N69-35719
NASA CR 105401

Report No. 03-69-28

Final Report

SOLAR CELL CONTACT DEPOSITION PARAMETER STUDY

(30 August 1968–28 February 1969)

Contract No. NAS5-11612
Goddard Space Flight Center
Contracting Officer: J. A. Maloney
Technical Monitor: John W. Fairbanks

Prepared by

Texas Instruments Incorporated
Components Group
P.O. Box 5012
Dallas, Texas 75222

Project Engineer: Gayle Morrison

for

Goddard Space Flight Center
Greenbelt, Maryland 20771

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SUMMARY

The purpose of this report is to present the progress achieved during a six month study contract, No. NAS5-11612, for NASA's Goddard Space Flight Center (GSFC). The objective of this contract is the improvement of vacuum deposition parameters for titanium-silver contacts deposited on silicon solar cells. The scope of this study program (phase 2 of a 3-phase program-reference NASA RFP 716-90066/285) includes identification of the relationship between various contact evaporation parameters and the humidity resistance of the solar cell contact.

Five groups of titanium-silver contacts have been evaporated on silicon solar cells while maintaining a different substrate temperature for each group. The substrate temperatures evaluated were 200°C, 150°C, 100°C, 50°C and 0°C. Electrical data are presented which indicate an improvement in the contact temperature-humidity resistance when the substrate temperature is lowered to 0°C. Electron microscope photos are presented which show the smaller grain size of the 0°C contract evaporation when compared to the other four groups.

Four groups of titanium-silver contacts with different thicknesses of silver have been evaporated on silicon solar cells. Silver thicknesses studied were 3, 5, 7, and 10 microns. Data presented show the silver thickness range of 5 microns to be the most reliable in high humidity-high temperature environments.

A study was made of the effect of different silver evaporation rates where silver was deposited at 0.29 μ/minute, 1.25 μ/minute, and 2.5 μ/minute rates. Data presented in this report indicate the slower rate of 0.29 μ/minute to produce the most stable contact following accelerated temperature and humidity storage.

To study the effect of residual pumping oil vapors normally found in oil diffusion pumped vacuum systems, a group of cells was fabricated using a turbo-molecular pumped vacuum system for contact evaporations. The cells exhibited no improvement when compared to standard production cells fabricated using oil diffusion pumped vacuum systems upon evaluation following accelerated temperature and humidity storage.

In order to evaluate a possible contributing factor to the temperature-humidity resistance of Ti-Ag contacts on silicon solar cells, TI processed four groups of cells on which the ambient gas during the contact sintering operation was changed. On the first group of cells, the standard forming gas ambient was used. Other ambients studied were hydrogen, nitrogen, and helium. Environmental exposure of these cells resulted in equal blistering of each of the four groups. One group of cells was sintered in a vacuum of 1 X 10^{-5} Torr. Data on these cells after environmental testing show no change from that normally seen on standard processed cells.

TI fabricated an experimental lot of silicon solar cells on which contacts were deposited using Ti and 5% Ge + 95% Ag. Accelerated temperature and humidity storage has caused no blistering of these contacts. Electrical evaluation of this contact system is under study.

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SECTION I

INTRODUCTION

A. OBJECTIVE

One of the biggest problems currently encountered with silicon solar cells is the power degradation attributable to the Ti-Ag contacts. The objective of this study program is to determine the extent of contribution of the various parameters involved with the Ti-Ag contact deposition.

B. SCOPE OF WORK

The program has involved the fabrication of a large number of experimental lots of silicon solar cells on which different evaporation parameters were used. Evaporation parameters evaluated and reported in this report are:

- Different substrate temperatures
- Different contact silver thicknesses
- Different evaporation rates
- Different sintering ambients
- Different vacuum pumping methods
- Added Ge to the Ti-Ag contact system

Cells with varied parameters were exposed to an accelerated temperature and humidity test and examined both mechanically and electrically.

SECTION II

TECHNICAL DISCUSSION

A. SAMPLE FABRICATION AND TEST

Every possible measure was taken to ensure that all samples were processed identically, except for the parameters varied for evaluation.

1. Material

Silicon blanks used were of the standard P-type 2-cm X 2-cm X 13-mil size with a base resistivity of 7 to 14 ohm-cm. Metals used in the contact evaporation are specified as being 99.99% pure.

2. Equipment and Methods

a. Evaporation

Solar cell contact metals were evaporation deposited using a Model 18 Consolidated Vacuum Corporation vacuum system for all experiments except the contact deposition which was made in an oil-free pumped vacuum using an Ultek RCS vacuum pumping system. Titanium charges were evaporated using tungsten coils and the silver charges were evaporated from tantalum boats. All evaporations were made in the upward direction, with the substrates facing downward from the top of the bell jar. For substrate temperatures from 50°C to 200°C, an infrared heating system was mounted directly to the substrate holders. For the evaporation made with a substrate temperature of 0°C, liquid nitrogen was circulated through copper coils which were attached directly to the substrate holders. Substrate temperatures were monitored with a West Model IN-3 potentiometer using an iron-constantan thermocouple located between the substrate holders and the substrate.

b. Electrical Test

For electrical output tests, a tungsten light source was used consisting of three tungsten flood lamps operated at a color temperature of 2800°K ± 50°K and adjusted to the height necessary to attain air-mass-zero (AMO) intensity. The light source intensity was calibrated using an in-house AMO working standard, which was calibrated with JPL balloon standard No. 185. The tungsten light source was chosen over a TI solar simulator for expediency and accuracy on the comparative nature of the testing. The electrical data from this testing are presented in the Experimental Results portion of this section and indicate the effect of each experiment on the degradation resistance of the sample solar cell's contacts. The electrical evaluation averages were determined from ten cells from each evaluation group.

c. Environmental

Accelerated storage life testing, consisting of ten days' storage at a temperature of 45°C and a relative humidity of 95% was performed on samples from each experiment. Storage life testing was performed using a Blue M model No. CF-7216A humidity chamber.

d. Electron Microscopy

Photos of grain structure and size of the deposited silver contacts were made using a TI R.C.A. EMU3 electron microscope.

e. Film Thickness

Titanium-silver contact thicknesses were monitored with a Taylor Hobson Model 3 Talysurf instrument.

f. Vacuum Sintering

For this experiment the solar cells with newly deposited contacts, ready for sintering, were sealed in a quartz tube evacuated to 1×10^{-5} **Torr** pressure. The sealed tube containing the solar cells was then passed through the sintering furnace for the normal process cycle. Figures 1 and 2 illustrate the equipment and methods used.

