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DEVELOPMENT OF TECHNIQUE FOR AR COATING AND NICKEL AND COPPER METALIZATION OF SOLAR CELLS

FINAL REPORT

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Prepared for:

JET PROPULSION LABORATORY
4800 Oak Grove Drive
Pasadena, CA 91109

PHOTOWATT INTERNATIONAL, INC.
2414 West 14th Street
Tempe, Arizona 85281

The JPL Low-Cost Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

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Approved by:

William Taylor

William E. Taylor
Technical Director

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1.0 SUMMARY STATEMENT

Solar cells were made with a variety of base metal screen printing inks applied over silicon nitride AR coating and copper electroplated. Fritted and fritless nickel and fritless tin base printing inks were evaluated. Conversion efficiencies as high as 9% were observed with fritted nickel ink contacts, however, curve shapes were generally poor, reflecting high series resistance.

Problems encountered in addition to high series resistance included loss of adhesion of the nickel contacts during plating and poor adhesion, oxidation and inferior curve shapes with the tin base contacts.

2.0 INTRODUCTION

This Final Technical Progress Report covers work performed during the period May 15, 1982 through September 30, 1982. The scope of the program covers the assessment of solar cell grid contacts formed by sreen printing conductive base metal printing inks onto a silicon nitride antireflective layer. Electroplated copper was applied to the thick film metalization to reduce the sheet resistivity.

The work can best be understood in terms of two major problems:

- Attack of the thick film deposit by the plating solution.
- Contact to the silicon through the silicon nitride by the printed and fired conductive ink.

Printing inks evaluated can be catagorized into two broad classes:

- Nickel printing inks (fritted and fritless),
- Tin based printing inks (fritless)

Silver fluoride, teflon powder, titanium hydride, zinc chloride, silver phosphate and silver were tested as addative agents to promote adhesion and penetration of the silicon nitride.

The nickel inks appear promising with respect to contacting the silicon surface through the silicon nitride but lost adhesion on exposure to the plating solution. The tin base inks were difficult to fire on. Hydrogen bearing firing atmospheres resulted in poor adhesion. Carbon monoxide bearing atmospheres and pure nitrogen resulted in contacts which were difficult to plate with a tendency to lose adhesion during plating. Solar cells made with the tin base printing inks were generally inferior to those made with the nickel printing inks.

No clear cut advantages were seen for any of the addatives with the possible exception of silver. Ionic agents such as silver fluoride and zinc chloride tended to exacerbate the plating problems.

3.0 TECHNICAL DISCUSSION

3.1 Introduction

The approach to low cost base metal solar cells for this program was that of screen printing metal conductive inks over a silicon nitride antireflective coating followed by electroplating with copper to reduce grid line resistance. Nickel inks were initially selected for investigation. The work was later extended to include other metals such as tin and tin-molybdenum. Brush plating was selected for applying the copper plate. Brush plating was performed by Vanguard Pacific Company of Santa Monica, California. After initial identification of problems the plating activity was shifted to Photowatt, using the brush plating solutions with conventional bath plating methods.

3.2 Plating

The theory of brush plating is similar to bath plating but the procedure resembles arc welding. As can be seen from Figure 3.1, one lead of the plating rectifier is connected to the part to be plated, which acts as a cathode. The other lead fits into the work tool, called a "stylus", which is an anode of the proper size and shape to contact a good part of the area to be built up. The anode is wrapped with a swab and the solution is pumped onto the swab. With the current on, the anode swab is brushed over the area to be plated until the desired thickness of deposit has been achieved. Rates of deposition with this technique are extremely high. The resulting deposits are hard, low in porosity, very pure, easily solderable and of high conductivity. Porosity is 75% less than that obtained in a bath deposit of identical thickness. Brush plating is normally activated by reverse etching, which is easily achieved by simply reversing the process polarity with a substitution of etching or activating solution. The average rate of deposition of copper is about 1 - 2 mils/minute with current densities ranging from 2000 - 6000 Amp/hours per square foot. This is at least 100 times faster than normal electroplating techniques.

