

NON-NOBLE METAL BASED METALLIZATION SYSTEMS

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This paper presents the results of efforts to produce a nonsilver metallization system for silicon photovoltaic cells. The system uses a metallization system based on molybdenum, tin, and titanium hydride. The initial work in this system was done using the MIDFILM process. The MIDFILM process attains a line resolution comparable to photoresist methods with a process related to screen printing.

The surface to be processed is first coated with a thin layer of photopolymer material. Upon exposure to ultraviolet light through a suitable mask, the polymer in the non-pattern area crosslinks and becomes hard. The unexposed pattern areas remain tacky. The conductor material is then applied in the form of a dry mixture of metal which adheres to the tacky pattern area. The assemblage is then fired to ash the photopolymer and sinter the conductor powder.

Several compositions of powders were used in this research, the compositions are identified as follows:

TYPE	Mo	Ti	Sn	frit
A DP-E570	19.5	80.0	0.5	0
B DP-E571	50.0	49.5	0.5	0
C DP-E572	70.0	29.5	0.5	0
D DP-E573	49.0	49.0	2.0	0
E DP-E574	48.0	48.0	4.0	0
F DP-F503	19.5	80.0	0.5	5.0

The frit used was a Pb/borosilicate glass.

Initial work using the MIDFILM process was done using only type A paste. It was found that this resulted in cells with a very high series resistance. If the cell was then plated the cell improved. To decrease the series resistance a screen printed process was investigated. The metal powders were formulated into screenprinting pastes by Thick Film Systems using the same vehicle used in silver pastes. After screenprinting the cells are fired in air in an IR belt furnace to burn off the organic components of the vehicle. The cells are then sintered in a pure hydrogen atmosphere.

Paste types A&F gave the best results. Cells were fired at 500-550°C at a belt speed of 18"/min. through a heated zone of 18". The metallization has a blue-grey color which becomes metallic looking after the hydrogen sintering. Sintering was done at 600°C for 90 seconds. Figures 13-16 show a typical Mo/Ti cell as compared to a silver cell (neither are AR coated). Cells produced by this method pass tape pull tests but are difficult to solder to without removing the metallization. Sintering for longer times at higher temperature enhances adhesion but increases series resistance to unacceptable values.

Several different cleaning procedures prior to screenprinting were tried in an attempt to increase adhesion. Figure 17 shows the procedures. All procedures worked equally well (or poorly), procedure D is now used routinely and successfully for silver metallization cells.

CO was used in place of hydrogen as the reducing gas in another experiment. The cells had much higher series resistance as seen in figure 20. Adhesion between the metallization and the silicon was improved but particle to particle adhesion appeared to degrade. Soldering to the cells was impossible under all conditions.

In the next study wafers were coated with indium tin oxide (ITO) prior to metallization. The ITO was applied by reactive sputtering by Applied Film Labs Inc. The thickness varied from 512 to 783A with an index of refraction of 1.95. The reflected color varied with increasing thickness as follows: green bronze, bronze, purple, blue. The cells were reduced using hydrogen at 600°C. The hydrogen firing also reduced the ITO causing a milky appearance on the cells. Air firing of the cell brought back some of the color of the film and improve cell performance as is shown in figure 25. Attempt to fire the cells at 650°C led to severe shunting, figure 24 and 25. The particle adhesion for the ITO cells was still not adequate for soldering.

Future work will include sequential use of hydrogen and CO, and use of other paste additives.

Figure 2. Objectives

- OPTIMIZATION, EVALUATION AND DEMONSTRATION OF A NOVEL METALLIZATION SYSTEM

- Mo/Sn/TiH SYSTEM

- ITO CONDUCTIVE AR SYSTEMS

Figure 3. Approach

- SCREEN PRINTING

- AIR FIRING

- REDUCING ATMOSPHERE FIRING

- CONDUCTIVE AR COATING (ITO)

Figure 4. Metallization Paste Formulations

	A (RH 3659)	B	C	D	E	F
MOLYBDENUM (SYLVANIA 280-325)	19.5	50.0	70.0	49.0	48.0	19.5
TIN (ATLANTIC EQUIPMENT ENGINEERS SN 266)	80.0	49.5	29.5	49.0	48.0	80.0
TITANIUM HYDRIDE (FERRO PLANT FX-41)	0.5	0.5	0.5	2.0	4.0	0.5
LEAD/BOROSILICATE FRIT (THICK FILM SYSTEMS #3347)						5.0

ALL PASTES USE THICK FILM SYSTEMS ORGANIC VEHICLE

Figure 5. Initial Effort I

<u>PREFIRE</u>	500°C			550°C		
BELT SPEED	18"/MIN.	24	36	18	24	36
<u>FIRE</u>	600°C 30 MIN. IN 5% H ₂ /95% N ₂					

ORIGINAL DRAWING
OF POOR QUALITY

Figure 6.

