-71 were etched during fabrication. Cells B-7 and R-69 were etched in a solution of bromine in iso-propanol, and cells R-71 and B-9 were etched in dilute nitric acid, prior to the cuprous selenide evaporation.

#### TABLE IV

Cell No. 1	Area (cm <sup>2</sup> )	T Cu <sub>2</sub> Se (%)	V <sub>oc</sub> (V)	l <sub>sc</sub> (mA)	f	P <sub>mp</sub> (mW)	N (%)
R-65	0.88	69	0.51	9.5	0.52	2.50	2.84
R-66	0.77	71	0.54	4.6	0.58	1.37	1.77
B-3	0.76	71	0.51	9.0	0.53	2.44	3.2
<b>R</b> -67	0.66	71	0.53	7.2	0.486	1.86	2.8
B-5	0.78	69	0.56	9.1	0.484	2.44	3.1
R-68	0.69	69	0.51	8.3	0.574	2.45	3.55
B-6	0.69	69	0.44	7.4	0.352	1.15	1.67
R-69	0.64	70	0.44	7.1	0.456	1.40	2.19
<b>R-71</b>	0.66	70	0.34	4.6	0.556	0.91	1.38
B-7	0.66	70	0.42	7.0	0.530	1.59	2,40
B-9	0.68	70	0.35	3.8	0.572	0.75	1.10
<b>R-72</b>	0.69	74	0.48	4.8	0.659	1.50	2.19
R-73	0.66	74	0.48	4.4	0.634	1.28	1.94
B-10	0.72	74	0.49	3.6	0.566	1.00	1.39
B-11	0.72	74	0.51	5.0	0.571	1.44	2.00

#### PHOTOVOLTAIC RESPONSE OF SMALL-AREA CELLS

These results indicate that the leakage and short-circuiting, which had been associated with the evaporations of both the cuprous selenide and the gold grid in the earlier cells, have been significantly reduced in the cells prepared by the modified GaAs growth process. It appears that fabrication of small-area cells is now possible with a reasonable yield of working cells.

#### C. STABILITY

Although techniques were developed (in the earlier work) which retarded the degradation of the cuprous selenide-gallium arsenide barrier cells, no treatment was found which would always prevent eventual severe deterioration of the cell performance. Therefore, a study of the effects of post-fabrication treatments on cell performance and stability has been initiated.

Cells were completed up to and including the grid evaporation, and were measured for performance under tungsten illumination. Test cells were then treated with one or another of the following etches:

- 1. dilute (2%) nitric acid
- 2. dilute solution of bromine in iso-propanol

Control samples of unetched cells were also kept. Immediately after etching, cell performance was again evaluated under 100-mW cm<sup>-2</sup> tungsten illumination. The cells were placed in storage in low ( $\sim 10^{-3}$  Torr) vacuum and are periodically tested to determine their stability characteristics. While sufficient data are not yet available to permit evaluation of the above stability tests, it has been found that the bromine-iso-propanol etch produces an immediate degradation of cell performance.

#### **D. OTHER STUDIES**

During a short period in which the cuprous selenide flash evaporator was unavailable, a small effort was directed toward the fabrication of Al-InAs-GaAs-Pt barrier cells. Several cells of this type, with a pressed mesh grid, were successfully fabricated. All of these cells, when tested under 100-mW cm<sup>-2</sup> tungsten illumination, were characterized by a low ( $\sim 0.3$  V) opencircuit voltage. The cause of this reduction in open-circuit voltage is not fully understood. Since this cell structure did not appear more promising than the Cu<sub>1.8</sub>Se-GaAs structure, work in this area has been temporarily discontinued.

### IV. CONCLUSIONS AND RECOMMENDATIONS

It is now possible to form operating solar cells of  $Al/InAs/GaAs/Cu_{1.8}$ Se with usable yields by the application of adequate process control.

It is recommended that further work be concentrated in two areas.

#### A. EFFICIENCY

Until  $1-cm^2$  area cells with 5% sunlight efficiency can be made with a reasonable yield, there seems to be little point in attempting to make larger-area cells. Steps to be taken to improve cell efficiency are:

- 1. Optimize the GaAs film growth conditions to produce material giving higher cell efficiencies.
- 2. Examine the effects of an anti-reflection coating for the cell surface on the cell performance.
- 3. Optimize the grid structure used for current collection on the cell surface.

#### **B. STABILITY**

The causes for the cell instabilities should be examined by life-testing a number of cells fabricated with various structures, some on single-crystal GaAs. Optical and electrical analysis of cells which degrade should be performed to provide an insight into the mechanisms giving rise to cell degradation.

Combination of the results on the optimization of efficiency and on the cell stability should yield a cell structure most likely to meet the program objectives, and cells with this structure should then be life-tested under more stringent conditions.

## REFERENCES

- 1. P. Robinson, ''Transport of Gallium Arsenide by a Closed-Space Technique,'' RCA Review, Vol. 24, No. 4, p. 574, Dec. 1963.
- 2. S. G. Ellis et al., 'Materials and Methods for Large-Area Solar Cells,' NASA CR-54959, January 14, 1966.

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