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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Report 32-1362

Effects of Environmental Exposures on Silicon Solar Cells

Robert Moss
Paul Berman

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JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
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Preface

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Abstract

A series of environmental tests was performed on batches of silicon solar cells having titanium-silver contacts, with and without solder coating, to determine the effects of these environments on the mechanical and electrical properties of the cells. Cells with solder coating exhibited the largest electrical and mechanical degradations after exposure to a series of five thermal cycles from +135 to −196°C. Cells without solder coating exhibited the largest mechanical degradations after a 36-h exposure at 145°C. This latter exposure, however, did not result in significant electrical degradation. Thus, the presence of solder coating on solar cells can have a protective or deleterious effect, depending upon the environment. It was observed that either solder-coated or non-solder coated cells were capable of surviving all the environmental tests with essentially no degradation, indicating that problems were in the process controls rather than in the basic cell process. Analysis indicated that, in the case of solder-coated cells, the major problem was in the control of solder thickness and uniformity. In the case of non-solder coated cells, the major problem area was not identified; however, it is postulated that more than one mechanism is operating since it was not possible to correlate electrical degradation with contact pull-strength degradation.

Effects of Environmental Exposures on Silicon Solar Cells

I. Introduction

The loss of contact pull strength after exposure to various environments has been one of the major problems encountered by users of silicon solar cells (Refs. 1 and 2). This loss can be so severe in vacuum metallized silver over titanium (Ag–Ti) contacts that it is necessary to put a protective layer of lead-tin-silver solder (36 Pb–62 Sn–2Ag) over the contact strips. While this solder coating protects the Ag–Ti contacts from environmental attack, it creates other problems; i.e., added weight of solder, thermal shocking of the cell during solder dipping, and the increased possibility of solar-cell cracking or delamination during thermal cycling because of excessively heavy or uneven solder coating (Ref. 3). Therefore, a program was undertaken at JPL to determine the effects of various environments on solar cell contacts. The cells thus far analyzed represented two main types: N on P, 0.016-in.-thick cells with solder-coated Ag–Ti contacts and N on P, 0.008-in.-thick cells with nonsolder-coated Ag–Ti contacts. These two cell types were selected because of their importance to major JPL programs. The 0.016-in.-thick solder-coated cells are presently utilized on the *Mariner* Mars 1969 program and the 0.008-in.-non-solder-coated cells are presently used on the JPL Large Area Solar Array Technology Development Program. A summary of the experimental results is given in the following sections.

II. Solder-Coated, 0.016-in.-Thick Cells

These cells were procured for the *Mariner* Mars 1969 program, and a good deal of information has been obtained as a result of the screening requirements imposed on each lot of production cells (screened to an Acceptable Quality Level (AQL) of 2.5). The environmental screening requirements (Ref. 4) consist of exposure to temperature and humidity, thermal shock, vacuum-temperature, ultraviolet-radiation, high-temperature, and ethylene oxide environments. The actual environmental tests to which the *Mariner* Mars 1969 cells were subjected are shown in Appendix A. Electrical measurements performed before and after each environmental test indicate that the only significant electrical degradations occur as a result of the thermal shock test. Pull strength tests on the *Mariner* Mars 1969 cells were performed subsequent to the entire series of environmental tests by soldering a gold-plated Kovar tab to the contact and pulling in a direction perpendicular to the cell face. It is not possible, from these tests, to determine the effect of *each* environment on the pull strength. The cells, however, can withstand a pull of greater than 500 g subsequent to the series of environmental exposures.

Environmental tests were performed on 14 evaluation cells obtained from each of the three major cell suppliers prior to the *Mariner* Mars 1969 program and, in this case,

the gold-plated Kovar pull-tabs had already been soldered to the cell faces in the JPL tunnel oven. The results of the tests on the three groups of evaluation cells are shown in Table 1. The thermal cycle exposure was by far the most severe environment. This was further observed during the *Mariner* Mars 1969 production lot cell screening where cracking of the silicon often resulted under the contacts. Consequently, a major effort was undertaken to determine the exact reasons for this behavior and to minimize or avoid the problem.