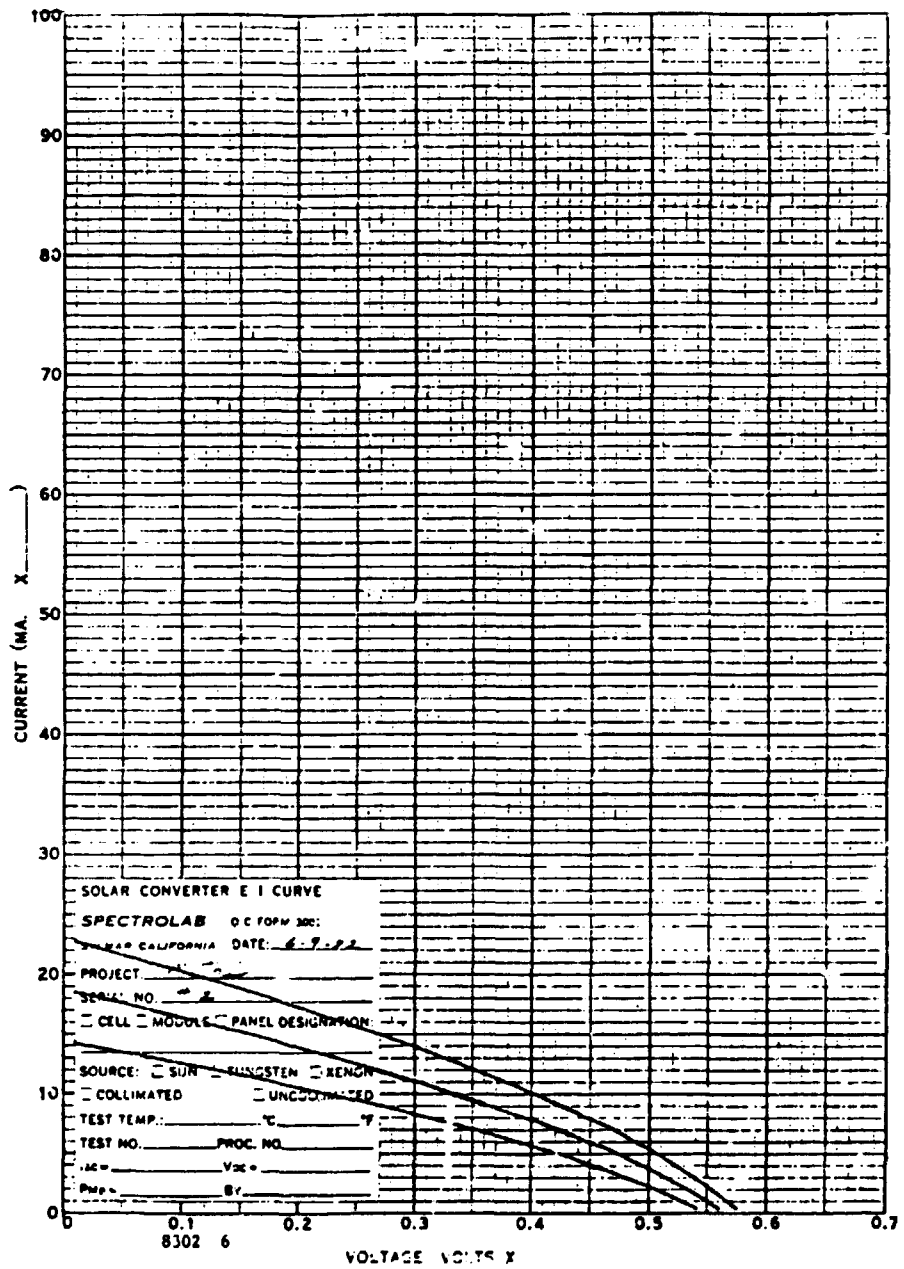


Figure 7. Initial Effort II

<u>PREFIRE</u>	450°			500°	
	9	18	24	9	18

FIRE AT 650°C

5% H₂/95% N₂

5, 10, AND 15 MIN.

Figure 8.

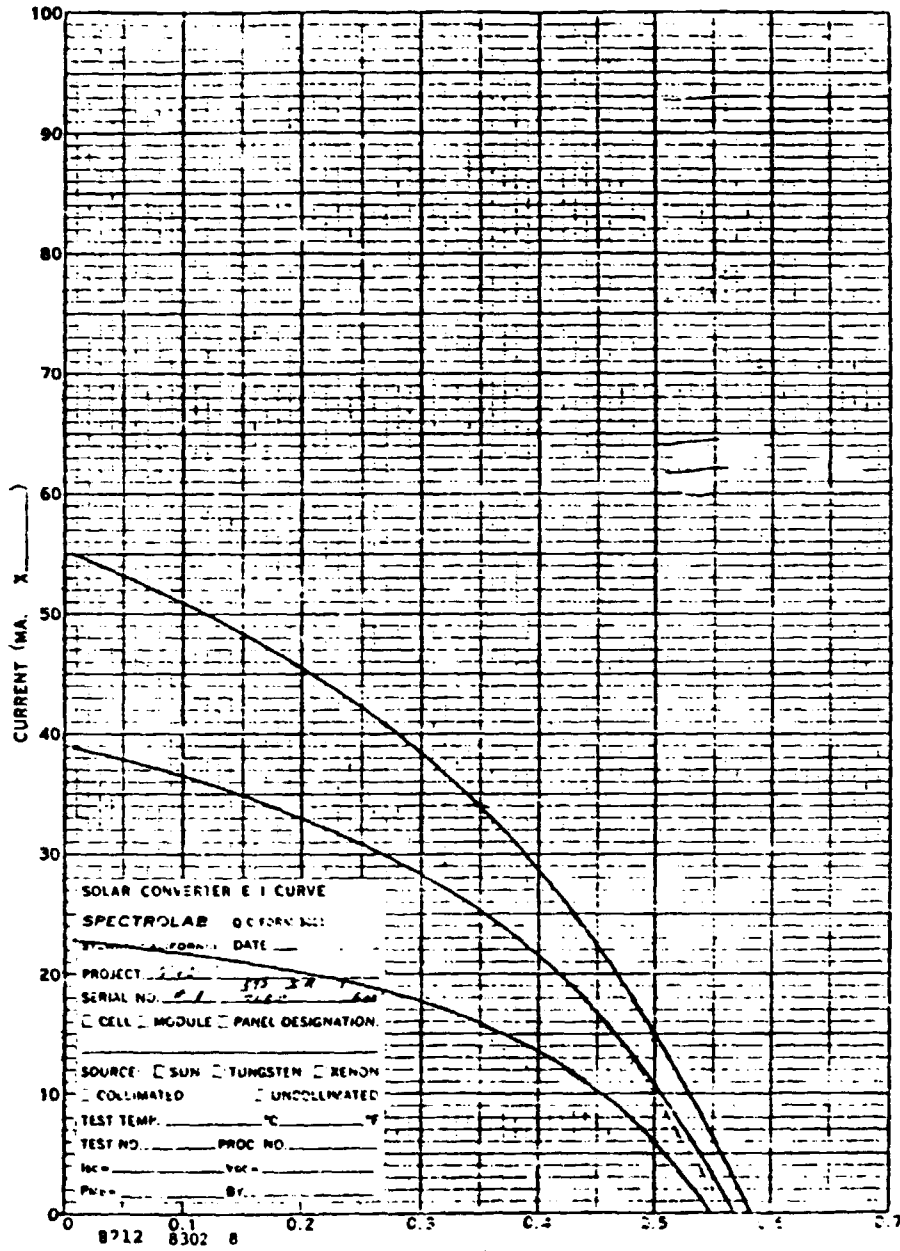


Figure 9. Initial Effort III

PREFIRE

400°, 450°, 550°
AT 24°/MIN.

FIRE

550°, 600°
30 MIN., 200% H₂

CELLS SHOWED METALLIC-LIKE CONTACTS

Figure 10. Firing Sequences

- 1) 18°/MIN. 500°C PREFIRE, 1 MIN. 575°C H₂ FIRE
- 2) 18°/MIN. 500°C PREFIRE, 1 MIN. 600°C H₂ FIRE
- 3) 9°/MIN. 500°C PREFIRE, 1 MIN. 575°C H₂ FIRE
- 4) 9°/MIN. 500°C PREFIRE, 1 MIN. 600°C H₂ FIRE

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Figure 11.

