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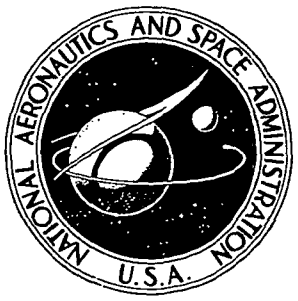

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A RELIABLE ALL-SILVER FRONT CONTACT FOR SILICON SOLAR CELLS

by John H. Lamneck, Jr., and Lawrence Schwartz

Lewis Research Center

Cleveland, Ohio 44135

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16. Abstract

The feasibility of making an adherent and moisture degradation resistant silver-only front contact to silicon solar cells was demonstrated. Optimum fabrication processes and process sequences were determined for making such contacts. These contacts were found to also have good electrical characteristics. A back contact of aluminum-silver was also developed. This proved very satisfactory for low-temperature applications.

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SUMMARY

Present day titanium-silver contacts to silicon solar cells are susceptible to degradation by atmospheric humidity. Presumably the titanium layer is the point of attack. Attempts by several investigators to apply a silver-only front contact were unsuccessful. However, at NASA Lewis Research Center, the feasibility of such a contact was demonstrated and optimum fabrication processes were determined. Contacts made by the optimized processes were found to be adherent and to have good electrical and humidity resistant characteristics.

A back contact of aluminum-silver was developed in conjunction with the work on the silver-only front contact. It was also adherent and humidity resistant, and when applied in two-steps was very satisfactory for extremely low-temperature applications.

INTRODUCTION

Unreliable contact adherence to silicon solar cells has been a continuing problem since the manufacture of the first cells. Originally, electroless nickel was used; since 1960, titanium-silver has been used. For several years the practice was to completely cover these contacts with solder. The main disadvantage to the use of solder was the severe stress induced between the contact and silicon when subjected to thermal cycling. This stress either fractured the silicon or caused contact delamination. To circumvent this problem and to gain a weight advantage, cells with only small solder covered areas where connections were made came into use. However, without the protective solder layer, contact degradation became a common occurrence under storage conditions.

Environmental testing at Heliotek (private communication) and other laboratories since 1965 has produced the following conclusions regarding contact adherence: (1) Cells that degrade rapidly under storage conditions result from poor quality control during manufacture; (2) all titanium-silver solderless cells are degraded by exposure to an environment of high humidity at high temperatures; and (3) degradation rate increases

with increasing temperature or humidity.

The mechanism of the degradation is still being investigated. The most popular theory is that the silver layer is porous and that moisture penetrates into the titanium where an electrochemical reaction occurs. Fisher and Gereth (ref. 1) claim that this results in a negative exchange potential at the interface and that a thin layer of palladium deposited between the titanium and silver shifts the exchange potential and eliminates the degradation.

Solar cell work at NASA Lewis Research Center had suggested that silver alone could function as a front contact on silicon although some researchers had stated that such a contact could not be made (refs. 1 and 2). A front contact of only silver would eliminate the corroding layer of titanium and avoid the potential poisoning of shallow junctions by iron and copper impurities in the titanium.

A program was initiated at this laboratory to determine the feasibility of an all-silver front contact to silicon solar cells. A back contact of aluminum-silver was developed simultaneously. Work was concentrated on the widely used 10-ohm-centimeter, boron-doped, n on p silicon cell of the Czochralski variety diffused with phosphorus oxychloride ($POCl_3$) for 20 to 30 minutes at 850° to 860° C. Development included investigations of processing variables from the treatment of the undiffused wafer to the application of the antireflection coating on the completed cell. The contacts were evaluated by tape testing after exposure to a temperature of 80° C at 95 percent relative humidity for 96 hours (4 days). Mechanical pull tests were also performed. The electrical characteristics of the cells were monitored to assure that the cells had been properly fabricated and continued to be useful after each nondestructive environmental test.

EXPERIMENTAL

Materials

The nominal 10-ohm-centimeter, boron-doped Czochralski silicon ingots were grown and cut into nominally 0.05-centimeter (20 mil) thick, 1- by 2-centimeter wafers, at Lewis Research Center. Resistivities varied from 7 to 14 ohm-centimeters.

The silver used to form the evaporated contacts was in the form of pellets of 99.9999 percent purity. The aluminum used was horizontally zone refined, cold swaged, and drawn into 1.27-millimeter (0.05-in.) diameter wire.

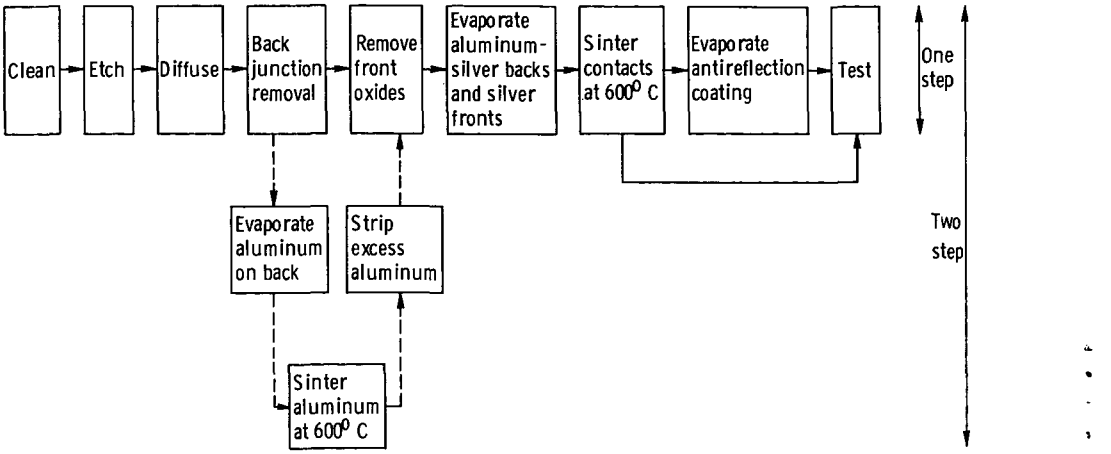


Figure 1. - Process flow chart for one- and two-step evaporation of contacts.