Table 1. Pull strength of cells after environmental exposure (average of 14 cells)

Test	Average pull strength, gm		
	Vendor A	Vendor B	Vendor C
Initial	1660	1730	1520
Temperature cycle (5 cycles)	1050	640	560
Humidity	1655	1460	1260
High temperature	1280	1170	960

The N on P solar cells are made from silicon blanks 2 cm long by 2 cm wide. The contacts are coated with 1 to 2 mils of 36 Pb–62 Sn–2 Ag solder by dipping the cells into a molten bath. The solder coating facilitates attachment of electrical connectors and protects the Ag–Ti from environmental attack. Eighty-five cells from the first *Mariner* Mars 1969 production lot (Lot 1) were subjected to thermal cycling consisting of five cycles from +135 to −196°C at a rate of at least 50°C/min. Medium to severe cracking and delamination at the edges and corners of the back contacts were observed on 38 of 85 cells (45%). Failure was in the silicon just below the contact interface. Examples of this type of failure are shown in Figs. 1a and 1b. The actual rate of temperature change for this test was at least 200°C/min. Additional testing of batches

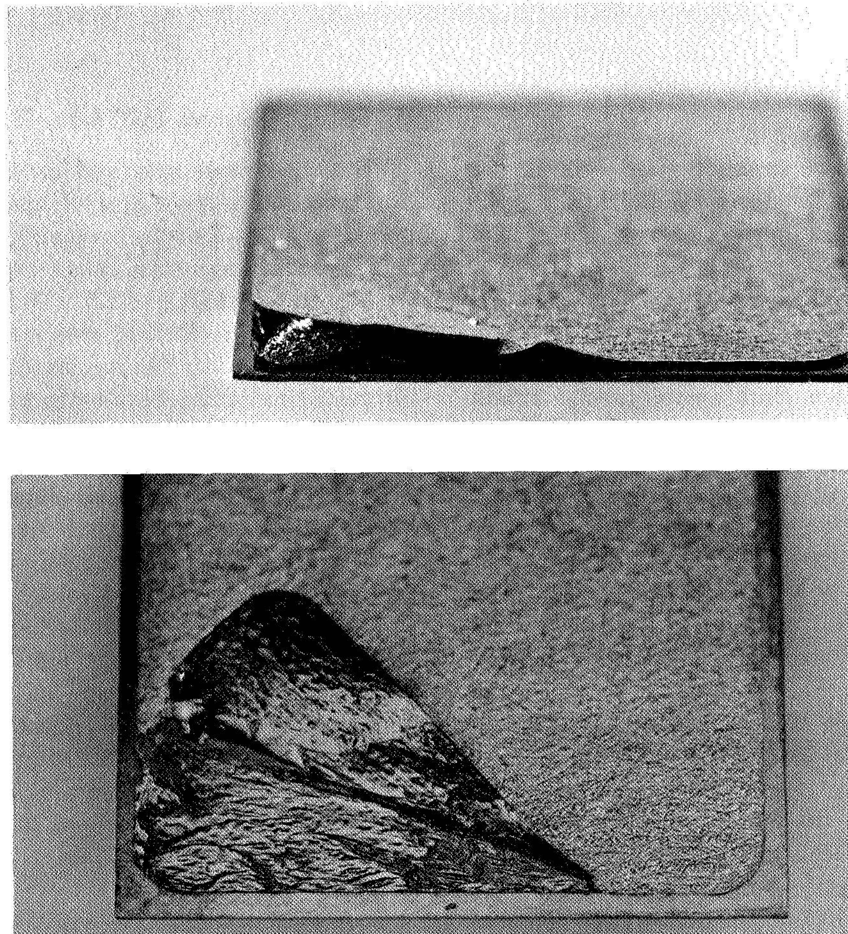

Fig. 1. Examples of silicon cracking as a result of temperature cycle

of 50 cells indicated that reduction in the rate of temperature change and rise in the *minimum* temperature from −196 to −100°C lowered, but did not eliminate, the severity and number of delaminations. Samples cycled to −75°C did not appear to delaminate; however, this temperature is not low enough to meet mission requirements. Soaking the cells for 5 h at +135°C and then at −196°C resulted in 20 and 10% delaminations, respectively. The solder coverage on the back contacts was uneven and heavy near the edges of the contact.