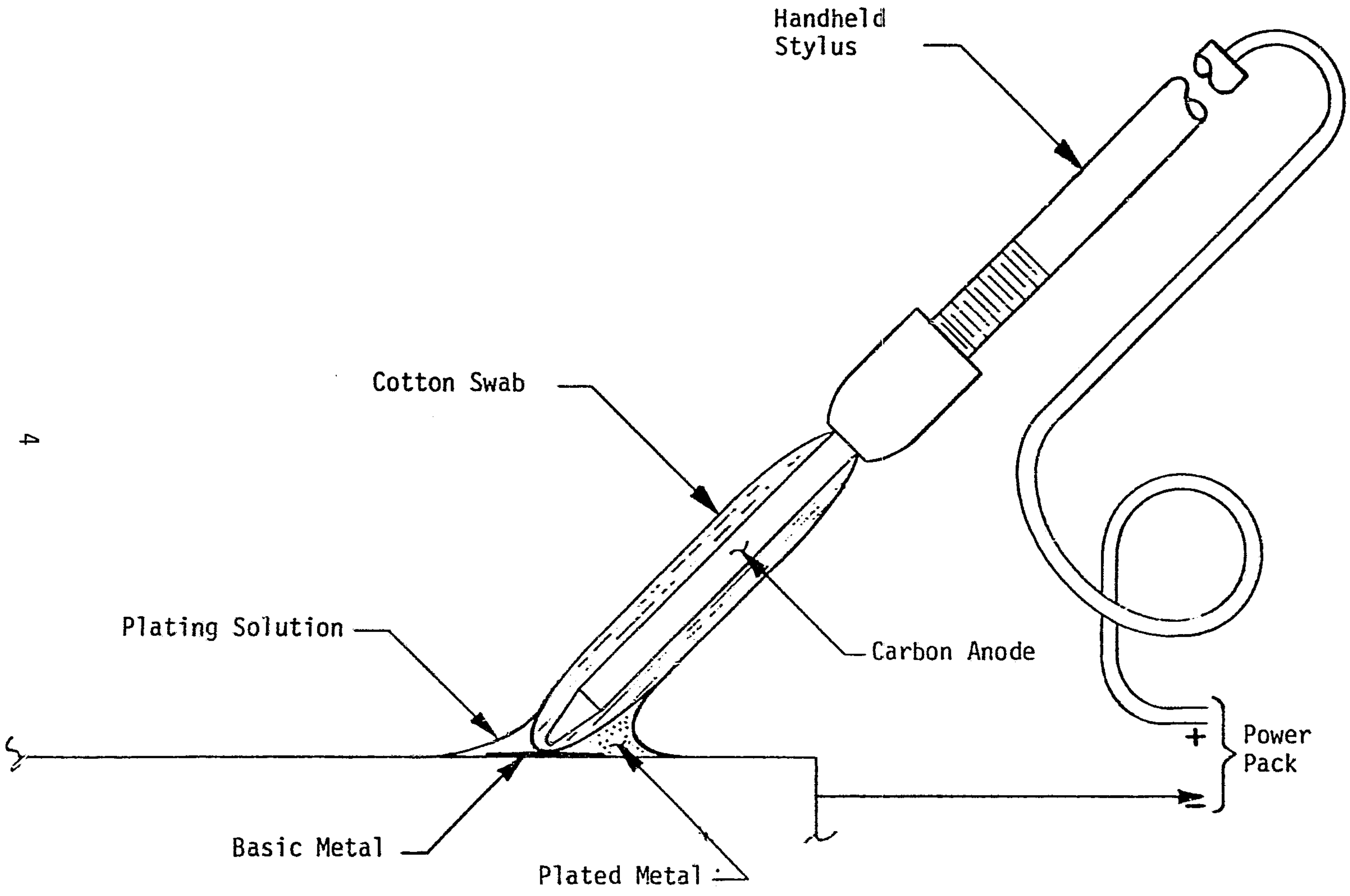

Figure 3.1 Schematic of Brush or Selective Plating Operation

Brush Plating Tests

Initial plating tests were performed at Vanguard Pacific using three nickle printing inks which were formulated by Electro-Science Laboratory. These printing inks contained a borosilicate frit. AgF was added to promote penetration of the silicon nitride.

After initial cell processing and printing, all inks were dryed at 125°C for 10 minutes. Three firing cycles, defined as follows were used:

625°C	Two minute heat-up, 10 minute soak for a total of 12 minutes.
650°C	Two minute heat-up, 10 minute soak for a total of 12 minutes.
700°C	Two minute heat-up, 5 minute soak for a total of 7 minutes.

All samples were given a tape test after firing, all samples indicated no lifting of nickel from Si_3N_4.

Brush copper plating was used to deposit copper on the front nickel and aluminum backs by Vanguard Pacific. Cells from the different Ni paste groups were returned to Photowatt for evaluation.

Pull test results of samples returned from Vanguard Pacific are presented in Table 3.1. The pull test values reported in Table 4 represent both the (90°) peel strength and shear strength of the metal layers when a flat ribbon (.002 X .062) was attached to the plated copper. A mildly activated flux was utilized to solder the ribbon to the cells.

Mechanical scratching and tape tests were applied to samples returned from Vanguard Pacific and results presented in Table 3.2. A visual and high power microscope inspection were performed on the returned samples and reported in Table 3.2. All cells examined showed loss of nickel and frit along the edges of the metallization after plating.