Cell Fabrication

One-step evaporation. - Figure 1 shows the process flow chart for a one-step evaporation of contacts. The 1- by 2- by 0.05-centimeter wafers were cleaned with organic solvents, concentrated sulfuric acid, and deionized water followed by chemical etching with a 2:3:1 solution of acetic acid, nitric acid, and hydrofluoric acid. Some were mechanically lapped with 1300-grit silicon carbide before cleaning. After chemical etching the wafers (now 0.035 to 0.04 cm thick) were thoroughly washed with hot and cold deionized water.

Diffusions were accomplished in a tube furnace heated to some temperature between 800° and 900° C. The specific temperature selected was determined by the desired sheet resistance of the diffused layer. Sheet resistances in the range of 50 to 200 ohms per square were investigated. Oxygen from the vaporization of liquid oxygen was used as a carrier gas for the phosphorus (n-type) dopant. The phosphorus source was either electronic grade phosphorus pentoxide or phosphorus oxychloride.

The unwanted junction that formed on the edges and back surface of the wafers during the diffusion step was then removed. First, the front surface was protected either by spreading the wafers on a halocarbon-waxed Teflon plate and then melting the wax or by coating the wafers with a solution of Apiezon W in trichloroethylene. Then the backs and edges were etched for 35 seconds with a 2:3:1 mixture of acetic acid, nitric acid, and hydrofluoric acid followed by water and organic solvent washes.

Next, the blue coating of phosphorus and silicon oxides was removed from the top n-type surface with a 0.5 percent hydrofluoric acid solution. The wafers were then washed several times with deionized water and isopropyl alcohol, spun dry for 10 to 15 minutes, placed in a holder, and covered with a mask (fig. 2). The holder was then

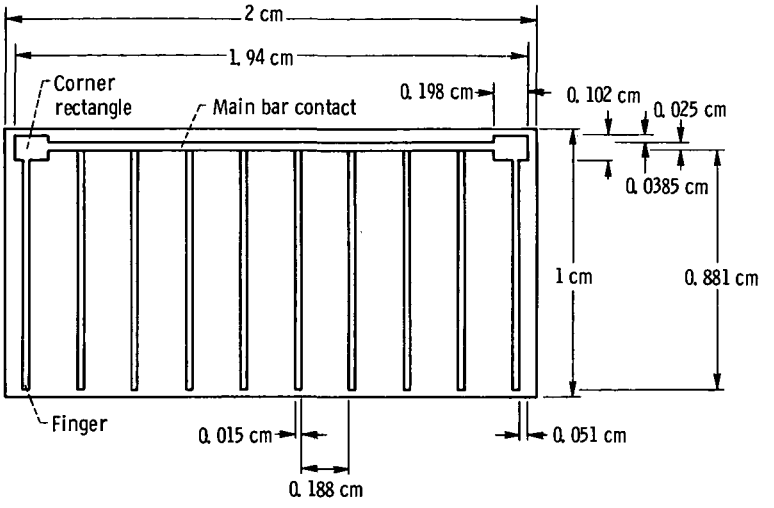


Figure 2. - Front contact geometry.

quickly loaded into a vacuum evaporator. Most runs involved 16 wafers in one cell holder.

The front and back contacts were applied in several different ways during this investigation. The procedure that resulted in the best front and back contacts was as follows: (1) The cells were placed inside the evaporator, which was evacuated to a pressure of at least 10^{-6} torr followed by a short soak. (2) The aluminum layer (0.06 to 0.07 μm) was evaporated onto the backs in 1 to 2 minutes. (3) A thin covering (0.5 to 1 μm) of silver was deposited on the fronts in 1 minute. (4) A silver layer (5 to 7 μm) was evaporated onto the backs in 10 to 15 minutes. (5) The remainder of the silver layer (6 to 9 μm) was deposited on the fronts in 10 to 15 minutes. (6) The cells were then permitted to cool for 45 minutes before they were removed from the evaporator.

After the contacts were applied to the cells, they were sintered in a furnace at a temperature between 500° and 700° C for 15 minutes to 1 hour in the presence of one of the following gases: argon, nitrogen, 94.4-percent argon - 5.6-percent hydrogen, or 94-percent nitrogen - 6-percent hydrogen (forming gas). The optimum sintering conditions were found to be 600° C for 35 minutes in the presence of forming gas. Antireflection coatings were then applied to some of the cells for an evaluation of the effects of these coatings on cell characteristics and contact adherence.

Two-step evaporation. - A departure from the procedure just described was used to assure an ohmic back contact on cells intended for low-temperature investigations. These cells were contacted in two steps as shown in figure 1. After the removal of the unwanted back junction, a layer of aluminum was deposited on the backs. This layer was sintered at 600° C for 35 minutes in an argon atmosphere during which some aluminum was alloyed into the silicon. A more positive (P^{+}) layer was thus formed which insured

ohmicity of the contact. The excess aluminum was then stripped from the backs with concentrated hydrochloric acid before removal of the blue-colored oxide coating from the fronts with dilute hydrofluoric acid. The remaining steps in the contact application were the same as for the one-step evaporation.

Tests and Criteria

After the contacts were applied to the cells, three electrical characteristics were measured:

(1) R_f - slope of the dark forward-biased cell diode voltage-current curve in the 300 to 400 milliampere range of forward current.

(2) n-value (diode equation constant) - 16.8 times the voltage difference of the dark forward-biased cell diode at currents of 10 and 1 milliamperes.

(3) I_r - value of current for the dark cell diode when biased in the reverse direction at a voltage of 0.6 volt.

All three characteristics were measured on a transistor curve tracer. Desirable values of R_f were less than 0.25 ohm and of I_r less than 10 microamperes. But values of I_r up to 100 microamperes were acceptable. Values of n less than 1.2 were excellent, and values in the range of 1.2 to 1.4 were good. The same characteristics were remeasured after application of silicon monoxide antireflection coatings.