Paste Type	Pre-Fire Speed @ 500°	Fire Temp. @ 1 min.	Cell #	V _{oc}	I _{sc}	I ₅₀₀	I ₄₅₀
A	9°	575	1	600	701	402	569
A	9°	575	2	598	677	390	490
A	9°	600	3	601	700	469	553
A	9°	600	4	597	696	458	548
A	10°	575	5	603	702	450	543
A	10°	575	7	599	560	286	359
A	10°	600	6	598	701	440	530
A	10°	600	8	602	703	461	550
B	9	575	9	600	687	377	488
B	9	575	11	598	676	297	398
B	9	600	10	600	689	369	478
B	9	600	12	597	644	282	371
B	10	575	13	602	681	345	451
B	10	575	14	602	681	331	438
B	10	600°	15	598	686	409	515
B	10	600°	16	596	692	389	497
C	9	575	20	594	617	194	266
C	9	575	17	589	369	105	150
C	9	600	19	592	668	246	345
C	9	600	18	587	300	90	123
C	10	575	21	597	684	305	415
C	10	575	23	598	667	285	388
C	10	600	22	600	687	359	463
C	10	600	24	596	680	347	458
D	9	575	26	598	684	330	447
D	9	575	25	599	681	320	429
D	9	600	28	598	676	320	435
D	9	600	27	599	678	351	455
D	10	575	31	596	686	346	464
D	10	575	29	598	682	336	448
D	10	600	32	601	691	378	441
D	10	600	30	600	694	393	502
E	9	575	33	596	668	260	356
E	9	575	34	596	639	229	312
E	9	600	35	596	674	265	363
E	9	600	36	598	677	262	417
E	10	575	37	597	672	295	396
E	10	575	38	598	669	286	385
E	10	600	39	597	690	333	440
E	10	600	40	600	685	318	420

Figure 12. Initial Optimization of Paste A

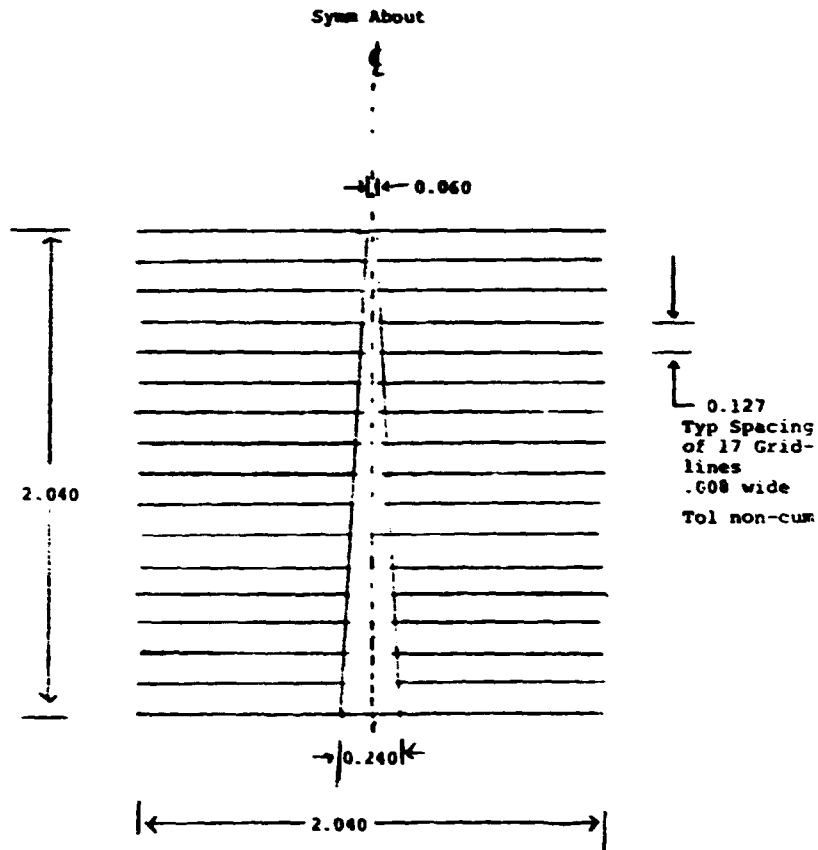
PREFIRE 18°/MIN. 500°C

 FIRE 1 MIN. 575°C

COMPARABLE TO SILVER PASTE CELLS

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Figure 13. Front Metallization Pattern



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Figure 14.