The results of these preliminary tests indicated poor adhesion, especially after plating. Modifications (F, G, H and D-1) of the D and E formulations intended to improve adhesion and improve electrical performance were obtained from Electro-Science Laboratories. These included such modifications as increased silver and reduced borosilica frit content. Tests of these pastes showed no improvement over the previous work.

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TABLE 3.1

MECHANICAL TEST RESULTS

CELL #/ Ni INK TYPE	FIRE CYCLE		Ni PASTE/Cu PLATE		Cu PLATE BACK SHEAR PULL STRENGTH (GRAMS)
	TEMP(C)	TIME(MINS)	FRONT SHEAR PULL STRENGTH (GRAMS)	90° PEEL STRENGTH (GRAMS)	
1-C	625	10	980	100	900
2-C	650	10	330	25	900
3-C	700	5	170	17	900
1-D	625	10	290	25	900
2-D	650	10	190	20	900
3-D	700	5	260	24	900
1-E	625	10	685	75	800
2-E	650	10	1000	120	900
3-E	700	5	600	65	900

TABLE 3.2

VISUAL & HIGH POWER EVALUATION RESULTS

Ni PASTE & CELL#	FIRE CYCLE		QUALITATIVE ADHESIVE TESTS		VISUAL & POWER INSPECTION	
	TEMP(C)	TIME(MIN)	BUSS	FINGER	Cu RESIDUE	Ni RESIDUE
1-C	625	10	OK	ML	YES	YES
2-C	650	10	OK	ML	YES	YES
3-C	700	5	ML	OK	YES	B
1-D	625	10	OK	ML	YES	NO
2-D	650	10	OK	L	YES	ETC
3-D	700	5	ML	L	YES	NO
1-E	625	10	OK	OK	YES	B
2-E	650	10	OK	ML	YES	YES
3-E	700	5	OK	ML	YES	YES

Notes: Codes and abbreviations for above columns: OK (test results successful); YES (Cu residue and/or Ni residue); NO (no visible Cu residue and/or Ni residue); ETC (nickel exposed through copper); B (Ni blistered); ML (minor lifting); L (lifting).

ESL also formulated a thick film nickel ink to be fired at high temperatures, 800°C, and in a reducing atmosphere. Cells were produced and printed with this high temperature nickel ink. Samples were dried at 125°C for 10 minutes and then fired at 800°C, 900°C and 950°C all in forming gas (N_2H_2) atmosphere. These samples exhibited good mechanical pull strengths. 50% HCL soak for one minute showed no effect on frit-coverage during soldering (80% of grid). Samples were sent to Vanguard for brush copper plating and were returned as being non-platable. Further testing was abandoned due to the inability to copper plate this particular nickel ink formulation.

Thermal Shock Tests

Thermal shock experiments were performed on D and E formulation samples after thick film fire-ins and brush copper plating. High temperature thermal shock failures were between the fired nickel and silicon nitride interface. Low temperature (LN_2) thermal shock did not cause failure. The nitride to nickel thick film and nickel thick film to copper interfaces remained intact after low temperature thermal shock.

Microscopic and SEM Evaluation

Microscopic and SEM evaluations of ESL thick films (D, E, F and G) were carried out using the following technique. A 100 mil wide ribbon wire (composition 60-40 tinned copper) was soldered to the brush plated copper buss of D and E formulated inks. The buss was subsequently removed by pulling the ribbon and the two exposed surfaces analyzed. The nickel pastes studied were fired at 700°C for 3 minutes after 125°C 10 minutes/dry cycle. See Figure 3.2 for areas studied. Observations are summarized in Table 3.3.

Reaction with Solutions

To determine the effects on adhesion of the cleaning solution (E/C) and alkaline and neutral copper solutions used by Vanguard Pacific, the following experiment was performed. The three solutions were heated in separate beakers and ESL nickel inks on solar cells were soaked at 90°C and various times after 125°C drying cycle and 700°C fire-in. Successive samples were soaked from 15 seconds to 30 seconds, at 5 second intervals.