B. EXPERIMENTAL RESULTS

1. Substrate Temperatures

For this experiment, solar cells were fabricated as per the normal TI process outlined in Figure 3. Contact evaporation substrate temperatures were closely monitored to assure close tolerance (+10°C/−5°C) to the different temperatures reported. Sample cells from each evaporation were subjected to a tape test prior to environmental testing, to assure good contact integrity at the start of testing. Contacts for this experiment were nominally 5-microns thick. Five groups of titanium-silver contacts were evaporated on silicon solar cells while maintaining substrate temperatures of:

Group D	200°C substrate temperature
Group C	150°C substrate temperature
Group B	100°C substrate temperature
Group A	50°C substrate temperature
Group E	0°C substrate temperature

As can be seen from the electron microscope photos in Figures 4, 5, and 6, the higher substrate temperatures allowed larger grain boundary growth during evaporation than did the lower substrate temperature of 0°C. It is felt that the 0°C substrate temperature held the surface mobility of the newly deposited Ag atoms to a minimum and thus discouraged a larger grain boundary growth. Electrical data on the five groups of cells, presented in Table I, indicate that the small grain size of

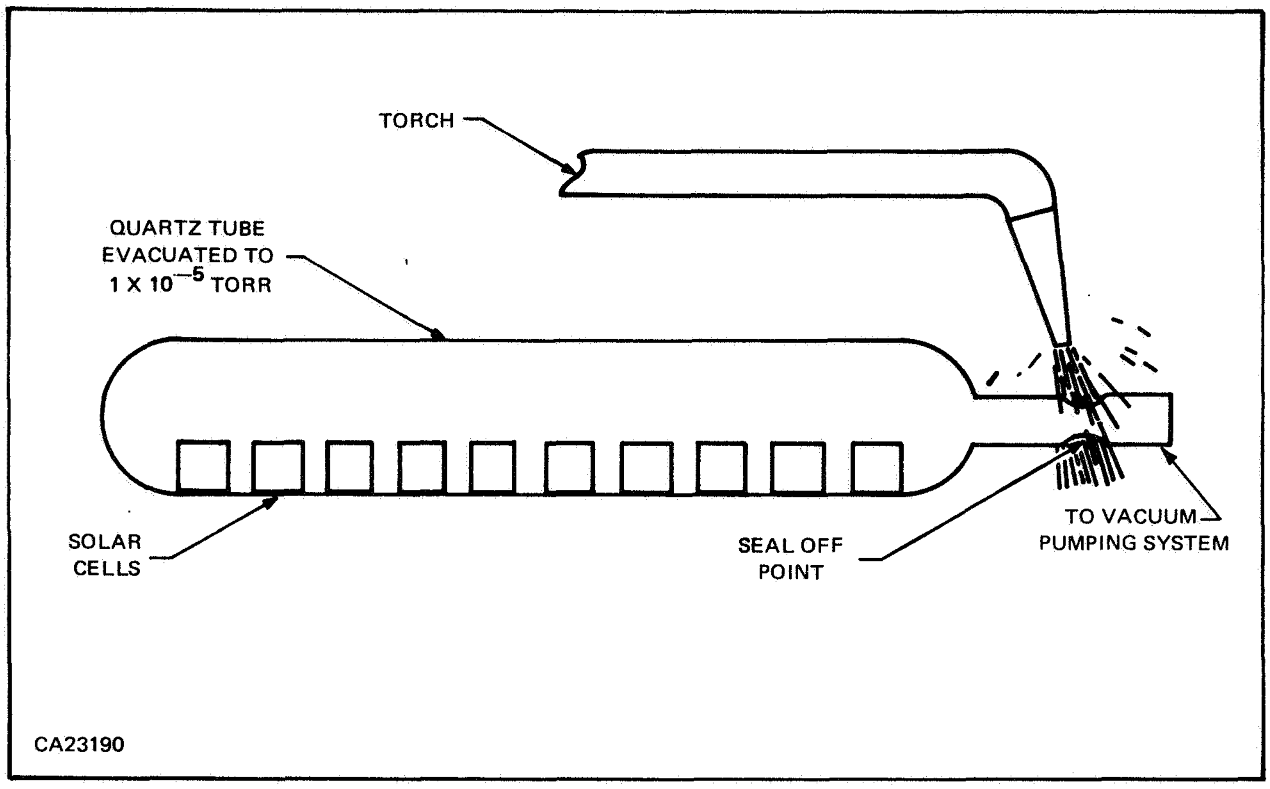


Figure 1. Tube Evacuation for Vacuum Sinter

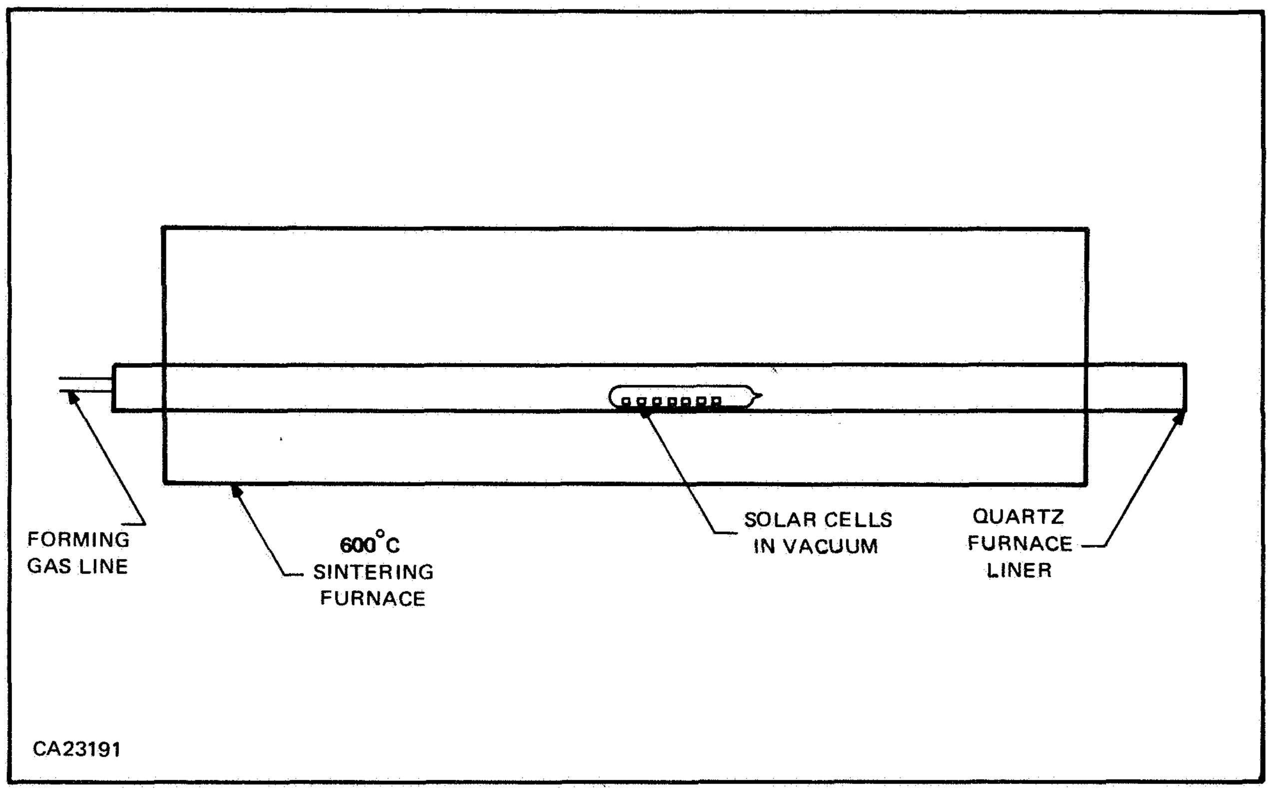


Figure 2. Vacuum Sintering

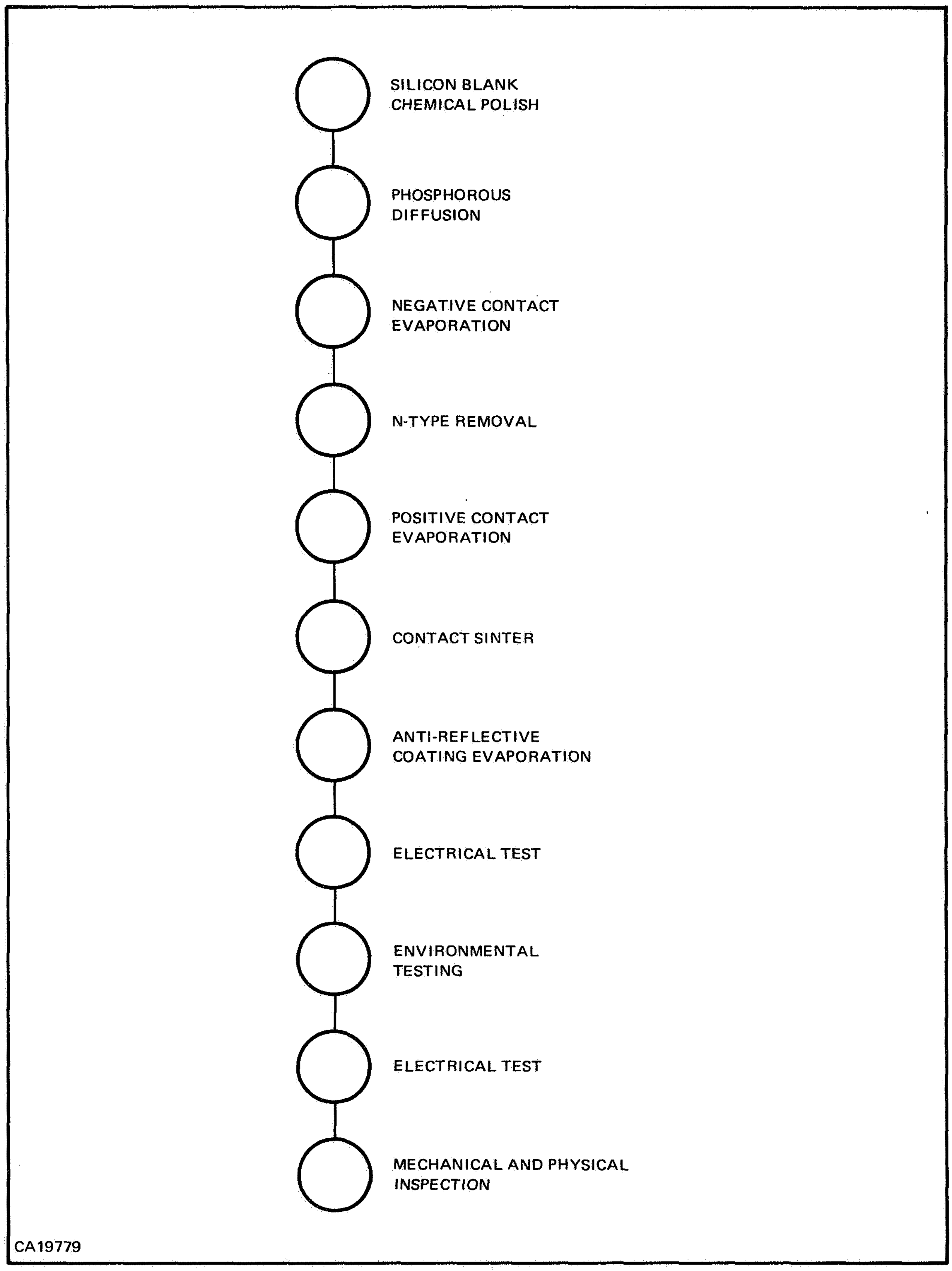
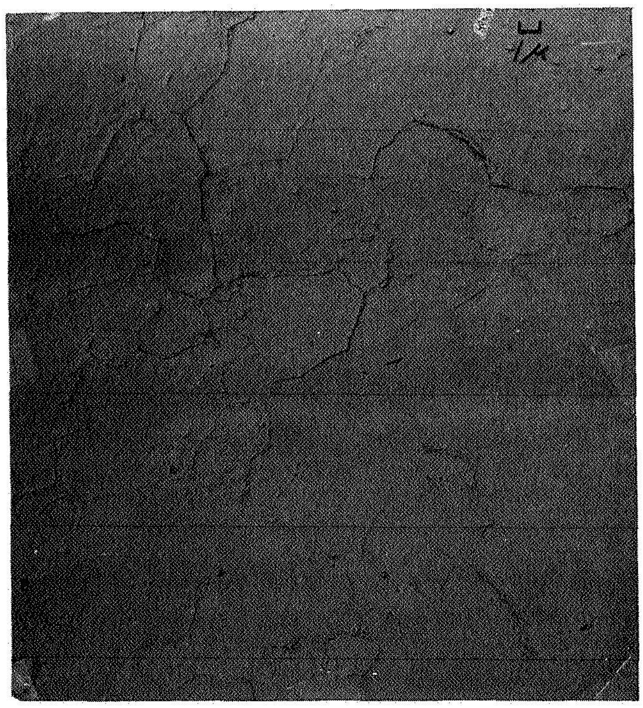
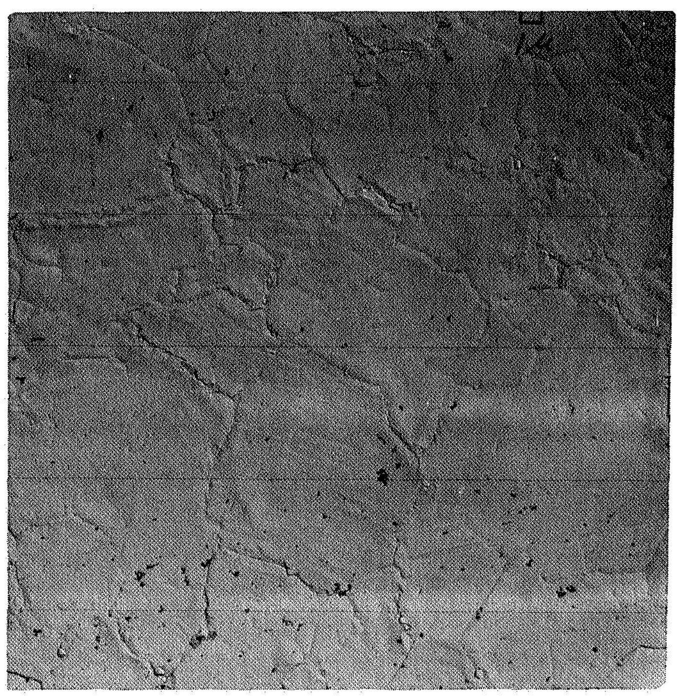


Figure 3. Process Flow Diagram



200°C CONTACT ELECTRON MICROSCOPE
PHOTO POSITIVE REPLICA



150°C CONTACT ELECTRON MICROSCOPE
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Figure 4. Electron Microscope Photos of Ag Contacts 200°C and 155°C Substrate

100°C CONTACT ELECTRON MICROSCOPE
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50°C CONTACT ELECTRON MICROSCOPE
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Figure 5. Electron Microscope Photos of Ag Contacts 100°C and 50°C Substrate


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0°C CONTACT ELECTRON MICROSCOPE