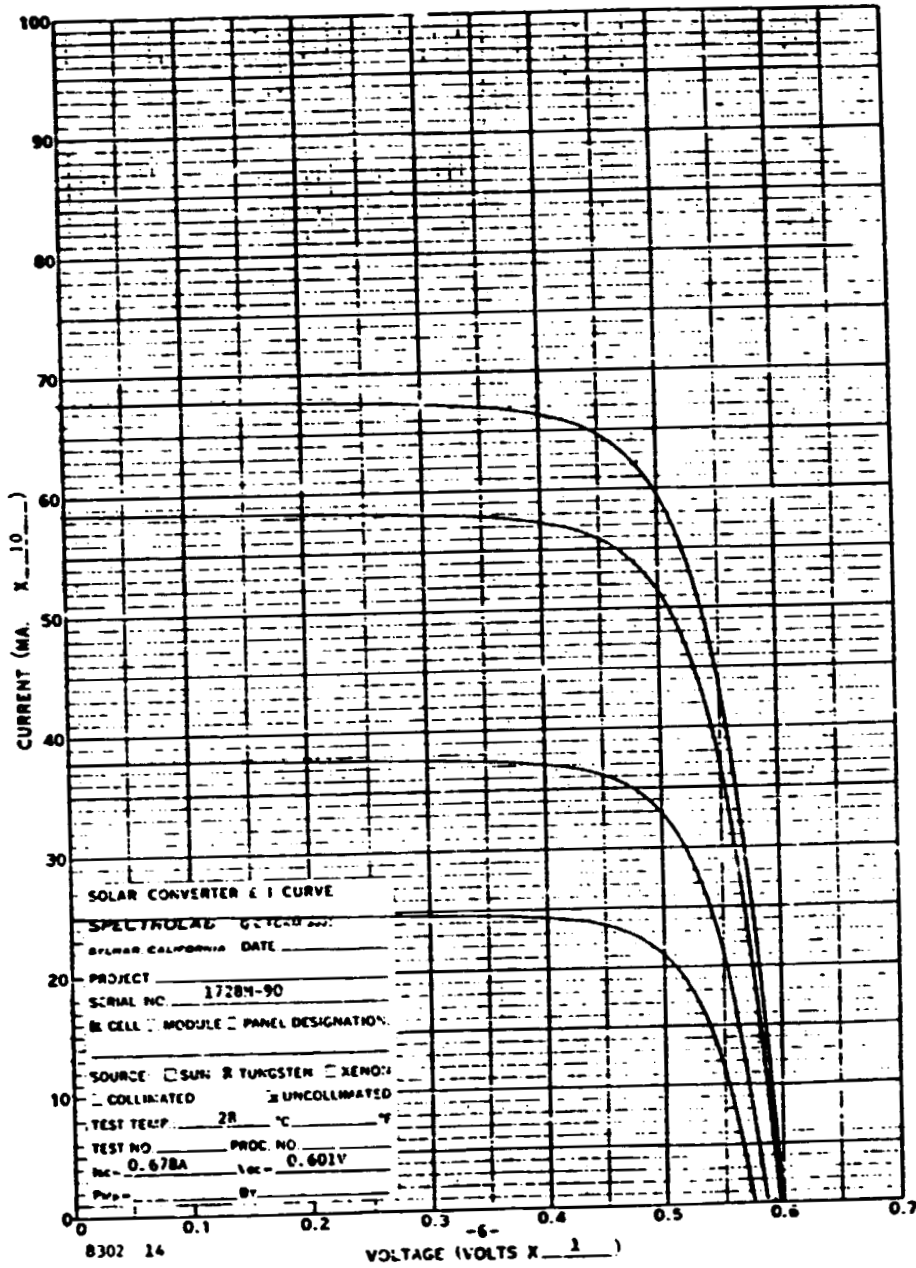


Figure 15. ORIGINAL PAGE OF POOR QUALITY

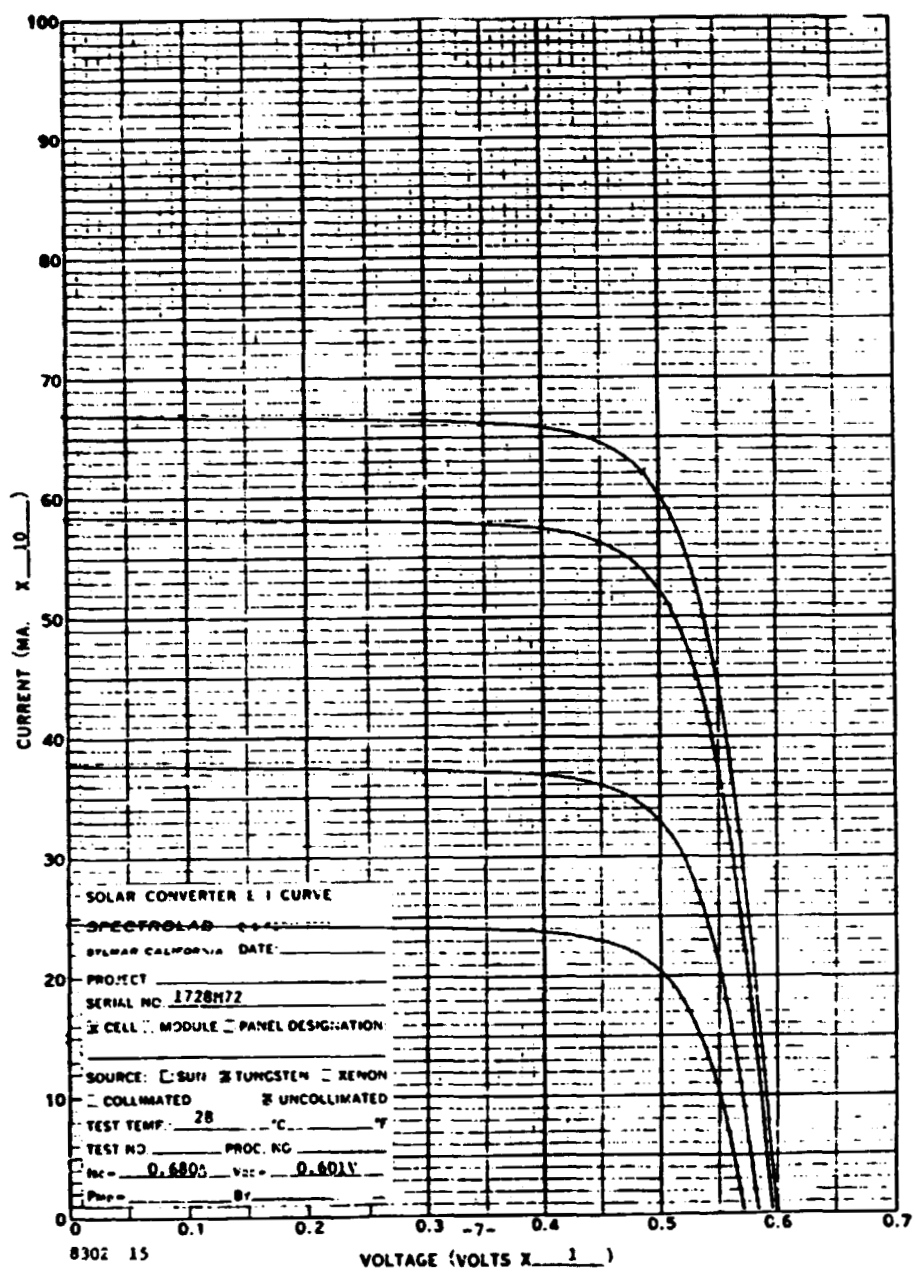


Figure 16. Mo-Sn versus Ag

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CELL	V_{oc}	I_{sc}	I_{500}	P_{MAX}	FF	E
1728M-90 (Mo/Sn)	.601	.678	.596	.229	.73	10.5%
1728M-72 (Ag)	.601	.680	.600	.302	.74	10.6%

Figure 17. Cleaning Procedures

A	B	C	D
10% HCL 1 MIN.	10% HCL 1 MIN.	10% HCL 1 MIN.	85°C H ₂ O/NH ₃ /H ₂ O ₂ 30 SEC.
H ₂ O RINSE	H ₂ O RINSE	H ₂ O RINSE	H ₂ O RINSE
10% HF 1 MIN.	10% HF 1 MIN.	10% HF 1 MIN.	
H ₂ O RINSE	H ₂ O RINSE	H ₂ O RINSE	
50% AcOH ~1 MIN.	H ₂ O/NH ₃ /H ₂ O ₂ 30 SEC.		
HOT H ₂ O RINSE	H ₂ O RINSE		
ACETONE 2 MIN.			
MEOH 2 MIN.			
HOT H ₂ O 2 MIN.			
H ₂ O, N ₂ 5 MIN.			

Figure 18. Problems

- POOR ADHESION
- FRIT DOES NOT APPRECIABLY WORK
- Si-POWDER BOND A PROBLEM
- SOLDERING A PROBLEM

Figure 19. CO as Reducing Gas

- CELLS HAVE HIGHER SERIES RESISTANCE
- PARTICLE TO SILICON ADHESION GOOD
- PARTICLE-TO-PARTICLE ADHESION POOR

Figure 20. ITO Studies

- APPLIED BEFORE METALLIZATION
- INDEX OF REFRACTION ~ 1.95
- THICKNESS VARIED 512 - 783 Å
- COLOR GREEN BRONZE - BRONZE - PURPLE - BLUE

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Figure 21.