Metallographic examination of as-received (i.e., prior to environmental tests) solar cells from a preproduction lot and Lot 1 revealed cracks in the silicon, usually below the deposited contact (Figs. 2a and 2b). The Lot 1 cells appeared to have larger and more extensive cracks after exposure.

The cell vendor attempted to solve the problem by controlling solder thickness and distribution on the back contacts. After solder dipping, each cell was hand-pressed on soft, absorbent material to smooth and thin the solder. This operation reduced cell delamination caused by thermal cycling to less than 20%; however, because it was a hand process, there still was some maldistribution of solder and some cell contact delaminations.

III. Examination to Determine Causes of Delamination

The first possible failure mechanism that was examined was thermal expansion mismatch between solder and silicon. This was the prime consideration because (1) it was found that solar cells which were not solder-coated could be thermal-cycled without delamination, (2) solder-coated cells with very thin uniform coatings also could be thermal-cycled without delamination, and (3) the literature revealed that the coefficient of expansion of solder is approximately 16 times as great as that of silicon (Refs. 5 through 7).

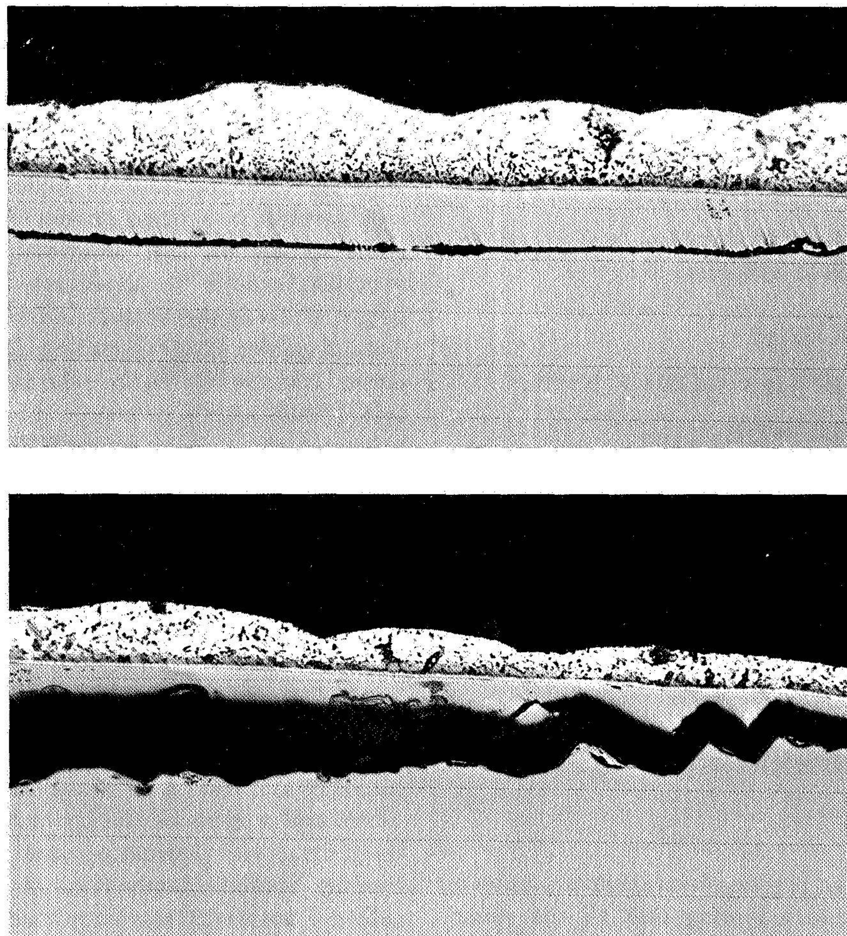

Fig. 2. Si cracks below contacts in as-received *Mariner* 1969 cells

A stress analysis was made of the solder-dipped solar cells by treating the cell and solder as a bimetallic strip and calculating the interfacial shear stress. In this configuration, the shear stresses at the interface are zero at the edge, increase rapidly to a maximum slightly in from the edge of the solder, and drop to zero asymptotically within $2t$ of the edge, where t is the sample thickness (Ref. 8). Therefore, heavy solder at the edges and corners can cause much greater strains during thermal cycling than an equivalent amount of solder uniformly distributed. To simplify the analysis, the solder coating was assumed uniform throughout and no yielding of either the solder or silicon took place under stress. The force at the interface caused by differential thermal expansion can be calculated from the equation:

$$F = \frac{(\alpha_2 - \alpha_1)\, T A_1 E_1 A_2 E_2}{(A_1 E_1 + A_2 E_2)\, W} \tag{1}$$

where

A_1 and A_2 = the areas of Si and solder respectively

W = sample width

E_1 and E_2 = corresponding moduli of elasticity

T = temperature

α = the coefficient of thermal expansion

Supplying values for these variables

$E_1 = 16.35 \times 10^6$ lb/in.^{2}

$A_1 = 0.79(16 \times 10^{-3})$ in.^{2} = 1.264×10^{-2} in.^{2}

$\alpha_1 = 1.5 \times 10^{-6}$ in./in./°C

$\alpha_2 = 24.7 \times 10^{-6}$ in./in./°C

$W = 0.79$ in.

$E_2 = 5 \times 10^6$ lb/in.^{2}

$A_2 = 0.75(t)$ in.^{2}

where

t = solder thickness, in.

T = 331°C

The maximum stress then is given by taking a parabola with minor axis of $2t$ and assuming that all the shear force is confined to a distance at the end of the interface equal to $2t$, where t = thickness. In this case, thickness is taken as total thickness of Si and solder. Equation (1) is modified to

$$\sigma = \frac{3\,(\alpha_2 - \alpha_1)\, T A_1 E_1 A_2 E_2}{4tW(A_1 E_1 + A_2 E_2)} \tag{2}$$

Inserting these values into Eq. (2), the results are:

σ_a = 1663.69 lb/in.^{2} for solder thickness = 0.001 in.

σ_b = 3087.60 lb/in.^{2} for solder thickness = 0.002 in.

σ_c = 5369.60 lb/in.^{2} for solder thickness = 0.004 in.

Although there is little data on stress-strain tensile properties of Si, some values of Si strength under cantilever beam loading were obtained at JPL as part of another program. The average shear strength of 227 Si solar cells tested was 4029 lb/in.^{2} under these loading conditions.

These calculations indicate that, as solder thickness increases, the induced shear stress from thermal expansion mismatch increases and this can be quite high in relation to the strength of Si. At thicknesses of 1 or 2 mils of solder, the Si stresses, while still appreciable, could be accepted since they are less than the failure stress of 4029 psi. However, a 4-mil solder layer at the cell edge would result in a stress greater than the average failure stress of the Si, and delamination would occur. This condition would be accentuated at corners since the corner stress is the vector sum of the edge stresses. For a 4-mil solder layer extending $2t$ along each edge, the corner stress is 7600 lb/in.^{2}; the same condition for a 2-mil solder layer results in a stress of 4365 lb/in.^{2}, or enough to exceed the average strength of the silicon.

Several cells were examined for cracks and stress patterns under the contact, and to determine whether such defects were localized. The solder and back contacts of several cells were removed by etching with a series of acid solutions. In several samples, this procedure exposed cracks just behind the edge of the contact which had not been found during microscopic examination. Other crack-free samples exhibited stress patterns which varied in intensity at different locations, but were greatest near the edges and corners of the contact. These are believed to be the traces of dislocation lines induced during thermal cycling. Similar examinations of non-solder coated solar cells did not reveal any subsurface cracks; stress patterns were much less severe and did not increase in severity near the edges of the contacts.

Another possible cause of delamination investigated was anomalies in the solder. Spectrographic analyses were made of a bar of virgin 36Pb–62Sn–2Ag solder, samples from the solder pot, and beads shaken from solar cells after dipping in the pot. Results are given in Table 2. Major differences are the increases in Pb content and slight decreases in Au, Sb, and Ca content in both the pot and cell shakeoff samples.