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Figure 6. Electron Microscope Photo of Ag Contacts 0°C

Table I. Substrate Temperature Evaluation—Electrical Data (Before and After Environmental Testing)

Group No. (Average)	I_{SC} (mA) Initial	I_{SC} (mA) Post	Δ (mA)	V_{OC} (mV) Initial	V_{OC} (mV) Post	Δ (mV)	I at 430 mV (mA) Initial	I at 430 mV (mA) Post	Δ (mA)
Group D 200°C	146.8	133.9	−12.9	557.3	552.9	−4.4	138.5	107.4	−31.1
Group C 150°C	150.0	152.1	+2.1	554.4	556.6	+2.2	141.13	134.08	−7.05
Group B 100°C	145.76	136.29	−9.47	552.6	551.0	−1.6	137.2	122.7	−14.5
Group A 50°C	147.7	140.53	−7.17	562.2	558.7	−3.5	140.4	94.82	−45.58
Group E 0°C	146.12	145.64	−0.48	555.9	553.4	−2.5	138.04	136.6	−1.44

the 0°C substrate cells is indeed more resistant to high temperature and humidity storage conditions. Minimizing the grain size of the Ag layer of the contact appears to be important in protecting the highly reactive Ti layer from moisture. Twenty cells from Group E (0°C substrate) have been shipped to NASA GSFC for evaluation.