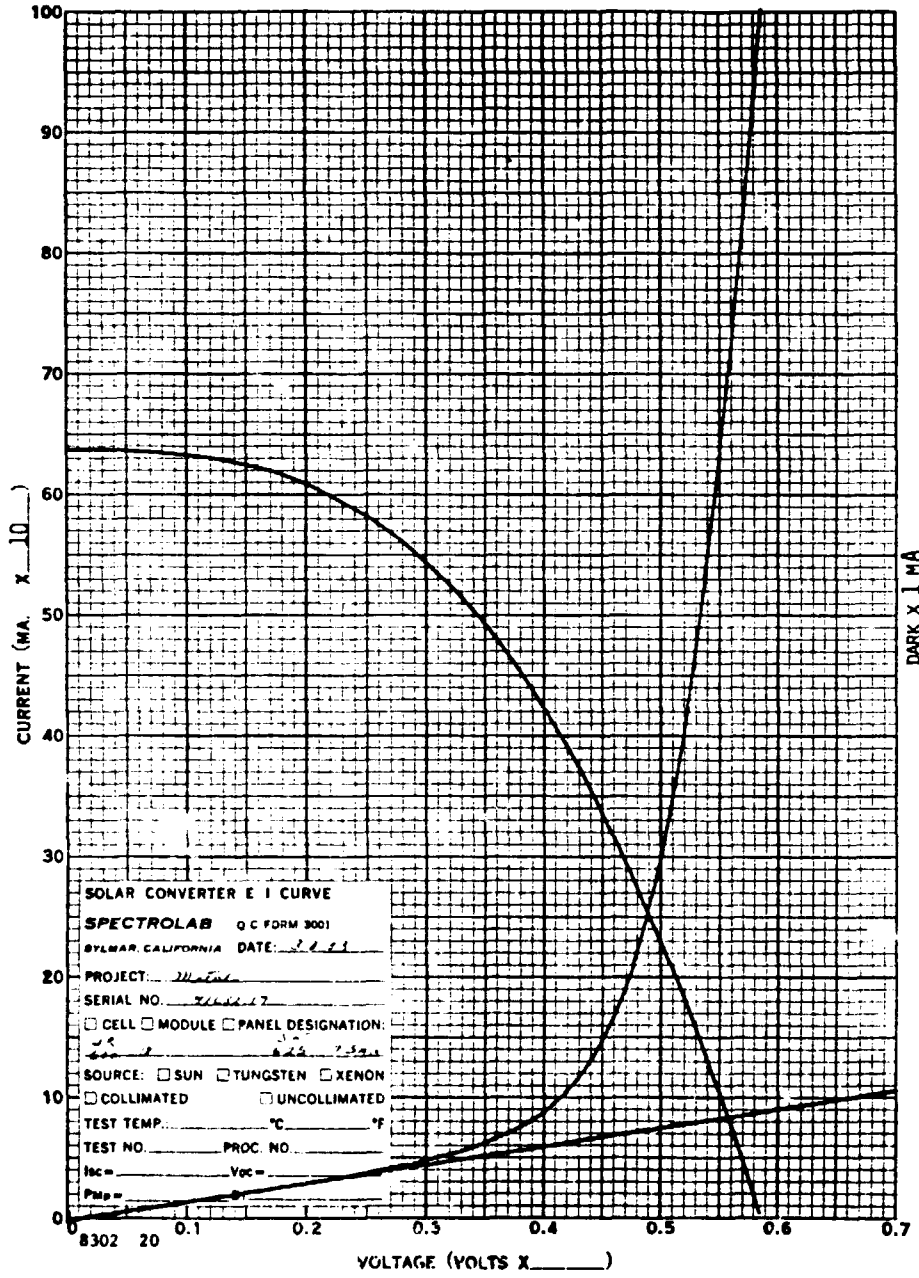
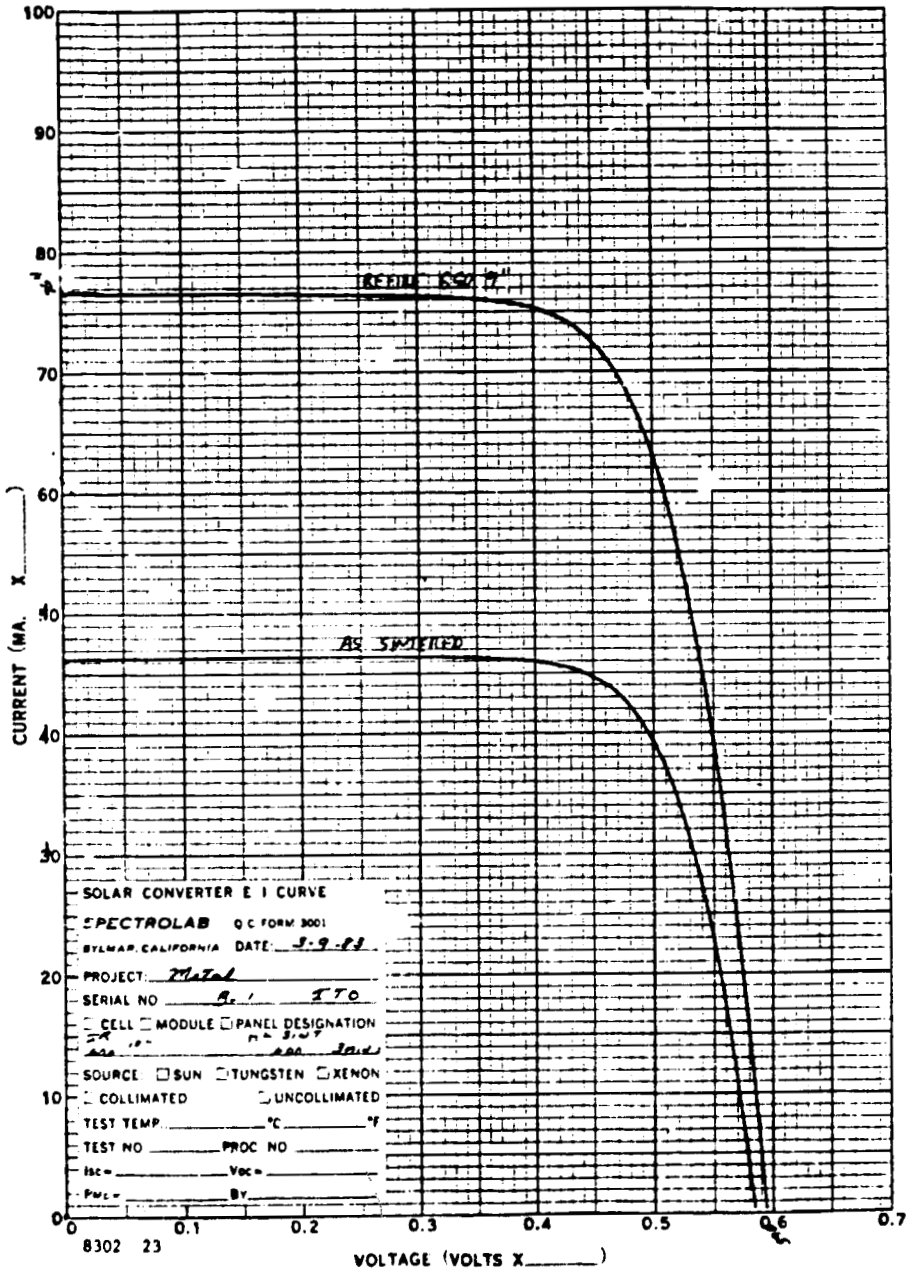