Both uncoated and silicon monoxide coated cells were placed in a controlled relative humidity chamber and kept at 80° C and 95 percent relative humidity for 96 hours. The cells were then tape tested on both sides with 1.9-centimeter (3/4-in.) wide Scotch polyester film tape number 850. Each cell was laid on a flat surface and covered with a section of tape that was rubbed to assure complete adherence. One corner of the tape was then grasped with the fingers and quickly peeled diagonally across the cell. This procedure was repeated three more times for each side of each cell so that all four corners of a cell received the initial pulling action.

A numerical rating system was devised to describe the extent of contact peeling effected by the tape test. Tables I and II explain this system for both the front and back contacts and include photographs of cells from each category.

Mechanical pull tests were performed on cells that had and had not been humidity tested. These cells were solder dipped only for this pull test. The humidity tested cells were cleaned in trichloroethylene before soldering. Soldering was accomplished by grasping the cell on the edges with a Teflon holder, dipping it into a hydrazine activated flux and then for about 10 seconds into molten solder. The solder was an alloy of 61.5 to 62.5 percent tin, 1.75 to 2.25 percent silver, 0.2 to 0.5 percent antimony, 0.25 percent maximum bismuth, and the remainder lead. A pulling wire (0.065-cm-diam tinned

TABLE I. - RATING SYSTEM FOR FRONT CONTACTS

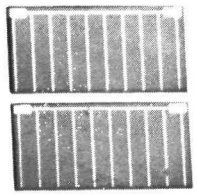
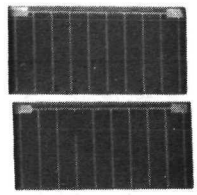
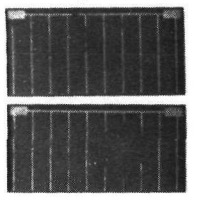
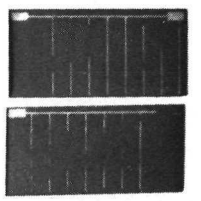
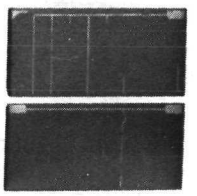
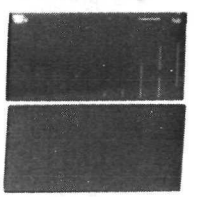
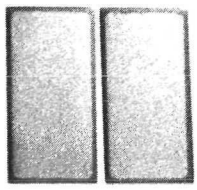
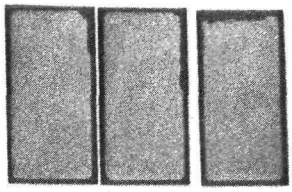
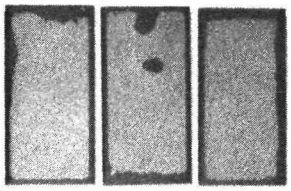
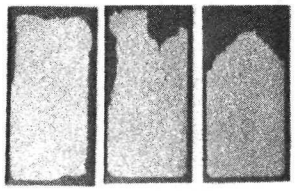
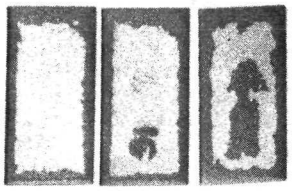
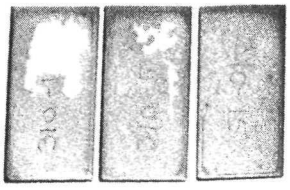
Rating	Examples	Extent of peeling
5		No more than one 1/2-mm break in one finger and located more than half way from the main contact
4		No breaks in main contact; slight peeling around one corner rectangle; and/or up to a 2-mm break in fingers
3		A very small break in main contact and/or up to 15 mm of finger peeling
2		Somewhat worse than for a 3 rating
1		Extensive peeling
0		Complete or nearly complete peeling

TABLE II. - RATING SYSTEM FOR BACK CONTACTS

Rating	Examples	Extent of peeling
5		No more than an indication of peeling around extreme outer edge of window
4		Very limited peeling around outer edges or one small spot in body of contact
3		Some peeling around edges or two or three small spots in body of contact
2		Up to 1/4 of contact surface removed
1		From 1/4 to 1/2 of contact surface removed
0		Over 1/2 of contact surface removed