Table 2. Chemical analyses of solder

Metal	Bar stock	Solder pot	Beads shaken from solar cells
Pb	36.0	44.0	44.0
Ag	2.1	2.5	1.7
Sn	balance	balance	balance
Sb	0.026	0.0077	0.0079
Au	0.064	None	none
Mg	0.00034	0.00013	0.00028
Si	0.019	trace	0.010
Fe	0.017	0.0021	0.0024
Bi	0.0036	0.0041	0.0043
Cu	0.0059	0.0042	0.0051
Ni	0.0013	0.0014	0.0011
Ca	0.0019	0.00067	0.00079
Al	trace	0.0005	0.0005
Zn	0.005	0.005	0.005
Others	none	none	none

Electron beam microprobe examination was made of solder from bar stock, the solder pot, and cell shakeoff. Homogeneity of solder from the pot and in smooth spots of the cell shakeoff samples was relatively good, although some Ag segregation is apparent in the cell shakeoff. Microprobe analyses were made of a cracked and an uncracked cell after thermal cycling. Both samples displayed extensive Ag micro-segregation, and lesser, but still appreciable, segregation of Pb and Sn.

Thermal expansion mismatch strains may be magnified if the composition of the solder varies appreciably. As shown in Table 2, such a variation does occur; Pb content on the cells is 44% as opposed to the nominal value of 36%. Since the coefficient of thermal expansion of Pb is almost 25% greater than that of Sn, the expansion of such a lead-rich alloy would be expected to increase, making thermal strain greater. Unfortunately, there is no specific value in the literature for the thermal expansion coefficient of a 44Pb – 54Sn – 2Ag alloy (as found on the cell shakeoff sample, Table 2). Therefore, quantitative values cannot be given. The micro-segregation which was found may have increased thermal strains since the coefficient of thermal expansion of Ag is approximately 2/3 that of Pb and 80% that of Sn. The actual behavior in any given case would be complex, but it is probable that any uneven distribution of components in the solder could result in greater than normal strains in the Si during thermal cycling or exposure to temperature extremes.

Some cracking may occur during the soldering operation. The thermal shock that occurs when a cell is dipped into molten solder, shaken to remove excess solder, and air-cooled may be sufficient to cause thermal stress cracking.

Delaminations may have been present in previous lots of solder-dipped solar cells, but were not as readily apparent. The unusually severe thermal shock to which Lot 1 was subjected, together with the gross solder unevenness, were responsible for making the cracks more apparent. Once alerted to the possible delamination problem, more exhaustive microscopic examination of additional thermally cycled cells showed that many of them contained fine delaminations which normally would have been overlooked. Slightly delaminated solar cells may have been used inadvertently on other flight programs since a microscopic examination, particularly oriented towards the observance of this type of defect, was required to locate most of the delaminated cells when thermal cycling was done under more normal conditions, i.e., 50°C/min rate of temperature change rather than 200°C/min.

The probability of delaminations can be reduced greatly or eliminated totally by proper material and process control. The critical factor is maintenance of a thin, uniform solder layer. Such control should be exercised by the solar cell suppliers.

IV. Non-Solder Coated, 0.008-in.-Thick Cells

These cells were procured for the JPL Large Area Solar Array Technology Development Program. The cells were N on P, nominally 0.008-in. thick, 2-cm wide by 2-cm long, with standard vacuum-metallized Ag–Ti contacts on the front and back. Cells from three production lots were divided into groups of 50 and examined

metallographically and electrically before and after exposure to various environments. They also were tested for contact pull strength and beam strength after environmental exposure.

The exposures used were: 36 h at 145°C; 5 cycles at 135°C to −196°C at a rate in excess of 50°C/min; 30 days at 95% relative humidity 24°C; 4 h at 0°C plus 4 h at 65°C at 95% relative humidity; 4 h at −125°C, plus 12 days at 125°C, 10^{-5}mm Hg; series of all the preceding exposures.

Metallographic examination revealed cracks on most of the cells between the Ag–Ti metallization and the Si, or in the Si just below the interface. Figure 3 shows a good interface and Fig. 4 shows an example of cracks in the Si just below the interface. No difference in type or severity of cracks was observed as a result of the various environmental treatments.