Figure 22. ITI Results

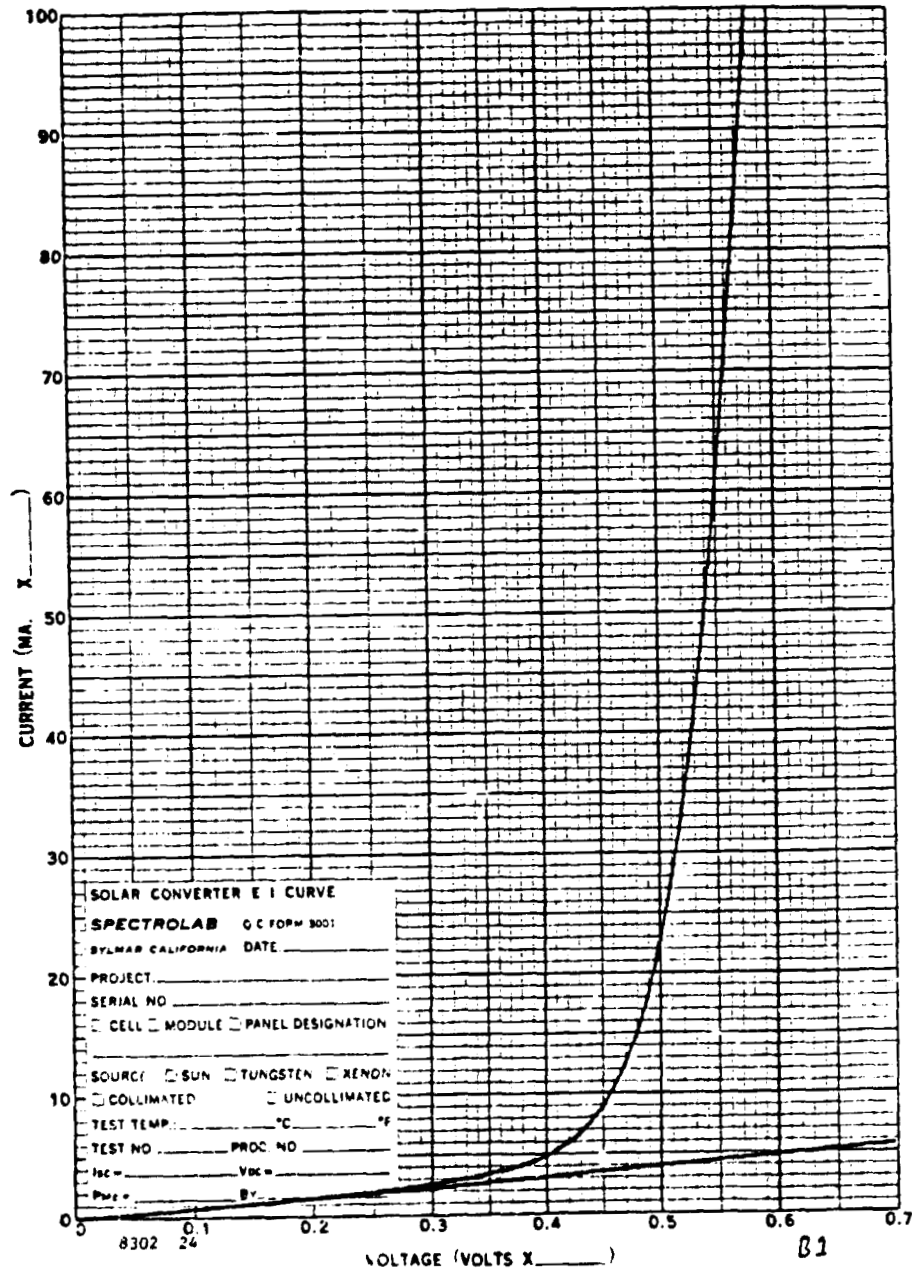
- GOOD ADHESION PARTICLES - ITO
- POOR ADHESION PARTICLE-PARTICLE
(REDUCED IN H₂)
- ITO AR VALUE IS DESTROYED BY REDUCING ATMOSPHERE
- REOXIDATION NECESSARY
- SHUNTING OCCURS ABOVE 600°C

Figure 23.



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Figure 24.



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Figure 25.

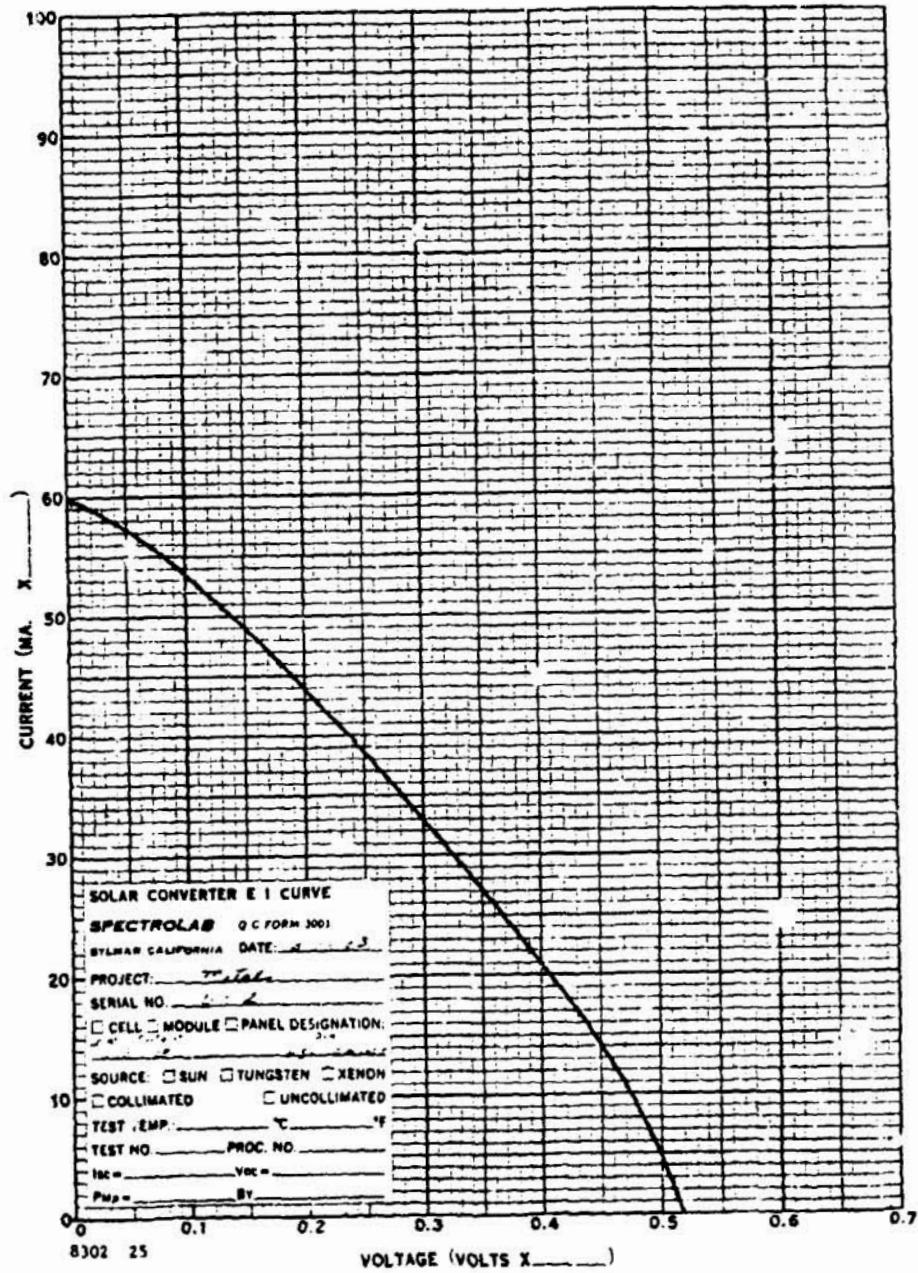


Figure 26.