It should be noted at this point that the contact sintering process (600°C) following contact deposition will affect the contact silver grain size and structure. Data presented in this report are on solar cell experimental groups which were sintered simultaneously so that the comparative evaluations may be considered valid.

2. Contact Silver Thickness

Four groups of silicon solar cells were fabricated on which the silver thickness of the contacts was deposited to 3, 5, 7, and 10 micron thicknesses. After storage in the accelerated temperature and humidity chamber, the 5-micron silver thickness group was visually superior in that it exhibited no blistering while 50% of the 3-micron group, 20% of the 7-micron group, and 10% of the 10-micron group had blistered cells. When the groups were tape tested following temperature and humidity storage, the 5-micron group still showed no contact delaminations, while the 3-micron group had delaminations on 50% (the same cells which exhibited blisters), the 7-micron group had delaminations on 50%, and the 10-micron group had delaminations on 70%. The fact that the thicker silver contacts showed fewer blisters after storage and more delaminations after tape testing indicates the presence of thick-film stresses and characteristic problems. The thicker silver appears to protect the thin Ti layer from moisture, but its bulk causes the narrow grid lines to separate from the silicon much more easily as evidenced by the number of post tape delaminations of the 10-micron group. Electrical evaluation data on the four groups are shown in Table II where the 5-micron group again appears to be the optimum thickness. Twenty cells from the 5-micron group have been shipped to NASA GSFC for evaluation.

Table II. Silver Thickness Evaluation–Electrical Data (Before and After Environmental Testing)

Group No. (Average)	I_{SC} (mA) Initial	I_{SC} (mA) Post	Δ (mA)	V_{OC} (mV) Initial	V_{OC} (mV) Post	Δ (mV)	I at 430 mV (mA) Initial	I at 430 mV (mA) Post	Δ (mA)
3 μ	144.79	145.01	+0.22	554.5	550.3	−4.2	134.68	110.82	−23.86
5 μ	143.54	143.74	+0.20	557.7	557.4	−0.3	136.16	133.59	− 2.57
7 μ	139.80	140.24	−0.44	555.5	555.5	0	131.58	128.31	− 3.27
10 μ	142.37	142.32	−0.05	553.0	548.9	−4.1	133.63	117.34	−16.29

3. Evaporation Rates

In addition to a study of various substrate temperatures during contact deposition, it was equally important to look at the temperature of the source metal during the evaporation process. An experiment was made in which the rate of evaporation of the silver was different on each of three groups of silicon solar cells. On the first group the source temperature was held at 1050°C, which resulted in a silver deposition rate of 0.29 μ/minute. On the second group, the source temperature was 1350°C and resulted in a deposition rate of 1.25 μ/minute. The third group had a source temperature of 1750°C and a high deposition rate of 2.5 μ/minute. On all three groups the substrate temperature was held at 30°C ± 5°C and the contact silver thickness was nominally 5 microns. Electron microscope analysis of the silver grain structure and size was conducted (Figures 7, 8, and 9). A definite trend can be seen when comparing the contact metal of the three groups. Grain boundary formation is noticeably absent on the 0.29-μ/minute group with the lower source temperature. Only the formation of small sites of single crystalline silver is different than the smooth dense contact. When looking at the 1.25-μ/minute contact in Figure 8, the beginning of grain boundary cracks and larger grain size is evident. Figure 9 shows the much enlarged grain size of the 2.5-μ/minute contacts deposited with the higher source temperature. Examination of the contacts following environmental storage revealed that 10% of the 0.29-μ/minute group, 50% of the 1.25-μ/minute group, and 100% of the 2.5-μ/minute group had some blistering on the contacts. Electrical evaluation of the three groups appears in Table III and also indicates the slower evaporation rate of 0.29 μ/minute to be superior to the higher rates. The cooler evaporated metal apparently reduces grain size growth in much the same manner as the cooled substrate. Twenty cells from the 0.29-μ/minute group have been shipped to NASA GSFC for evaluation.