Beam strength of the Si was determined to establish whether reductions in contact pull strength were caused by weakening the Si resulting from environmental exposure. This was done by measuring length, width, and thickness of each cell to be tested, then inserting the cell into a test fixture that maintained a constant beam length of 0.500 in. As anticipated, no exposure had any significant effect on the Si strength. Overall average strength was 42,794 g/in.^{2}.

Contact pull strength was measured by placing the cell vertically in a holding fixture and slowly pulling the soldered contact strap at 90 deg to the plane of the cell. A gram scale attached to the loading arm gave a direct

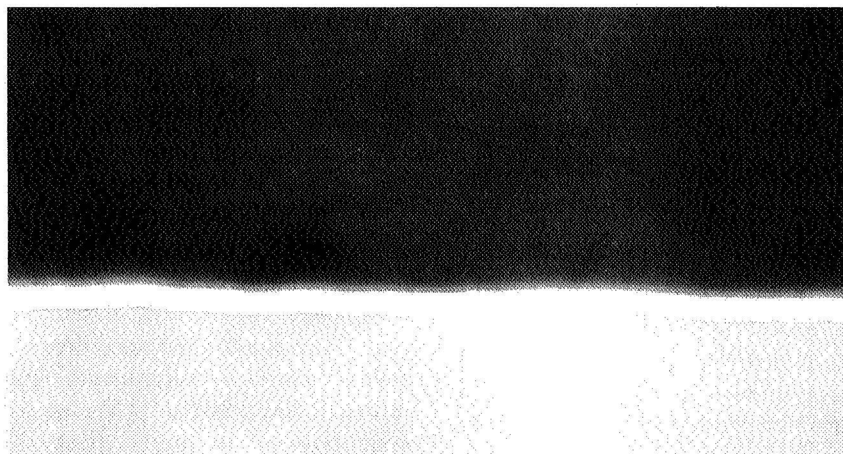

Fig. 3. Good interface between Si and contact

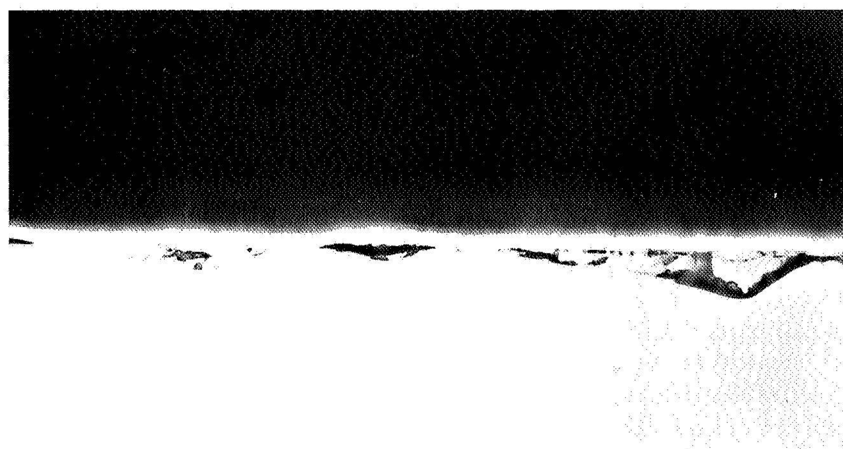

Fig. 4. Example of cracks in Si below Si-contact interface

contact strength reading at the point of failure. A computer program was developed which can be used to calculate average and standard deviation values of beam and contact strength for each lot of cells, and each environmental exposure. Comparisons of the averages and standard deviations (σ) may then be made at the 90% confidence level between the controls and any group of exposed cells, taking either all lots tested, or any one or more lots. This program was used to identify the significance of the various environmental exposures on Si beam strength and contact pull strength.

Table 3 gives the results of environmental exposure on contact pull strength and power at 0.480 V for all lots and a given exposure. Each of the tests indicated was made on as-received cells (i.e., without previous environmental exposure). Significant decreases in contact strength occurred after temperature-humidity (4 h, 0°C; 4 h, 65°C; 95% relative humidity), heat soak (36 h at 145°C), and the series of all five environmental exposures. Surprisingly, the 30-day room temperature humidity soak had no effect on contact strength, although it had been thought that high humidity was a major cause of contact failures.