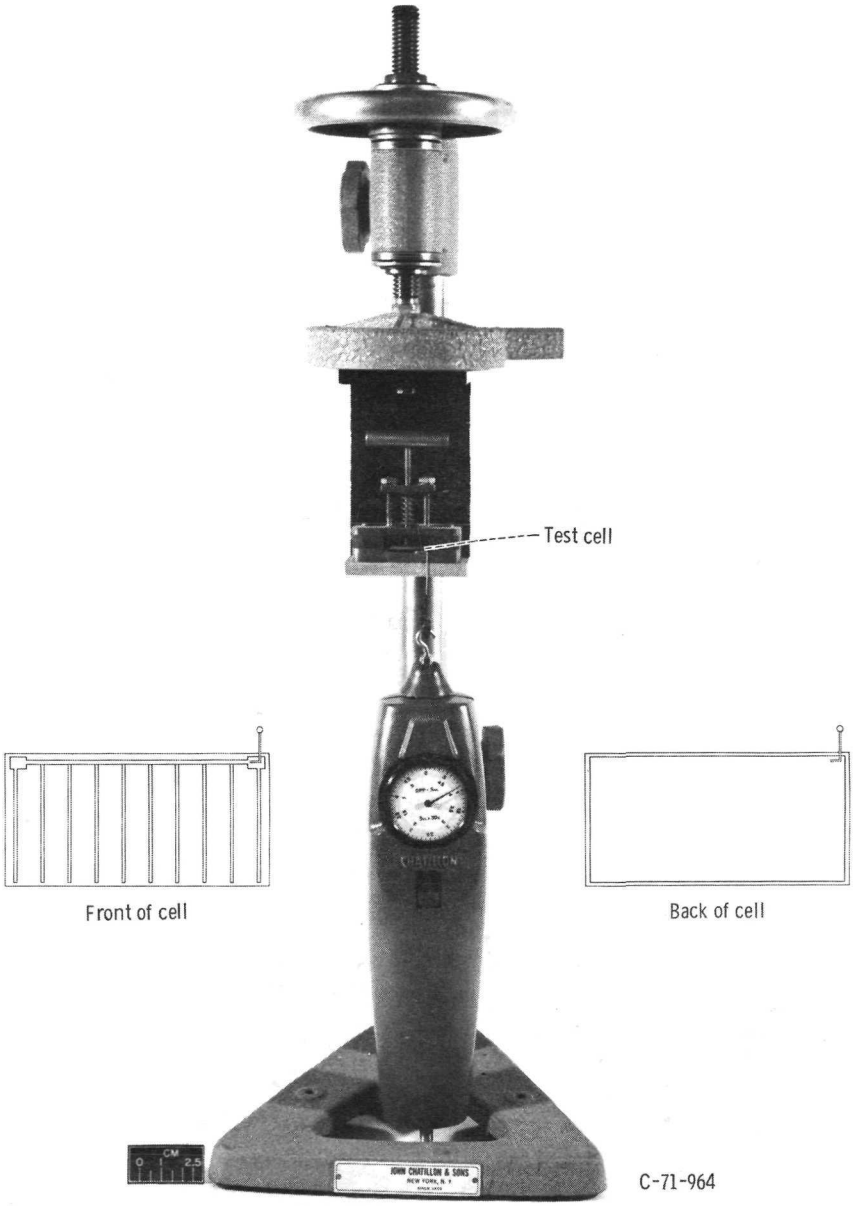


Figure 3. - Contact pulling apparatus and wire attachment points.

copper) was soldered to the cell and mechanically pulled until the wire and cell separated. A photograph of the apparatus is shown in figure 3. The force necessary to break the bond was measured on a push-pull dial gage of 5 kilogram capacity.

RESULTS AND EVALUATIONS

One-Step Evaporations

Tables III to XII contain data relating to the one-step evaporation of contacts. The effects of some of the processing variables on contact adherence and on cell electrical characteristics are discussed in this section.

Table III(a) describes the optimized cell processing steps; the data obtained from an evaluation of uncoated cells from one contacting run of 16 wafers using this process is shown in table III(b). Electrical measurements and humidity test results were excellent and are typical of what can be obtained from cells with the all-silver front contact. The data in table III(b) are included as part of group A of table IV. Table IV shows the effects of some of the processing variables on the characteristics of uncoated cells. The data in table IV lead to the following observations:

(1) Values of n and I_r were higher (undesirable) for cells protected by wax instead of Apiezon (groups C and D).

(2) Shortening the time from the dilute hydrofluoric acid wash to insertion into the contact evaporator from 40 minutes to 18 minutes did not have any significant effect on contact adherence (groups A and B).

(3) Lapping of the wafer surfaces improved adherence of the back contacts (groups A and C). The quality of the adherence is indicated by the humidity test data.

(4) Doubling the thickness of the aluminum layer had little or no effect on back adherence (groups A and G).

(5) Sintering with argon resulted in high n-values (groups D and I). Argon-hydrogen sintering also showed this same effect but to a much smaller degree (group D with F and A with E).

(6) A shortened sintering time had a slightly adverse effect on front and back adherence (groups B and H).

(7) Adherence for argon-hydrogen sintered cells was as good as for those sintered in forming gas (groups A and E).

Table V shows the effect on contact adherence of varying the concentration of the hydrofluoric acid used to remove the blue-colored oxide layer from the fronts of the cells. The optimum concentration for best adherence on both fronts and backs was 0.5 percent. Front adherence deteriorated rapidly with increasing concentration while back

TABLE III. - OPTIMIZED ONE-STEP CONTACT EVAPORATION PROCESS

(a) Cell processing steps

Step	Process
1	Lap wafers before etching
2	Diffuse wafers at 850° to 860° C for 25 min with $POCl_3$
3	Protect front surfaces of future cells with Apiezon
4	Etch backs and edges for 35 sec
5	Clean with organic solvents and deionized water
6	Remove blue-colored oxides from fronts with 0.5 percent HF
7	Load in evaporator and evacuate to at least 10^{-6} torr
8	Evaporate aluminum on backs
9	Evaporate silver on fronts and backs
10	Cool cells
11	Sinter at 600° C in forming gas for 35 minutes
12	Evaporate antireflection coatings on cells

(b) Typical cell characteristics

Cell (a)	Slope of forward current-voltage curve, R_f, ohms	Diode equation constant, n-value	Reverse current for dark cell diode, I_r, μA	Humidity and tape test rating	
				Fronts	Backs
1	0.22	1.14	3	(b)	(b)
2	.20	1.09	3	(b)	(b)
3	.20	1.21	7	5.0	4.0
4	.20	1.13	3	(b)	(b)
5	.21	1.13	70	5.0	5.0
6	.20	1.11	3	5.0	5.0
7	.20	1.09	3	(b)	(b)
8	.21	1.11	3	5.0	5.0
9	.21	1.16	174	4.0	5.0
10	.20	1.13	3	5.0	5.0
11	.20	1.13	3	(b)	(b)
12	.21	1.23	3	5.0	5.0
13	.21	1.13	3	(b)	(b)
14	.20	1.11	3	5.0	5.0
15	.20	1.11	3	5.0	5.0
16	.21	1.14	4	5.0	5.0
			av	4.9	4.9

[a]No antireflection coatings on cells.

[b]Used for other tests.

TABLE IV. - EFFECTS OF PROCESSING VARIABLES ON CELL CHARACTERISTICS

FOR ONE-STEP CONTACT EVAPORATION

[No antireflection coating; sintering temperature, 600° C.]