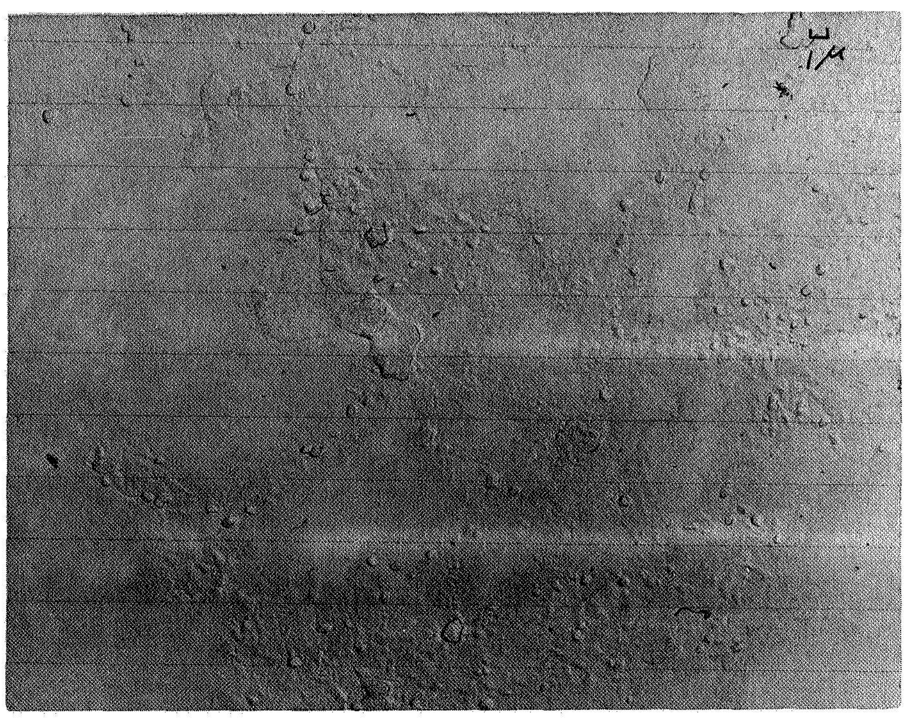

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Figure 7. Electron Microscope Photo of Ag Contacts 0.29-μ/min Evaporation Rate (2445X)

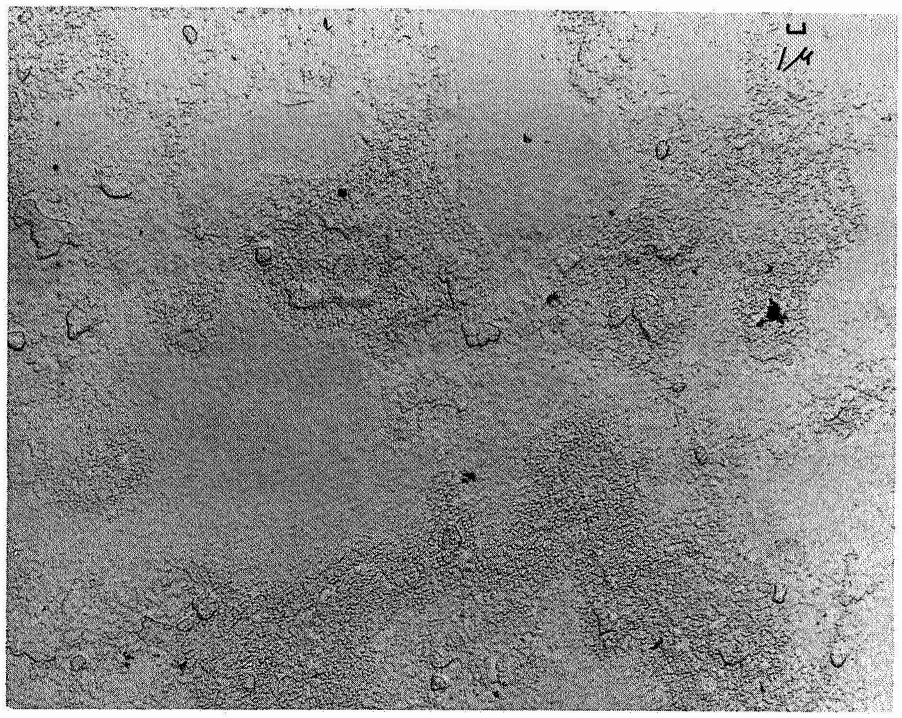

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Figure 8. Electron Microscope Photo of Ag Contacts 1.25-μ/min Evaporation Rate (2445X)

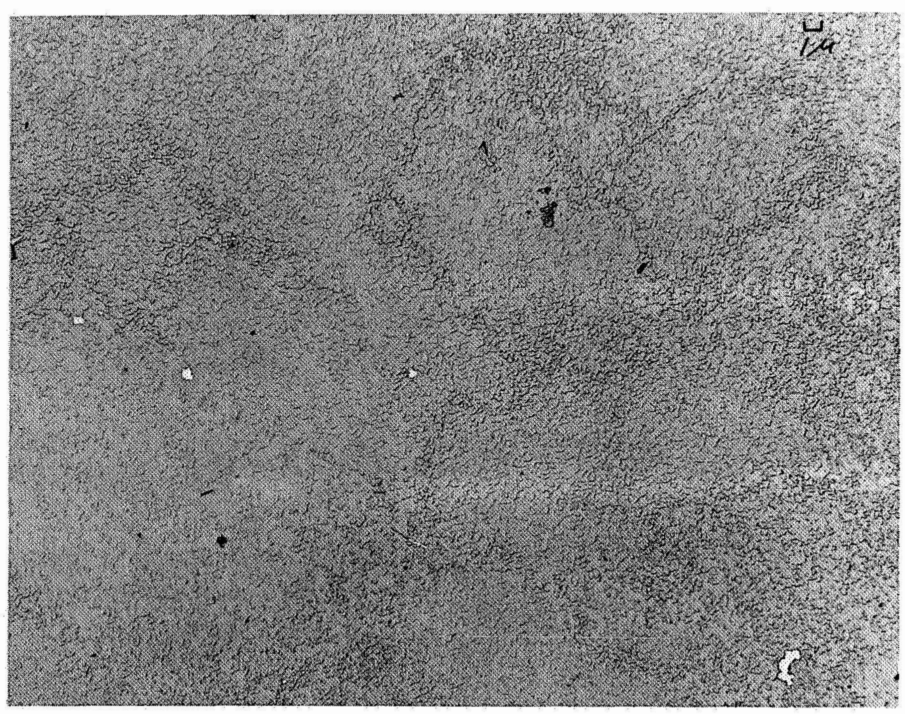

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Figure 9. Electron Microscope Photo of Ag Contacts 2.5-μ/min Evaporation Rate

Table III. Evaporation Rates Evaluation–Electrical Data (Before and After Environmental Testing)