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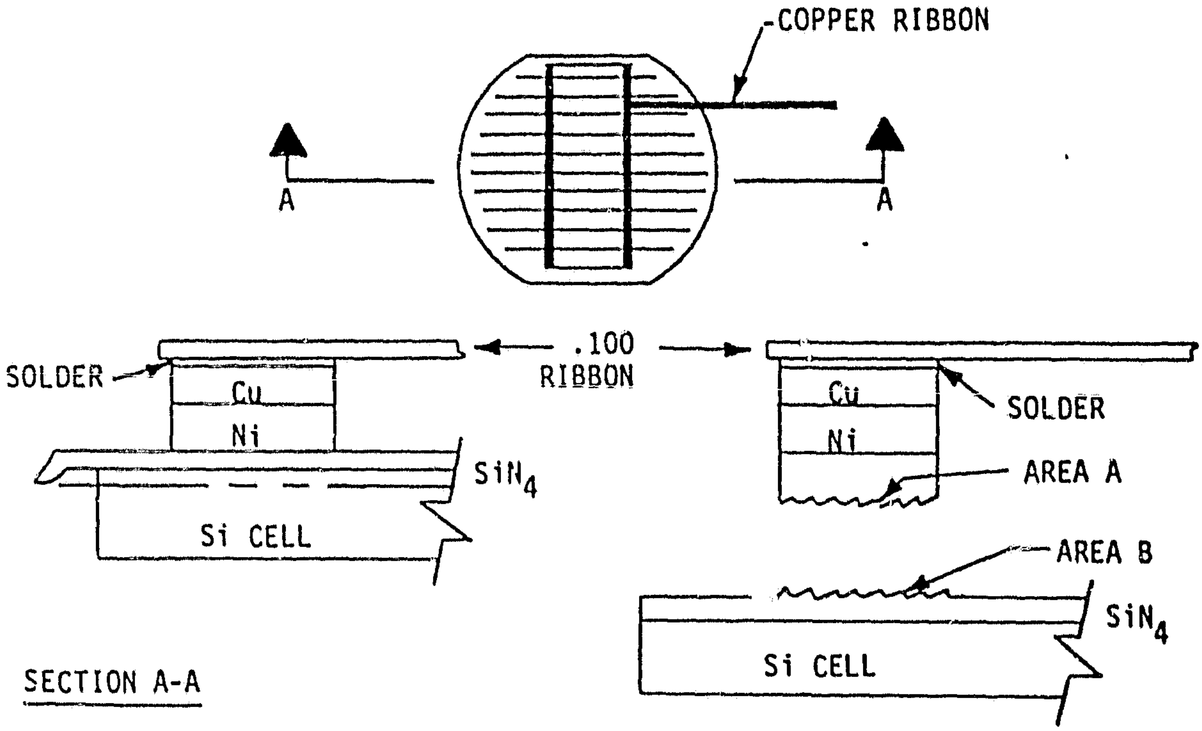

Figure 3.2. Sample preparation for microscopic and SEM examination.

TABLE 3.3

Microscopic & SEM Observations

Microscopic and SEM observations of thick film inks fired at 700°C for 3 minutes and brush plated with copper.

Ink D

1. Separation at the thick film/silicon nitride interface.
2. Prevalence of frit on the A surface with few nickel sites.
3. On surface A, medium concentrations of nickel, lead and silver, trace quantities of aluminum. Large concentration of silicon. No copper.

Ink E

1. Separation at the copper plate/fritted nickel interface.
2. Prevalence of frit on the surface of the grid with few nickel sites.
3. Porosity of the copper plate caused by limited number of nickel sites for plating.
4. Cracks in the grid.
5. On surface A, large concentration of silicon, medium concentration of lead. Trace quantities of silver, nickel and aluminum.

Ink F

1. Separation at the thick film/silicon nitride interface.
2. Large quantity of loose frit on surface B.

Ink G

1. Separation at the thick film/silicon nitride interface.
2. Loose frit on surface B.

Ink AA

1. Separation at the thick film/silicon nitride interface.
2. Loose frit on surface B.

Each sample was visually (high-power) inspected, and the height and width of grid patterns were measured in three places on cells before and after each soaking time. In all cases, maximum soaked samples appeared to have little or no decrease in height or width of nickel paste grid patterns. Samples were subjected to adhesive tape test and mechanical scratching.

ESL nickel thick film samples, subjected to E/C cleaning solution for 15 seconds, showed on visual (high-power) inspection a removal of frit along each side of the nickel stripe. After samples were soaked for 20 seconds, grids failed in adhesive tape tests and by mechanical scratching. After 25 seconds, nickel grids were being removed without adhesive tape test or scratching. Nickel grids were almost entirely gone on samples soaked for 30 seconds.

ESL nickel thick film subjected to alkaline copper solution showed removal of frit along each side of the nickel stripe after 15 seconds. As samples were soaked for 20 seconds, there was more frit removal and the nickel grids began to come off with adhesive tape test and mechanical scratching. By 25 seconds of soaking, nickel grids were being removed without adhesive tape test. Samples at 30 seconds showed that more than fifty percent (50%) of the nickel grids were entirely gone.

ESL nickel paste samples subjected to neutral copper solution survived all testing with a very minor frit breakdown from 15 to 25 seconds. At 30 seconds, adhesive tape test and mechanical scratching started to remove the nickel grid patterns.