The electrical characteristics of the cells were obtained under a tungsten simulator having a color temperature of 2800°K at a cell temperature of 28 ±1°C. The simulator was calibrated to correspond to a solar intensity of approximately 100 mW/cm^2 by means of balloon flight standard cells. The tungsten light was utilized because of its good stability, control cells indicating a deviation of less than ±1% for cells of the type considered. The 12-day exposure in vacuum to a temperature of 125°C and the combined exposure to all environments indicated the greatest electrical degradation. The former test did not indicate a very significant degradation in contact strength, however, while the 36-h test at 145°C showed significant loss in contact strength, but no significant electrical degradation. It should be pointed out that there were very large deviations from the average degradation value in all tests except Tests 2 (36 h at 145°C) and 4 (thermal cycle). Test 5 (4 h, 0°C + 4 h, 65°C at 95% relative humidity) yielded zero to 25% power degradation and Tests 3, 6, and 7 yielded from 0 to 15% power degradation. The drastic spreads indicate that control of processing variables is extremely important in determining the behavior of solar cells in these environments, since the tests indicate that some cells are capable of surviving the environments with no electrical degradation while others exhibit severe electrical degradation.

V. Conclusions

A. Solder-Coated, 0.016-in.-Thick Cells

1. The presence of 0.004 in. of solder on the edge of a 0.016-in.-thick solar cell probably will cause cracking and delamination during thermal cycling between 135 and −196°C because of thermal expansion mismatch.

2. The presence of 0.002 in. of solder at the corner of a 0.016-in.-thick solar cell will probably cause Si cracking and delamination under the contact during the same exposure.

Table 3. Effects of environmental exposure on contact strength and power at 0.480 V of 8-mil solderless cells

Test No.	Exposure	Pull strength average, gm (33 cells each test)	Standard deviation, σ	Average electrical degradation at 0.480 V, % (13 cells each test)
1	Controls	644.33	31.819	
2	36 h, 145°C	433.33	32.476	1.3
3	30-day, 95% relative humidity at 24°C	659.33	46.852	1.4
4	5 cycles 135 to −196°C	622.00	46.012	1.5
5	4 h, 0° + 4 h, 65°C, all lots 95% relative humidity	579.33	57.440	1.8
6	4 h, −125°C, 12 days 125°C, 10^{-5} torr	588.33	43.899	3.2
7	All exposures combined	363.33	40.594	2.7

3. Secondary defects, such as deviations from nominal solder content, solder segregation, microcracks, or strain fields in the Si could contribute to failures when the solder thickness and location give marginal conditions for survival during thermal cycling.

4. Heavy layers of solder and uneven solder coverage should be avoided, particularly at edges and corners.

5. Rate of cycling affects severity of delamination; however, some delamination was seen even at the minimum permissible rate of 50–55°C/min.

6. Delaminations occurred when the lowest temperature during thermal cycling was −100°C or below.

7. Most of the as-received cells contain some subsurface microcracks which can contribute to delamination because of thermal expansion mismatch stresses during environmental testing.

B. Non-Solder Coated, 0.008-in.-Thick Cells

1. Loss in contact strength is not caused by weakening of the silicon, but primarily by a decrease in adherence of the Ag–Ti to the Si.

2. The thermal cycle test did not give rise to any significant decrease in either contact pull strength or electrical output. This is consistent with the analysis of the 0.016-in.-thick solder-coated cells which indicated that the major reason for the degradation of this type of cell after thermal cycling was the thermal expansion mismatch between the solder and the silicon, especially when there was an excess of solder at the edges.

3. Exposure to 95% relative humidity at a temperature of 24°C for 30 days did not result in significant mechanical or electrical degradation. Exposure to 4 h at 0°C plus 4 h at 65°C, 95% relative humidity indicated some contact strength degradation. Furthermore, this latter test gave the largest spread in values for both contact strength and electrical degradation of any test, as indicated by the standard deviation.

4. It appears that high humidities alone do not result in degradation of contact pull strength; however, the combination of higher temperature and high humidity can be important. There is apparently a variation in degradation from cell to cell as a result of temperature-humidity exposure, leading to the belief that, through proper process control, it is possible to reduce the deleterious effects of high humidity-temperature environments on contact adherence and electrical performance.