Processing variables							
Group	Lapped ?	Sheet resistance range, ohm/sq	Coating for back junction removal	Wafer preparation time	Back contact aluminum thickness, μm	Sintering	
						Gas	Time, min
A	Yes	52 - 87	Apiezon	Normal	0.06 - 0.07	Forming gas	35
B	Yes	58 - 64	Apiezon	Short[a]	↓	↓	↓
C	No	61 - 66	Apiezon	Normal			
D	No	55 - 78	Wax	↓		↓	
E	Yes	52 - 64	Apiezon			Argon, hydrogen	
F	No	66 - 77	Wax		↓	Argon, hydrogen	
G	Yes	52 - 64	Apiezon	↓	.12 - 0.14	Forming gas	↓
H	Yes	58 - 64	Apiezon	Short[a]	.06 - 0.07	Forming gas	15
I	No	56 - 66	Wax	Normal	.06 - 0.07	Argon	35

Cell characteristics									
Group	Number of evaporation runs	Number of cells					Humidity and tape test ratings		
		Total	With n-value -		With I_r -		Fronts	Backs	Number of cells
			<1.2	From 1.2 to 1.4	<10 μA	<100 μA			
A	3	48	37	10	43	45	4.9	4.8	25
B	3	48	29	14	35	46	4.9	4.8	22
C	2	23	16	3	18	23	4.8	4.2	14
D	5	55	1	37	14	30	4.8	3.7	55
E	3	48	27	12	35	42	4.9	4.7	33
F	1	10	0	2	0	1	4.9	4.8	10
G	2	32	23	8	23	31	4.8	4.6	22
H	1	16	10	6	13	15	4.6	4.5	8
I	2	26	0	3	6	17	4.5	4.3	20

[a]The short preparation time eliminated two of the three water rinses and the drying step.

TABLE V. - EFFECTS OF CONCENTRATION OF HYDROFLUORIC ACID ON CONTACT ADHERENCE

[All groups were sintered at 580° to 620° C in argon and are one-step evaporations with no antireflection coatings.]

Group	Hydrofluoric acid concentration, percent	Humidity and tape test ratings		
		Fronts	Backs	Number of cells
J	0.25	4.6	4.3	14
K	.5	4.7	4.8	16
L	1.0	4.0	4.7	↓
M	2.0	3.4	4.4	↓
N	5.0	3.1	4.4	↓
O	10.0	1.4	4.2	↓

TABLE VI. - EFFECT OF PREMATURE REMOVAL OF BLUE COLORED OXIDE LAYER FROM FRONT SURFACE OF WAFERS

[No antireflection coatings used.]

Group	Cell number	Slope of forward current-voltage curve, R_f, ohm	Diode equation constant, n-value	Reverse current for dark cell diode, I_r, μA	Humidity and tape test ratings		Blue colored oxide removal relative to back junction removal
					Fronts	Backs	
P	1	0.21	1.11	3	5.0	4.0	After
	3	.20	1.13	3	↓	5.0	↓
	9	.22	1.23	4	↓	5.0	↓
	14	.23	1.14	22	↓	4.0	↓
	16	.21	1.24	6	↓	3.0	↓
	--	----	----	--	5.0 av	4.2 av	-----
Q	6	0.9	1.73	9	0	4.0	Before
	7	1.25	1.95	3	↓	↓	↓
	8	.6	1.75	43	↓	↓	↓
	11	.92	1.71	3	↓	↓	↓
	15	.82	1.71	25	↓	5.0	↓
	--	----	----	--	↓	4.2 av	------
R[a]	2	0.22	2.22	114	0	4.0	Before
	4	.38	1.56	5	↓	5.0	↓
	5	.25	2.28	93	↓	4.0	↓
	10	.32	1.75	9	↓	5.0	↓
	12	.23	2.60	12	↓	5.0	↓
	13	.24	2.60	16	↓	4.0	↓
	--	----	----	---	↓	4.5 av	------

[a]An additional 0.5 percent HF treatment was given after back junction removal.

adherence was only slightly affected. The wafers used for this evaluation were not lapped and were coated with wax for back junction removal.

Table VI shows the importance of delaying the removal of the blue-colored oxide layer until just before front contact application. In each case 0.5 percent hydrofluoric acid was used to remove the oxide. Group P cells were prepared in the normal manner with the blue-colored oxide removed after the back junction was removed. Groups Q and R were prepared by removing the blue-colored oxide before the back junction was removed. For group R, but not group Q, there was a similar hydrofluoric acid treatment following back junction removal as well. This group was intended to show that a delayed hydrofluoric acid treatment alone was not the important criterion for good contact adherence. The contacts then were applied to all three groups in the same one-step evaporation.

The fronts completely peeled on humidity and tape testing on all the cells whose oxide layer was removed before back etching. Back adherence was only slightly affected, if at all, but R_f and n-values were much higher for such cells. Also, the I_r values were slightly higher.

Table VII summarizes the effects of sintering in different atmospheres. All four gases resulted in excellent front contacts but the two reducing atmospheres (groups S and V) yielded more adherent back contacts and also gave much better n-values. Forming gas was slightly better than argon-hydrogen with respect to n and I_r.

Table VIII demonstrates the importance of sintering temperatures. Results from 550° to 700° C in forming gas are shown. The cells processed at 600° C have the most adherent contacts and the best n-values. The back contact at 550° C is poor because the aluminum-silicon eutectic temperature of 577° C was not reached. Adherence of the front contact had deteriorated appreciably by 700° C.

TABLE VII. - EFFECT OF VARIOUS SINTERING GASES ON CELL CHARACTERISTICS

[Number of cells per group, 16; identical wafers used for each group; no antireflection coatings on cells; sintering temperature, 600° C; sintering duration, 35 min.]

Group	Sintering gas	Slope of forward current-voltage curve, R_f, ohm	Number of cells				Humidity and tape test ratings		
			With n-value		With I_r		Fronts	Backs	Number of cells
			<1.2	From 1.2 to 1.4	<10 μA	<100 μA			
S	Forming gas	0.20 - 0.22	14	2	14	15	4.9	4.9	10
T	Argon	.21 - 0.23	1	14	12	15	4.9	4.1	12
U	Nitrogen	.21 - 0.24	5	10	12	14	5.0	4.5	12
V	Argon-hydrogen	.21 - 0.23	12	2	10	15	4.8	4.8	12

TABLE VIII. - EFFECT OF SINTERING TEMPERATURE ON CELL CHARACTERISTICS

[Number of cells per group, 16; identical wafers for each group; no antireflection coatings used on cells; sintering gas, forming gas; sintering duration, 35 min.]