Group No. (Average)	I_{SC} (mA) Initial	I_{SC} (mA) Post	Δ (mA)	V_{OC} (mV) Initial	V_{OC} (mV) Post	Δ (mV)	I at 430 mV (mA) Initial	I at 430 mV (mA) Post	Δ (mA)
0.29 μ	140.7	140.2	–0.5	532.9	533.1	+0.2	124.4	120.7	–3.7
1.25 μ	141.6	140.1	–1.5	532.9	531.7	–1.2	123.3	116.5	–6.8
2.5 μ	145.6	144.7	–0.9	538.2	540.2	+2.0	130.8	122.0	–8.8

4. Turbo-Molecular Evaporation

An important portion of this study program was an evaluation of the contact deposition vacuum equipment. Most metal contact depositions are performed in vacuum systems which use an oil diffusion pumping technique. In systems using oil diffusion pumping, oil is heated to its vaporizing temperature and then condensed on cooled surfaces within the pump. When the vaporized oil condenses, gas molecules are trapped in the oil droplets and are forced to the bottom of the pump where they are disposed of by mechanical pumping. In this type system, such as the CVC-18, the metal deposition area is subjected to random oil vapors which, if serious enough, will prevent contact metal adherence to the substrates, and in most systems small traces of residual oil can be detected even when good contact adherence is achieved.

In an effort to study the seriousness of residual oil in the contact deposition area, a group of solar cell contacts were evaporated in an Ultek RCS vacuum system which uses a completely oil-free pumping technique. The Ultek system uses cryogenic pumping to remove the bulk gases for a rough vacuum and utilizes a sublimated titanium gettering technique to reach an evaporation pressure of 1×10^{-7} Torr. The solar cells with contacts evaporated in the Ultek system were subjected to the temperature and humidity storage chamber for 10 days. After storage the cells were evaluated and found to have the same characteristic contact blisters as have been observed on cells with contacts evaporated in the CVC-18 oil diffusion pumped system. Twenty cells with Ti-Ag contacts evaporated in the Ultek system have been shipped to NASA GSFC for evaluation.

5. Sintering Gases

A group of silicon solar cells having blistered Ti-Ag contacts were subjected to a mass-spectrometer residual gas analysis. Hydrogen was found to be concentrated in the Ti-Ag contact blisters. This analysis was performed by evacuating the analysis chamber and then crushing the blistered contact samples. It was then felt that hydrogen from the forming gas (10% H_2 + 90% N_2) could possibly diffuse into the contact during the sintering operation and contribute to the appearance of blisters after exposure to temperature and humidity. In order to evaluate a possible contributing factor to the temperature-humidity resistance of Ti-Ag contacts on silicon solar cells, TI processed four groups of cells on which the ambient gas during the contact sintering operation was changed. Separate groups of cells were sintered using ambients of forming gas, hydrogen, nitrogen and helium. Environmental exposure of these cells resulted in equal blistering of each of the four groups as shown in Figure 10. The presence or absence of hydrogen during the sintering process apparently does not contribute to the temperature-humidity resistance of Ti-Ag contacts on silicon solar cells. It is now felt that the concentrated hydrogen found in the blistered areas is a result of the chemical reaction on the contact where moisture acts as a catalyst.

6. Vacuum Sinter

To evaluate the possibility that any gases entrapped during the contact sintering operation are contributing to the failure mode, a group of cells have been processed using a vacuum contact sintering technique. To accomplish this experiment, the solar cells were sealed in an evacuated quartz tube, as described in Figure 1, and then passed through the sintering furnace as shown in Figure 2. After environmental testing, the group of cells exhibited only one milliamp of electrical degradation at the maximum power operating point (430 mV) but the contacts were still showing blisters identical to those of the contacts sintered in the different gas ambients shown in Figure 10. Twenty cells sintered in a vacuum have been shipped to NASA GSFC for evaluation. Table IV shows the vacuum sinter electrical data before and after environmental testing.

7. Ti-(Ag+Ge) Contacts

In an effort to alter any electrochemical potential which may be present in the pure Ti-Ag solar cell contact, TI fabricated a group of solar cells with Ti-(Ag+Ge) contacts. The germanium (approximately 2% by weight) was added to the silver charge in the evaporator and was deposited at the same time as the silver. An electron microscope photo of the silver-plus-germanium contact is shown in Figure 11. The small amount of germanium is easily visible in the photo. It is also noticeable that the Ge impurity in the Ag contact has retarded any large grain growth. The cells have been through environmental storage and do not exhibit any blistering on the contacts. Electrical evaluations have not been performed.