5. Large variations in electrical degradation (from 0 to 15% power degradation at 0.480 V) were also observed in the 30-day-humidity, high-temperature vacuum, and combined series tests. This again indicates that poor control of process parameters is responsible for mechanical and electrical degradations experienced as a result of exposure to these environments, since some cells were able to survive without exhibiting degradation.

6. Because environments that gave rise to significant degradation in contact pull strength did not necessarily give rise to significant power degradation (and vice versa), in all probability at least two degradation mechanisms are involved. If only one mechanism were involved, it should be possible to correlate electrical power and mechanical contact strength degradations and to predict the magnitude of one from measurement of the other.

Appendix A

Environmental Screening Requirements as per JPL Specification SS500608

The following environmental screening requirements have been excerpted from JPL Specification SS500608.

4.5 Testing.

4.5.1 Lot. For purposes of sampling, a lot shall consist of 6,000 cells for Types A and C, or 3,000 cells for Types B and D delivered at one time unless otherwise specified by JPL.

4.5.2 JPL inspection. For the purpose of inspection, Military Standard MIL-STD-105D normal for an AQL of 2.5 percent defective shall be used. These cells are subject to all acceptance tests. On completion of tests all cells shall be in conformance with requirements of this specification; if not, the lot shall be rejected.

4.5.3 Temperature and humidity. The cells shall be placed in a test chamber and the air temperature and humidity lowered to 5°C and greater than 95 percent respectively. The air temperature shall then be lowered to 0°C. The cells shall soak at this temperature for four hours. The air temperature and humidity shall then be raised to 65°C and greater than 95 percent, respectively. The cells shall soak at this temperature for 48 hours. At the completion of this test, the cells shall conform to the requirements of 3.3 and 3.4.

4.5.4 Thermal shock. The cells shall be subjected to five temperature cycles between the extremes of 135°C and -196°C. The cells shall remain at the extremes for a minimum of one hour. The temperature rate of change shall be no less than 50°C per minute. At the completion of the test, the cells shall conform to 3.3 and 3.4.

4.5.5 Vacuum-temperature. The cells shall be tested in a vacuum chamber and the pressure of 10^{-5} mm Hg or less. The cell temperature shall be maintained at -125°C for four hours and 125°C for 12 days. Upon completion of the test, the cells shall be tested for satisfactory operation, and shall conform to 3.3 and 3.4.

4.5.6 Ultraviolet radiation test. The cells shall be placed in a vacuum chamber at a pressure of 10^{-5} mm Hg and subjected to high intensity ultraviolet radiation for a period equivalent to 200 sun hours. The cells shall be tested for satisfactory operation, with no apparent degradation as a result of this test.

4.5.7 Shape factor. The change in current from the short circuit current point to the current at 400 millivolts shall be less than 4.0 milliamperes for cell Types A and C and 8.0 milliamperes for cell Types B and D.

4.5.8 Spectral response. Spectral response measurements based on a constant energy wave length input shall be made on 20 cells selected at random from each lot. Tolerances on the response shall be mutually agreed on by the manufacturer and JPL. These measurements shall serve to detect changes in the properties of the cells which may seriously affect the design of solar panels. Copies of these response measurements shall be delivered to JPL prior to, or at the same time as delivery of the lot.

4.5.9 High temperature. The cells shall be placed in a chamber and the temperature raised to 145°C; and shall remain at this temperature for a period of 36 hours. Upon completion of this period, the cells shall be allowed to return to ambient room temperature, and shall conform with the requirements of 3.3 and 3.4.

4.5.10 Ethylene oxide. The cells shall be placed in a chamber and allowed to stabilize at 43 ±12°C. The Ethylene Oxide-Freon 12 gas mixture shall then be introduced into the chamber in such a manner as to produce an ethylene oxide concentration of 450 mg/l (25 percent by volume, 11 percent by weight). Sufficient water vapor shall then be added to the gas mixture to raise the relative humidity to about 35 percent but less than 90 percent, for a test period that shall be 32 hours. At the end of the test the ethylene oxide mixture shall be purged from the chamber with dry air or N_2. The cells shall then be removed from the chamber, and shall conform with the requirements of 3.3 and 3.4.

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