Group	Sintering temperature, °C	Slope of forward current-voltage curve, R_f, ohm	Number of cells				Humidity and tape test ratings		
			With n-value		With I_r		Fronts	Backs	Number of cells
			<1.2	From 1.2 to 1.4	<10 μA	<100 μA			
W	550	0.21 - 0.23	7	8	15	15	4.8	1.4	12
X	600	.20 - 0.22	14	2	14	15	4.9	4.9	10
Y	650	.21 - 0.23	6	7	11	13	4.5	3.7	12
Z	700	.23 - 0.25	11	3	7	13	3.8	4.5	12

Table IX indicates the effect of humidity on the cell characteristics, R_f, n, I_r, and contact adherence. These cells were prepared by the optimized procedure shown in table III(a) and were not coated. The electrical characteristics were not adversely affected by the humidity exposure and, in the cases of some individual cells, were even significantly improved. Improvements may have been effected by the removal of edge contaminants during the humidity exposure. Contact adherence of all cells was excellent.

Pull test data are shown in table X. These tests were performed on four categories of cells: (1) no antireflection coating and no humidity testing, (2) no antireflection coating but humidity testing, (3) a silicon monoxide antireflection coating and no humidity testing, and (4) a silicon monoxide coating and humidity testing. Results were very good for all categories on both fronts and backs. Variances in the thicknesses of cells would affect the data when failure was due to silicon breakage. This breakage was more prevalent on testing the front contact because the pulling wire was attached closer to the edge of the cell.

Table XI lists some experimental data on a group of cells made by the optimized procedure and to which an antireflection coating had been applied. These cells are comparable with those uncoated cells in tables III and IX. Curves of voltage against current output were measured at ambient temperature under a quartz-iodine lamp light source whose intensity was set with a calibrated cell to a value equal to that of air mass zero (AM0). Both fill factors and efficiencies were equal to or better than the values acceptable for present day silicon solar cells.

Table XII shows the effect of diffusion temperature on cell characteristics and contact adherence. The bulk of the cells tested for this report were diffused at 850° to 865° C and had sheet resistances of 50 to 89 ohms per square. However, some cells were also diffused at 840°, 820°, and 800° C and had sheet resistances of approximately 100, 150, and 230 ohms per square, respectively.

TABLE IX. - EFFECT OF HUMIDITY ON CELL CHARACTERISTICS FOR OPTIMIZED ONE-STEP CONTACT EVAPORATION RUN

[Wafers were diffused at 854° C, some with $POCl_3$ and some with P_2O_5. They were coated with Apiezon for back etching and sintered for 35 min at 600° C in argon-hydrogen. No antireflection coatings were used on the cells.]

Cell number	Before humidity and tape testing			After humidity and tape testing			Humidity and tape test ratings	
	Slope of forward current-voltage curve, R_f, ohm	Diode equation constant, n-value	Reverse current for dark cell diode, I_r, μA	Slope of forward current-voltage curve, R_f, ohm	Diode equation constant, n-value	Reverse current for dark cell diode, I_r, μA	Fronts	Backs
1	0.23	3.94	128	0.23	1.28	5	5.0	5.0
2	↓	1.71	12	↓	1.23	3	↓	5.0
3	↓	1.13	4	↓	1.14	15	↓	4.0
4	↓	1.11	3	↓	1.13	3	↓	5.0
5	↓	1.11	3	↓	1.11	3	↓	↓
6	↓	2.74	32	↓	1.13	4	↓	↓
7	↓	1.11	3	↓	1.11	4	↓	↓
8	↓	1.09	↓	↓	1.11	3	↓	4.0
9	↓	1.13	↓	↓	1.11	4	↓	4.0
10	.22	1.09	↓	↓	1.09	3	↓	5.0
11	.22	5.88	970	↓	1.39	9	4.0	5.0
12	.23	1.85	13	↓	1.23	12	5.0	4.0
13	↓	1.09	3	↓	1.09	3	↓	4.0
14	↓	5.55	540	↓	3.94	102	↓	5.0
15	↓	1.11	3	↓	1.13	3	↓	5.0
16	↓	1.09	3	.25	1.23	4	↓	4.0
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TABLE X. - PULL TESTS ON ONE-STEP CONTACTED CELLS

Cell number	Humidity tested ?	Pull test					
		Fronts			Backs		
		Force		Comment	Force		Comment
		N	g		N	g	
No antireflection coating							
1	Yes	14.5	1475	Silicon broke	26.8	2730	Wire pulled loose
2	↓	20.7	2110	↓	25.3	2575	Wire pulled loose
3		19.6	2000		25.5	2600	Wire pulled loose
4		20.4	2080		32.9	3350	Silicon broke
5		12.7	1300		24.5	2500	Wire pulled loose
6		29.4	3000	Wire pulled loose	28.4	2900	Silicon broke
7	No	16.0	1630	Silicon broke	16.9	1720	Wire pulled loose
8	↓	18.6	1900	↓	42.2	4300	Wire pulled loose
9		13.7	1400		28.0	2850	Wire pulled loose
10		17.2	1750		39.7	4050	Silicon broke
11		32.4	3300		25.5	2600	Silicon broke
12		26.0	2650		49.0	5000	Silicon broke
Silicon Monoxide antireflection coating applied							
13	Yes	24.0	2450	Silicon broke	28.0	2850	Silicon broke
14	↓	17.7	1800	↓	32.9	3350	Wire pulled loose
15		16.2	1650		21.6	2200	Silicon broke
16		23.5	2400		39.7	4050	Wire pulled loose
17		24.5	2500		49.0	5000	Wire pulled loose
18		15.2	1550		22.6	2300	Silicon broke
19	No	10.8	1100	Silicon broke	23.0	2350	Silicon broke
20	↓	19.6	2000	Silicon broke	31.9	3250	Silicon broke
21		20.6	2100	Silicon broke	28.9	2950	Silicon broke
22		20.6	2100	Wire pulled loose	30.4	3100	Wire pulled loose
23		14.7	1500	Silicon broke	32.4	3300	Wire pulled loose
24		17.2	1750	Silicon broke	32.9	3350	Silicon broke