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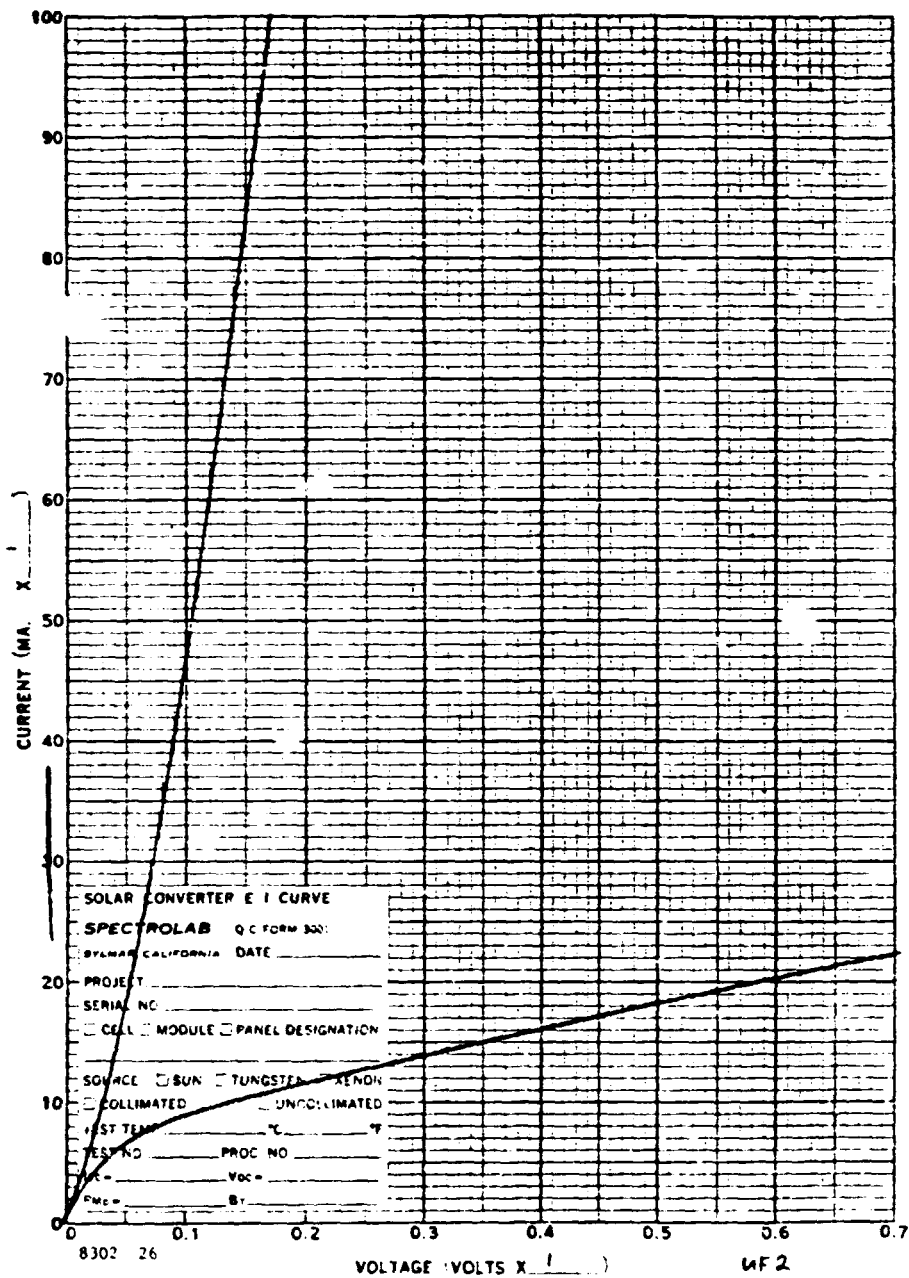


Figure 27. Discussion

- CO PROMOTES GOOD SILICON-PARTICLE ADHESION
POOR PARTICLE-PARTICLE ADHESION
- H₂ PROMOTES BETTER PARTICLE-TO-PARTICLE ADHESION BUT STILL NOT
GOOD ENOUGH
- PARTICLE-TO-ITO ADHESION GOOD
- ITO EASILY REDUCED AT 600°C IN H₂
- ITO SHUNTS CELLS AT 650°C

Figure 28. Future Work

- SEQUENTIAL USE OF H₂ AND CO REDUCTION
- SEM EVALUATIONS
- OTHER PASTE ADDITIVES?

DISCUSSION

SOMBERG: Did you try any without titanium hydride?

GARCIA: In this study we have not tried them without the titanium hydride. In the mid-film work we did try some without titanium hydride and the results were terrible compared with the ones that did have a little titanium hydride.

SOMBERG: My other question is: when you soldered to the cell, you said there was failure. Were you able to tell where failure was occurring?

GARCIA: It failed in different ways. In cells that were fired in hydrogen, the failure was between the metallization and the silicon. It appeared to just come straight off the silicon. When it was fired in carbon monoxide you divoted the silicon but you didn't get particle-to-particle adhesion; it wasn't very good. It appears you were just making contact with a couple of particles and pulling those out of the silicon, but the particles were not sticking to one another. There wasn't much congruity to the metallization.

LAVENDEL: I might comment on the function of titanium hydride in your system. Believe it or not, I am going back to a problem that I had once with armors. Quite a distance between armors and solar cells, but the problem we were trying to solve at that time was to get to a structure that would be composed of aluminum oxide particles or plates built together with very thin metal films, and lo and behold, one of the best systems was tin titanium hydride. It is because, at these temperatures that you mentioned, titanium hydride decomposes; titanium dissolves in tin and you have a liquid metal that wets and bonds to the ceramic surface, oxide ceramic surface. You say that in the case of hydrogen firing, you don't get a good adherence of your metallization, of bonds of your metallization to silicon. I would propose that you don't get it because you have a very clean silicon surface. If you had traces of silicon oxide on it, then you have that tin-titanium liquid wetting the surface and bonding. If you remove the oxide completely, you don't have bonding. If you use carbon monoxide, you would probably restore very thin oxide film on your silicon and you restore bonding.

GARCIA: Well, one thing we did try was no cleaning at all, which I would assume would leave some oxide on the cell. That didn't help. We also tried putting a big oxide on there by just dipping the solar cells in hydrogen peroxide. I was not sure if that would put oxide on, but I thought it might. That didn't help either. So I am not sure that was the problem.