Fritless Nickel Ink

Tests were made of Thick Film Systems (TFS) 5522 Oxyfire fritless nickel with 0, 2 and 5% silver fluoride fired in oxygen for 25 minutes at 500°C followed by 10 minutes at 650°C in forming gas. The sample with no fluoride added had good adhesion both before and after copper plating. Addition of silver fluoride resulted in loss of adhesion during plating. When fired at 800°C and 850°C for short periods, adhesion degraded during plating for all of these inks. 5522 nickel was also tested with 0.5% teflon added and fired at 750, 800 and 850°C. These compositions had good adhesion as fired but lost adhesion during plating. 5522 nickel with additions of 2 and 5% silver phosphate had fair adhesion as fired but could not be plated.

Fritless Tin Base Inks

Several fritless tin base printing inks were formulated and tested. These inks were all very sensitive to oxidation. By careful attention to furnace leaks and purging it was possible to eliminate oxidation by firing in forming gas (90% N_2 10% H_2). Under these conditions these inks did not adhere to the silicon nitride surface. Varying degrees of adhesion were obtained with a nitrogen atmosphere as are reported in Table 3.3. Visual and microscopic examination suggested a slight degree of oxidation. It will be noted that there is a general, but not universal tendency for adhesion to degrade during plating. This tendency is consistant with the hypothesis that bonding in these cases is associated with oxide layers which can be attacked by the plating solution.

In all cases plating was difficult and non-uniform. Compositions which included silver fluoride were most easily plated but suffered from extensive spreading of the grid lines. This spreading was of a feathery nature and appeared to be associated with the formation of thin conductive layers or filiments adjacent to the grid lines.

Samples were fired with a selection of tin base inks under a reducing atmosphere of CO in nitrogen. These experiments were performed at Electrink, Inc. with the assistance of Dr. Joseph Parker and Dr. Bernd Ross. The adhesion observed (Table 3.4) was much superior to that previously obtained with forming gas, and equal to or better than that in nitrogen. However, adhesion had deteriorated after plating, especially for the inks containing silver fluoride. The samples fired in the CO atmosphere showed no visible evidence of oxidation when examined under the microscope at high power.

TABLE 3.4

MECHANICAL ATTRIBUTES OF FRITLESS TIN BASE PRINTING INKS FIRED ON SILICON-NITRIDE

COMPOSITION	TIME MIN.	TEMP °C	ATM.	TAPE TEST ADHESION	
				BEFORE PLATING	AFTER PLATING
80 Sn 18 Mo 2 TiH_3	5	650	N_2	Good	Fair
80 Sn 18 Mo 2 TiH_3	3	800	N_2	Fair	Fair
	5	800	N_2	Fair	Fair
	10	800	N_2	Fair	Fair
(Sn/Mo TiH_3) + 2% AgF	1 - 3	700	N_2	Fair	Poor
(Sn/Mo/TiH_3) + 10% Ag	3 & 10	600	N_2	Good	Poor
	3 & 10	700	N_2	Fair	Poor
(Sn/Mo/TiH_3) + 20% Ag	5	700	N_2	Fair	Fair
	3	800	N_2	Fair	Fair
	5	800	N_2	Fair	Fair
Sn + 2% TiH_3	3	800	N_2	Fair	Fair
Sn + 1% AgF	10 & 15	700	N_2	Good	Good
	20	700	N_2	Good	Good
	2 - 10	800	N_2	Good	Good
Sn + 10% Ag	15	750	N_2	Good	Good
	10	800	N_2	Good	Good
Sn + 10% Ag	10	800	CO	Good	Good
Sn + 1% AgF	5	800	CO	Good	Poor
Sn + 10% + 1% AgF	5	800	CO	Good	Poor

3.3 Nickel Printing Inks

Electro-Science Laboratories Inks

Several special nickel printing inks were prepared by Electro-Science Laboratories designated A, B, C, D, E, F, H and D-1. These formulations contained one of 3 borosilicate frit blends and with AgF added to promote penetration of the silicon nitride. The inks differed in amounts of frit and AgF. Subsequent attempts by another vendor to blend AgF with fritted conductive inks were accompanied by exothermic heating which was attributed to reaction of the AgF with frit. Although ESL did not report any exothermic effects, it is likely that most, if not all, of the AgF in fritted inks is consumed by reaction with the frit, either during mixing or in the firing process.

Printing inks A and B were used for initial evaluations which led to the subsequent formulation of inks C, D and E. Electrical characteristics obtained with inks A and B after copper plating are reported in Tables 3.5 and 3.6.

Based on the preliminary results three new inks were formulated by ESL to improve the physical contract strength and electrical parameters:

- Ink C - Original ink with an increase in borosilicate and AgF.
- Ink D - Original ink with an increase in borosilicate and AgF.
- Ink E - New composition of borosilicate frit.