TABLE XI. - SOME CHARACTERISTICS OF ANTIREFLECTION-COATED ONE-STEP CONTACTED CELLS

Cell number	Slope of forward current-voltage curve, R_f, ohm	Diode equation constant, n-value	Reverse current for dark cell diode, I_r, μA	Fill factor, percent	Efficiency, percent	Humidity and tape test ratings	
						Fronts	Backs
1	0.23	1.24	16	75.4	11.1	(a)	(a)
2	.24	1.19	4	76.0	11.1	5.0	5.0
3	.23	1.24	3	75.8	11.3	(a)	(a)
4	.24	1.23	7	76.3	11.3	5.0	5.0
5	.26	1.29	3	75.7	11.4	5.0	4.0
6	↓	1.23	3	76.2	11.4	4.0	4.0
7	↓	1.23	3	78.0	11.1	5.0	4.0
8	↓	1.24	4	75.7	11.0	5.0	5.0
9	.25	1.24	8	75.6	11.1	(a)	(a)
10	.23	1.21	3	75.7	11.0	5.0	4.0
11	.23	1.13	4	75.7	11.0	5.0	5.0
--	----	----	--	----	----	4.9 av	4.5 av

[a]Used for other tests.

TABLE XII. - EFFECT OF DIFFUSION TEMPERATURE ON CELL CHARACTERISTICS AND CONTACT ADHERENCE

[Number of cells per group, 16. The wafers were lapped and diffused with $POCl_3$ for 25 to 30 min. They were coated with Apiezon for back etching and sintered for 35 min at 600° C in forming gas. No antireflection coatings were used.]

Group	Wafer diffusion temperature, °C	Number of cells				Humidity and tape test ratings		
		With n-value		With I_r		Fronts	Backs	Number of cells
		<1.2	From 1.2 to 1.4	<10 μA	<100 μA			
AA	854	14	2	14	15	4.9	4.9	10
BB	840	8	6	9	13	4.9	4.4	16
CC	820	11	3	12	14	3.9	3.8	16
DD	800	2	4	9	16	2.0	3.3	16

Front contact adherence of the 840° C diffused cells was as good as that for the 850° to 865° C diffused cells, but became progressively worse as the diffusion temperature was decreased, first to 820° C and then to 800° C. Back contact adherence also decreased. Values of n were higher for the 800° C cells because of the shallower and more nonideal junction.

Quantities of one-step silver-only evaporated cells were supplied to two manufacturers and several users of solar cells. Test data obtained by the two manufacturers after humidity exposure and tape testing showed no peeling on any of the front contacts under the following conditions: (1) Ten cells for 15 days at 45° C and 90 percent RH (private communication from P. Payne, Heliotek Division of Textron, Inc., Sylmar, Calif.); (2) 10 cells for 4 days at 65° C and 95 percent RH (private communication from K. Ling, Centralab Semiconductor Division of Globe-Union, Inc., El Monte, Calif.); and (3) two cells for 1 week, two cells for 2 weeks, and two cells for 3 weeks at 80° C and 95 percent RH (private communication from K. Ling). These results are consistent with those obtained at Lewis. No data were received from the users.

For purposes of comparison, many groups of commercial space-quality cells (a total of 64 cells) were humidity tested for 4 days at 80° C and 95 percent relative humidity and were then tape tested. This test is more severe than commercial cells are required to pass. All the front contacts were rated at 2.4 or lower, and the back contacts were rated from 4.3 to 2.1.

Two-Step Evaporations

Table XIII shows the effects of processing variables on the uncoated cell characteristics for two-step evaporations. As with one-step evaporated cells, protecting the fronts with Apiezon instead of wax leads to much lower values of n and I_r. Changes due to shortened workup times and to the use of forming gas rather than argon in the first sintering are too small to indicate definite trends. However, argon is to be preferred in this first sintering as it leaves a much less discolored surface after sintering and after the hydrochloric acid stripping etch.

Table XIV shows the results obtained from evaluating two-step contacted and uncoated cells. The data at 77 K (-196° C) were obtained by spring-clamping each cell between two brass plates and immersing the cell and plates in liquid nitrogen. The very low values of R_f at low temperatures show that the contacts to the cells were ohmic. Most of the cells exhibited excellent voltage-current curve shapes with none of the double slope or broken-knee effects described in reference 3.

Table XV lists the pull test data on contacts to two-step evaporated cells. The same four categories as for the one-step cells were tested. Results were very satisfactory

TABLE XIII. - EFFECTS OF PROCESSING VARIABLES ON CELL CHARACTERISTICS

FOR TWO-STEP CONTACT EVAPORATION

[No antireflection coating used; sintering time, 35 min; sintering temperature, 600° C.]

Processing variables						
Group	Sheet resistance range, ohm/sq	Coating for back junction removal	Wafer preparation time	Amount of aluminum on backs, μm	Sintering gas	
					First step	Second step
EE	26 - 110	Wax	Normal	0.06 - 0.07	Argon	Argon
FF	56 - 66	Wax	↓	.12 - 0.14	Argon	Forming gas
GG	56 - 77	Wax	↓	.12 - 0.14	Forming gas	↓
HH	57 - 64	Apiezon	↓	.06 - 0.07	Forming gas	↓
II	52 - 64	Apiezon	Short[a]	↓	Forming gas	↓
JJ	52 - 66	Apiezon	Short[a]	↓	Argon	↓
KK	52 - 64	Apiezon	Normal	↓	Argon	↓

Cell characteristics								
Group	Number of cells					Humidity and tape test ratings		
	Total	With n-value		With I_r		Fronts	Backs	Number of cells
		<1.2	From 1.2 to 1.4	<10 μA	<100 μA			
EE	16	0	8	0	6	4.9	4.1	16
FF	14	0	8	1	8	4.6	4.3	14
GG	16	0	1	0	1	4.6	4.6	16
HH	↓	7	7	11	16	4.6	4.8	10
II	↓	5	7	7	13	4.5	4.5	8
JJ	↓	11	4	8	15	4.9	4.7	7
KK	↓	9	3	8	14	5.0	4.9	8

[a]The shortened preparation time eliminated two of the three water rinses and the drying step.