BEAVIS: Of course when you put it in hydrogen like that, if it is really pure hydrogen, what happens is that the oxide reduces, because there is oxide there anyway in the beginning. Have you tried any with putting water -- in other words, wet hydrogen? That will certainly keep the silicon in the oxidized state. I am not sure what the free energies for tin oxide are, I don't remember right off hand, but it would certainly keep the silicon oxide on the surface if you have water in it.

GARCIA: We have not tried that.

BEAVIS: That is a classic way, by the way, of doing those sorts of things.
It is just wet hydrogen.

BICKLER: Bernd Ross had concluded that it is the hydrogen occupying the free silicon sites and preventing the chemical bonding to the silicon, it is not the lack of the oxide, carbon monoxide is sufficiently reducing to handle that aspect of the thing but it's occupancy of silicon sites by hydrogen, quite similar to some of these hydrogen involvements with silicon we are seeing in polycrystalline cells.

BURGER: If I remember the original work with the moly-tin systems, wasn't that molybdenum pentoxide and titanium resinate with pure tin?

GARCIA: I am not aware of that. I didn't worry about that.

GALLAGHER: In the original Midfilm program, we used both moly trioxide and moly metal.

GARCIA: This wasn't at the end of the Midfilm contract.

GALLAGHER: That is the one we are talking about, where we used moly metal and molytin.

GARCIA: Yes, we did. But we didn't use a resinate.

GALLAGHER: Yes, there was a resinate in it.

GARCIA: There was? Maybe.

WONG: I have a question for Don (Bickler). This will clear up my mind on the hydrogen business. Are you saying that the free surface of the silicon has a lot of dangling bonds and the hydrogen wants to satisfy those dangling bonds? And becomes stable so that it won't react any more with other --

BICKLER: That is the understanding to date.

AMICK: I would think that picture at 600° is very unlikely because amorphous silicon goes to pieces at something like 500° and you lose the hydrogen at the surface even down at 400° in firing.

BICKLER: Well, it goes through all the temperatures in the furnace. It is still in the hydrogen atmosphere as it comes back out.

AMICK: But at the time you are actually trying to form the bond, it is at high temperatures.

GALLAGHER: Well, actually, Bernd Ross did some nuclear resonance studies with SUNY wherein he not only showed that hydrogen had taken care of dangling bonds at the surface but there was actually hydrogen within the structure to some depth. Depth being in Angstroms.

AMICK: After you come back down to room temperature, I can believe the hydrogen was in there; the question is, whether it's at the surface interfering with something, at the temperature at which you are trying to put it in.

GALLAGHER: I don't know - all I know is that the samples were done in both hydrogen and CO and sent (to SUN and he performed this experiment and we got back curves that said there is hydrogen in there and hydrogen absorbs --

BICKLER: He was working with copper; it wasn't molytin. He experienced the same problem and it was because of that experience that Alex (Garcia) --

GARCIA: That is why I went to the carbon monoxide.

TAYLOR: We have been looking at this question also and have looked at systems in which we fire the molybdenum tin and also we have looked at other metalizations in a forming gas-type atmosphere and we have observed the same loss of, or failure to develop, adhesion there even when you go down to very low concentrations of hydrogen in the molecular atmosphere, down below 1% hydrogen.

BLAKE: One of the things we noticed in the study of the effect of hydrogen on adhesion is that we could take silver bonds that were very strong and pass all the tests, expose the bonds to hydrogen at elevated temperatures, and get a complete release with no trace of adhesion. So we felt that hydrogen was insinuating itself between the bond in some way that we were not aware of and causing a release of the bond that we had previously.

SOMBERG: What temperature would it take to do that?

BLAKE: Oh, about 550° and up.

TAYLOR: We have seen that same thing going on in sintered aluminum firing. We fired in a very weak hydrogen atmosphere at 550° to 600° temperature.

BLAKE: It is that observation that caused us to start to do more work with SUNY to find out whether or not hydrogen is present on the surfaces. I don't think it is all that conclusive at this stage. We have to get more work done on it.

GARCIA: I might say that the cells we are firing in carbon monoxide wet the silicon very nicely and on microscopic appearance they looked very good. They look like a very good coating, whereas on the ones where the hydrogen was used, the film was much more rough and appeared to be more particulate in nature, instead of a real film.

HOGAN: Two questions. First of all, what was the series resistance on the cells?

GARCIA: On the good cells, the series resistance was about 30 to 40 milliohms. Bad cells could get up as high as you wanted it. But the cells I showed you, that showed good curve shape, I would say between 30

and 60 milliohms for that cell, which is something we feel is acceptable for that size cell.

HOGAN: The other question was: with the ITO, what was the sheet resistivity as received, and also after you reoxidized?

GARCIA: We didn't make those measurements. I believe that 150 ohm-cm is the number. I'm not sure what it is.

GALLAGHER: Tell them how long you have had them, maybe that would explain.

GARCIA: I did this work last week. So we really haven't done too much work on these films.

HOGAN: That might be something that you would want to look at.

GARCIA: Yes. The thing is, we found that there is sufficient conductivity so that we don't have a problem with series resistance. Just by analyzing the curve shape and everything, we are saying there is enough conductivity. We are more interested, I think, in the adhesion-promoting abilities underneath it than on the conductivity of the cell. It helps, but I don't think that that extra boost in conductivity might make that much difference.

NICOLET: Two questions. What is this system's advantage over the silver system?

GARCIA: Well, in theory, it should be cheaper. We had originally hoped that this could be done using a forming gas atmosphere and could be done in a conventional IR furnace of some sort.

NICOLET: Second question. Did you ever solve the solubility problem?

GARCIA: We have not solved the solubility problem yet.

NICOLET: Why don't you get good soldering? It appears you have plenty of tin.

GARCIA: I don't know. We are still not getting good sintering from particle to particle with good adhesion on the final product.

TAYLOR: Have you done any scanning electron microscope work on these films?

GARCIA: No. That's our next task.

TAYLOR: We did some work with tin-nickel mixtures and in examining those under scanning electron microscope, we discovered that the tin has a terrible propensity for agglomeration. We got real fine tin particles there but you can't find them, they are all in big boulder-agglomerated particles. That agglomeration tendency might be playing some kind of a role in what you are seeing here.

GARCIA: That is possible.

PARKER: Do you know whether you are getting any compounds of molytin that might interfere with your tinning?

GARCIA: I don't know.

STEIN: Did you see any difference in solder wettability between the 80% tin and the very low tin? In other words, does that play a role?

GARCIA: We did try some solder tests to the B through E pastes and they weren't good. I didn't look at them that carefully but they could not be soldered either. The closest to soldering was using the hydrogen firing of the A paste. Then you could actually solder to the metallization and the metallization would stick together even though it wouldn't be on the cell. You could hold it in your hand, and I made a pretty little doodad I stuck on my door.

TAYLOR: How about trying some just pure tin and see if you could solder that?

GARCIA: That's a thought. Try pure tin. I might try that.