Cells were fabricated using C, D and E inks with three firing cycles:

- 625°C - Two minute heat-up, 10 minute soak for a total of 12 minutes.
- 650°C - Two minute heat-up, 10 minute soak for a total of 12 min0 utes.
- 700°C - Two minute heat-up, 5 minute soak for a total of 7 minutes.

Electrical test results of the samples returned from Vanguard Pacific after plating are presented in Table 3.7. From the electrical test results, fill factor, I_{sc} (per cm^2) and efficiency were calculated and are also reported in Table 3.7.

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TABLE 3.5

ELECTRICAL TEST RESULTS

OF 3" CELLS USING LOT A INK

CELL NUMBER	Isc(mA/cm^2)	Voc(VOLTS)	FIRE CYCLE		
			FURNACE TYPE	TEMP(C)	TIME (MIN)
1	22	0.523	IR Belt	625	5
2	23	0.552	IR Belt	625	5
3	13	0.427	IR Belt	625	10
4	25	0.522	Box	700	10
5	-0-	0.551	Box	700	1
6	4.2	0.545	Box	700	1

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TABLE 3.6

ELECTRICAL TEST RESULTS

OF 3" CELLS USING LOT B INK

CELL NUMBER	Isc(mA/cm^2)	Voc(VOLTS)	FIRE CYCLE		
			FURNACE TYPE	TEMP(C)	TIME (MIN)
1	20	0.448	IR Belt	625	5
2	25	0.564	IR Belt	625	5
3	-0-	0.544	IR Belt	625	5
4	20	0.505	IR Belt	625	10
5	21	0.555	IR Belt	625	10
6	11	0.183	Box	700	1
7	24	0.572	Box	700	1

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TABLE 3.7

ELECTRICAL TEST RESULTS
FOR ESL NICKEL INKS

CELL # INK	FIRE TEMP(C)	FIRE TIME(MIN)	$I_{sc}(mA/cm^2)$	Voc(VOLTS)	F.F.	EFF(%)
1-C	625	10	23	0.55	0.31	3.64
2-C	650	10	25	0.56	0.39	4.90
3-C	700	5	25	0.54	0.40	5.35
1-D	625	10	18	0.45	0.26	2.14
2-D	650	10	25	0.57	0.62	8.78
3-D	700	5	25	0.58	0.63	9.27
1-E	625	10	24	0.56	0.36	2.39
2-E	650	10	25	0.56	0.48	6.40
3-E	700	5	24	0.57	0.65	8.99

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The ESL fritted inks had all suffered loss of adhesion during the plating step as described in Section 3.2. Modifications (F, G, H, and D-1) of the D and E formulations intended to improve adhesion and improve electrical performance were obtained from Electro-Science Laboratories. These included such modifications as increased AgF and reduced borosilica frit content. Tests of these pastes showed no improvement with respect to either electrical performance or resistance to plating solution.

Effect of Increased Silver Content

Six groups of cells were produced using the Photowatt International, Inc. solar cell process and ESL thick nickel inks with silver added to observe the effects of increasing silver and decreasing borosilicate frit on D & E formulated nickel inks. D and E ink formulations were utilized with 5%, 10%, and 20% silver by weight in the form of EMCA Ag 7069 printing ink. Twelve samples in each group were dried at 125°C for 10 minutes, and then individually fired at 650°C, 700°C, and 750°C, from 3 minutes to 6 minutes for each temperature. IV curves were taken on nickel fired cells and then samples were copper plated, and again IV curves taken. All IV curves revealed very poor fill factors due to high series resistance. At the higher temperatures and longer times, 20% silver cells indicated low shunt resistance and V_{oc} had decreased to the 350 MV level. The IV curve for paste E with 5% silver fired at 700°C for 6 minutes shown in Figure 3.3 is typical of the curves obtained for all samples. All samples had poor adhesion after plating.

An additional ink (AA) formulated at Photowatt by blending 30% of Electro Materials Corporation Ag 7069 with Thick Film Systems Nickel ink #5517 was tested in a similar series. This formulation produced much better results as shown by the curves in Figure 3.4. These results were repeated in independent experiments performed at various times over a three month period. This formulation also showed degradation of adhesion during the plating step. SEM examination of the ink/silicon nitride interface after exposure to the copper plating solution revealed prevalence of frit at the interface, with evidence of loose frit residues.