TABLE XIV. - SOME CHARACTERISTICS OF TWO-STEP CONTACTED CELLS

[No antireflection coatings used.]

Cell	Temperature, °C						Humidity and tape test ratings	
	25			-196				
	Slope of forward current-voltage curve, R_f, ohm	Diode equation constant, n-value	Reverse current for dark cell diode, I_r, μA	Slope of forward current-voltage curve, R_f, ohm	Diode equation constant, n-value	Reverse current for dark cell diode, I_r, μA	Fronts	Backs
1	0.22	1.13	8	<0.01	1.08	2	(a)	(a)
2	.21	1.23	3	↓	2.35	2	4.0	4.0
3	.21	1.26	11	↓	2.92	4	5.0	5.0
4	.20	1.24	7	↓	2.42	3	5.0	5.0
5	.21	1.09	16	↓	.44	7	(a)	(a)
6	.21	1.21	5	↓	.91	2	(a)	(a)
7	.20	1.19	12	↓	1.18	↓	4.0	5.0
8	.22	1.14	4	↓	1.18	↓	(a)	(a)
9	.22	1.13	3	↓	.50	↓	(a)	(a)
10	.21	1.11	2	↓	1.28	↓	5.0	5.0
11	.21	1.23	3	↓	2.45	↓	3.0	5.0
12	.21	1.14	6	↓	.94	↓	(a)	(a)
13	.22	1.11	3	↓	.50	↓	↓	↓
14	.22	1.08	4	↓	.30	↓	↓	↓
15	.23	1.09	11	↓	.84	3	↓	↓
16	.20	1.11	3	↓	.30	2	↓	↓
--	----	----	--	----	----	-	4.3 av	4.8 av

[a]Used for other tests.

TABLE XV. - PULL TESTS ON TWO-STEP CONTACTED CELLS

Cell	Humidity tested ?	Pull tests					
		Fronts			Backs		
		Force		Comment	Force		Comment
		N	g		N	g	
No antireflection coating							
1	Yes	13.2	1350	Silicon broke	29.4	3000	Peeling with some silicon
2	↓	22.6	2300	↓	29.4	3000	delamination
3		11.8	1200		37.3	3800	↓
4		24.0	2450		38.2	3900	
5		22.1	2250		45.1	4600	
6	↓	13.2	1350	↓	39.2	4000	Silicon broke
7	No	12.7	1300	Silicon broke	21.1	2150	Peeling with some silicon
8	↓	8.8	900	↓	37.3	3800	delamination
9		18.6	1900		34.3	3500	↓
10		24.5	2500		17.2	1750	
11		12.7	1300		22.6	2300	Silicon broke
12	↓	15.2	1550	↓	20.1	2050	Silicon broke
Silicon monoxide antireflection coating applied							
13	Yes	8.3	850	Silicon broke	7.8	<800	Peeled
14	↓	18.6	1900	Wire pulled loose	↓	↓	↓
15		15.2	1550	Silicon broke			
16		20.6	2100	↓			
17		20.1	2050				
18	↓	17.2	1750	↓			
19	No	21.2	2160	Silicon broke	18.6	1900	Silicon broke
20	↓	10.8	1100	↓	19.1	1950	Silicon broke
21		13.7	1400		24.0	2450	Wire pulled loose
22		8.8	900		19.1	1950	Peeling with some silicon delamination
23		5.9	600		43.6	4450	Silicon broke
24	↓	10.8	1100	↓	53.9	5500	Silicon broke

except for the backs of the antireflection coated cells that had been humidity and tape tested. On these cells the entire backs could be peeled off by hand once a corner had been loosened. The reasons for this result are not clear.

DISCUSSION

The manner in which the silver layer is bonded to the silicon surface is not known. Silver is not soluble in silicon at the temperatures of sintering. The attraction could be by physical forces alone or it could be aided by the phosphorus diffused into the surface layer. The fact that wafers of high sheet resistance (low phosphorus concentration) or those treated with the higher concentrations of hydrofluoric acid (more phosphorus removed from surface) resulted in cells with nonadherent contacts suggests that phosphorus plays a part in the bonding mechanism.

However, the phosphorus could be acting to decrease the rate of oxidation of the silicon surface thereby enabling the silver to make an intimate contact to silicon. This would be impossible if a thick oxide layer were formed. When the diffused oxide layer was prematurely removed from the front surface of the wafer (i.e., before removal of the back junction) the contact again was nonadherent. In this case, the additional processing time would have allowed more oxide to form before the silver contact was applied. Contamination of the exposed top surface before contacting could also have been a factor causing the nonadherent contacts when the diffused oxide layer was removed early in the processing.

Wafers coated with Apiezon yielded cells with much better n and I_r values. This was due to the improved edge etching of the Apiezon-coated cells. With the wax plate method a portion of the edges is protected from the back-etchant and the cell junction therefore extends over the edges. This can lead to imperfect and leaky junctions at the edges and high n and I_r values.

CONCLUSIONS

The feasibility of a silver-only front contact to silicon solar cells has been demonstrated. This contact is adherent and has excellent electrical and humidity-resistant characteristics. Processing steps are not critical except for the scheduling of the removal of the blue-colored oxide layer and the concentration of hydrofluoric acid used to remove it. The contact was not adherent on cells diffused at temperatures much lower than 840° C. Forming gas was the most suitable sintering gas and sintering temperature should be approximately 600° C.

A satisfactory back contact was obtained from a thin layer of aluminum covered with silver. An ohmic contact at low temperatures was obtained by initially alloying aluminum into the back surface.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 4, 1972,
113-33.

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