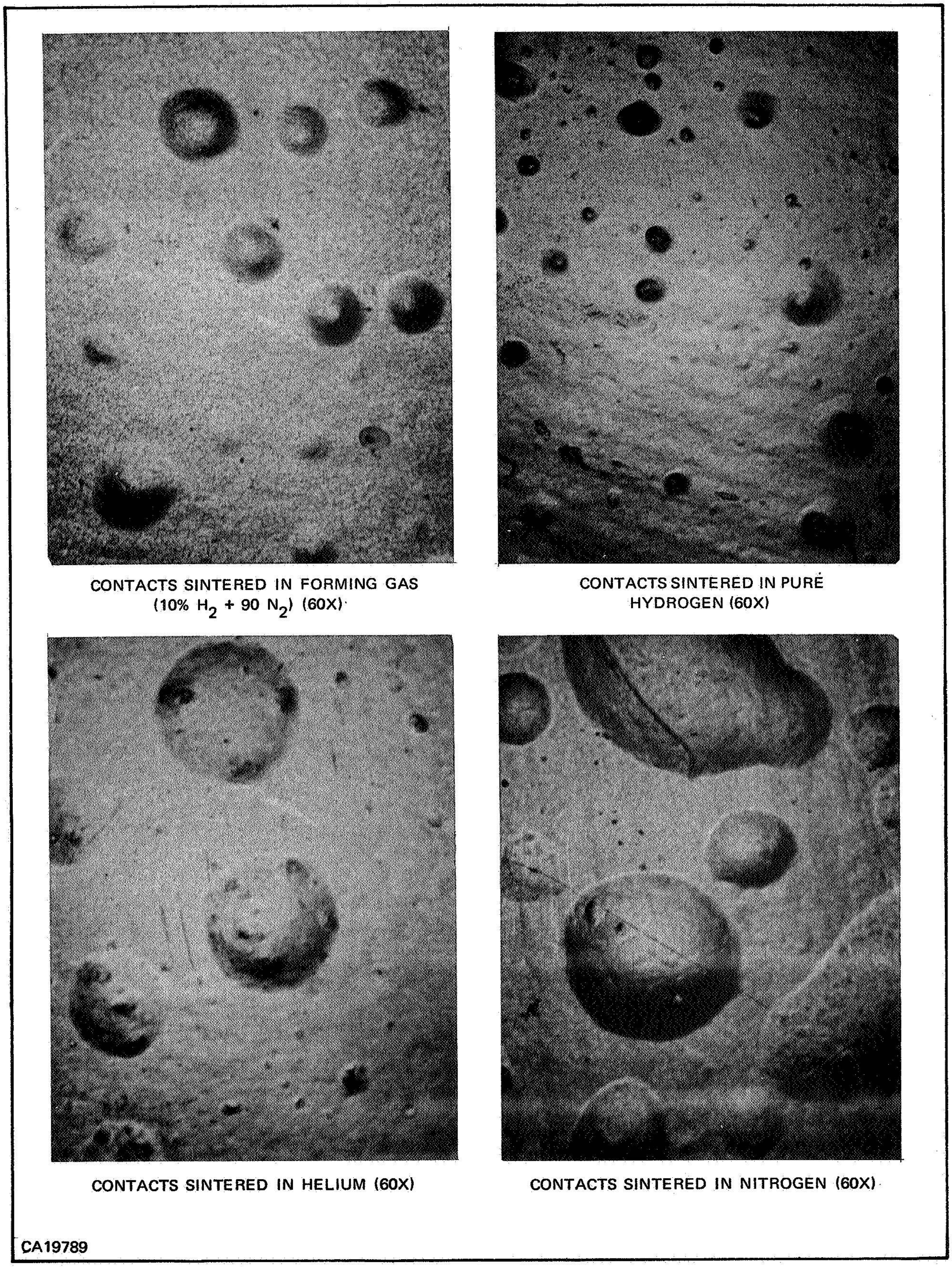

Figure 10. Contacts Sintered in Different Ambient Gases

Table IV. Vacuum Sinter Evaluation—Electrical Data

I_{SC} (mA) Initial	I_{SC} (mA) Post	Δ (mA)	V_{OC} (mV) Initial	V_{OC} (mV) Post	Δ (mV)	I at 430 mV (mA) Initial	I at 430 mV (mA) Post	Δ (mA)
140.4	140.0	−0.4	535.6	531.6	−4.0	120.4	119.0	−1.4

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Figure 11. Electron Microscope Photo of Ag+Ge Contacts

SECTION III

NEW TECHNOLOGY

New technology reported includes the evaporation of Ti-Ag contacts onto silicon solar cells while maintaining a substrate temperature of 0°C. This technique resulted in a silver grain structure considerably different than was previously experienced. This contact shows some evidence of improvement on the Ti-Ag contact temperature and humidity resistance. Solar cells with this type of contact evaporation have been submitted to NASA GSFC for final evaluation.

As additional new technology studied during this contract, TI would like to report the use of Ti-(Ag+Ge) contacts on silicon solar cells. The addition of an impurity to the Ag portion of the contact system appears to alter any electrochemical potential present as well as retard an undesirable large grain size and grain boundary growth.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

Evaluations performed during this contract indicate that evaporation substrate temperatures contribute to the optimization of the temperature-humidity resistance of the Ti-Ag contacts on silicon solar cells by influencing the grain size and structure of the evaporated metal. Experimental results show that contacts deposited at reduced substrate temperatures exhibit smaller grain size and a higher degree of temperature-humidity resistance.

Contact silver thickness does have an effect on the temperature and humidity resistance of the contact. The thicker silver more effectively protects the reactive Ti layer from moisture but stress problems appear when the contact approaches thick film thicknesses. A silver thickness of 5 microns appears to be optimum.

Different evaporation rates affect the contact in much the same way as different substrate temperatures. Slow silver deposition rates (0.29 μ/minute) reduce chances of large grain growth as does a substrate cooled to 0°C, while fast deposition rates (2.5 μ/minute) cause the appearance of large grain growth. Slow evaporation rates resulting in small grain size are desirable.

While contamination in any form is certainly not desirable, the contacts deposited in an oil-free vacuum pumping system do not show temperature and humidity resistance superior to contacts deposited in an oil diffusion pumped system.

Sintering ambient gases, including vacuum sintering, do not have an effect on the temperature and humidity resistance of the Ti-Ag contacts on silicon solar cells.

Brief evaluations of the tri-metal solar cell contact at TI [Ti-(Ag+Ge)] offer hope of increased temperature and humidity resistance. The addition of an impurity, such as Ge, to the silver contact promises to change any electrochemical potential present as well as retard unwanted large grain size and grain boundary growth.

It is recommended that additional effort be put on the development of a new contact metal system for silicon solar cells. Optimization of the deposition parameters of the Ti-Ag contact system will not produce a contact which is as reliable as that achieved by the addition of a third metal or development of a system using metals other than Ti and Ag.