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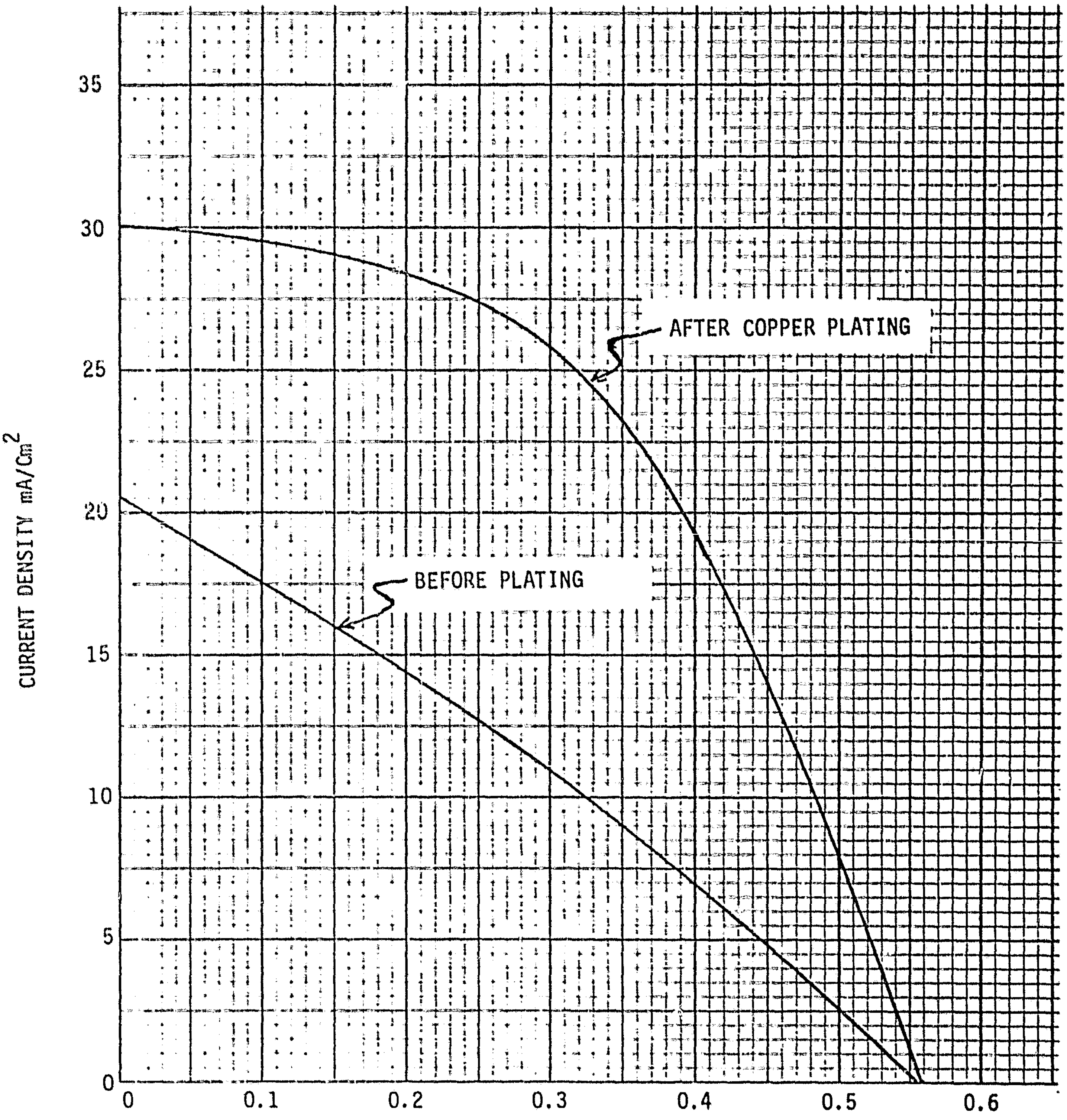

Figure 3.3. ESL paste E + 5% EMCA Ag 7069 fired at 700^{o}C for 6 minutes.

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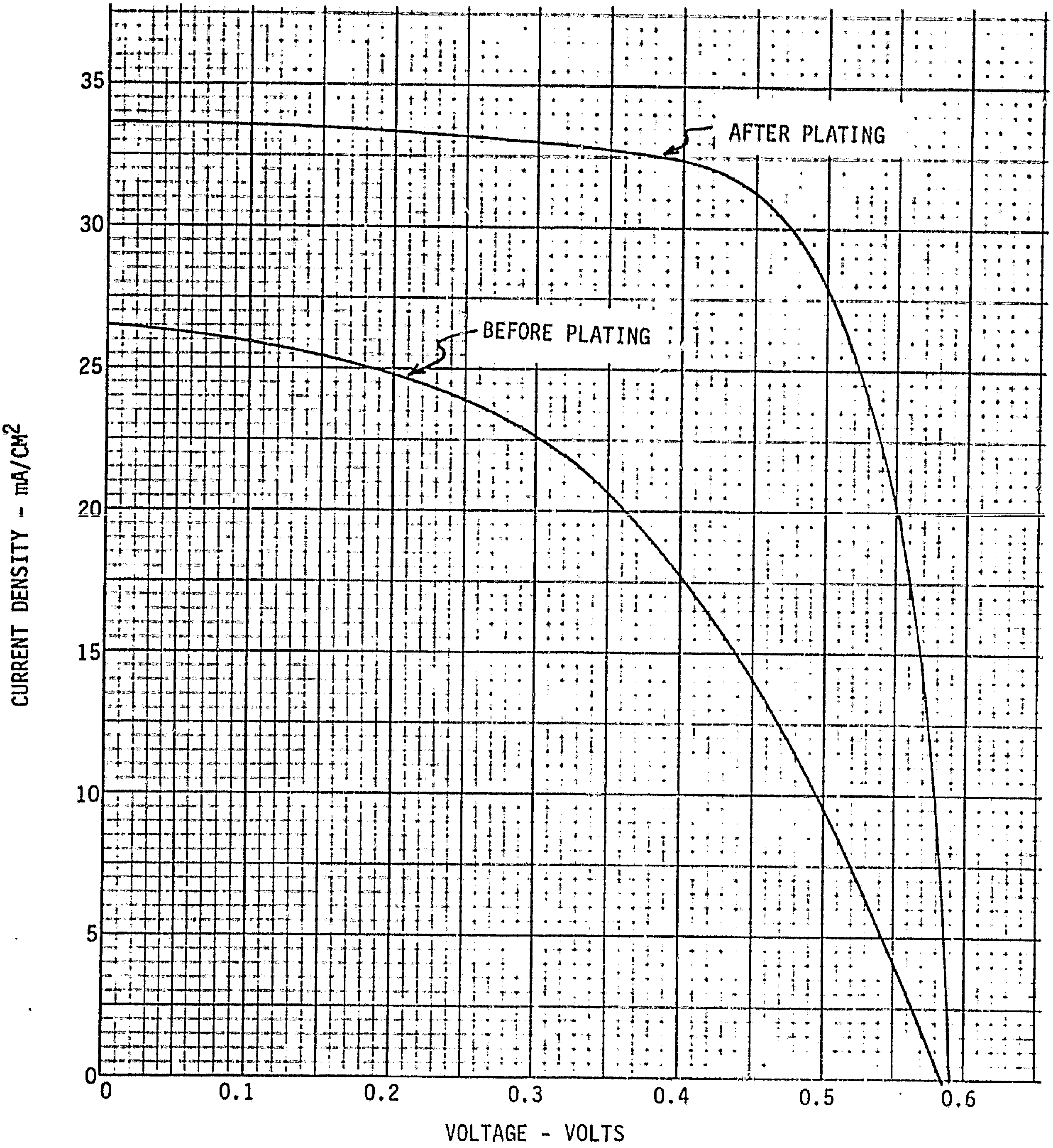

Figure 3.4. TFS Ni 5517 + 30% EMCA Ag 7069 fired at 700°C for 5 minutes.

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Fritless Nickel

Preliminary experiments with TFS 5522 Oxyfire fritless nickel with 0, 2, and 5% silver fluoride were fired in oxygen for 25 minutes at 500°C followed by 10 minutes at 650°C in forming gas. All samples were shorted with no electrical output. When fired at 800° and 850° for short periods, some electrical output was obtained. Grid lines lost adhesion during plating, and IV curves could only be obtained in the unplated condition. IV curves obtained with the unmodified TFS 5522 ink are shown in Figure 3.5 and as modified by 5% silver fluoride in Figure 3.6. An attempt to replicate the 45 second curve for the unmodified ink resulted in the indicated curve in Figure 3.5. Although the replicate curve has a poorer fill factor, this is largely due to a higher short circuit current. In the replication experiment, the optimum firing time was 45 seconds. Longer firing time resulted in shorting and collapse of the curve back toward the origin. This metallization lost adhesion in plating except for the unmodified ink with long firing time.

Similar results were obtained with 5522 nickel spiked with 0.5% teflon powder (DuPont DLX6000) (Figure 3.7). There was a slight change in the silicon nitride color believed to be caused by reaction of the AR coating with teflon vapors. Cells made with 5522 nickel blended with 2 and 5% silver phosphate had no photocurrent or photovoltage and could not be plated.

3.4 Tin Base Fritless Printing Inks

A variety of tin base conducting inks were tested in an attempt to avoid the loss of adhesion due to attack of frit by the plating solution. The inks were formulated by blending single component fritless inks containing tin, molybdenum and nickel which were obtained from Thick Film Systems. Tin ink was obtained with and without 2% titanium hydride added as a flux. A similar ink containing silver fluoride was used as an additive to promote penetration of the silicon nitride. Zinc chloride added as an alcohol solution and Teflon (DuPont DLX 6000) added as a fine

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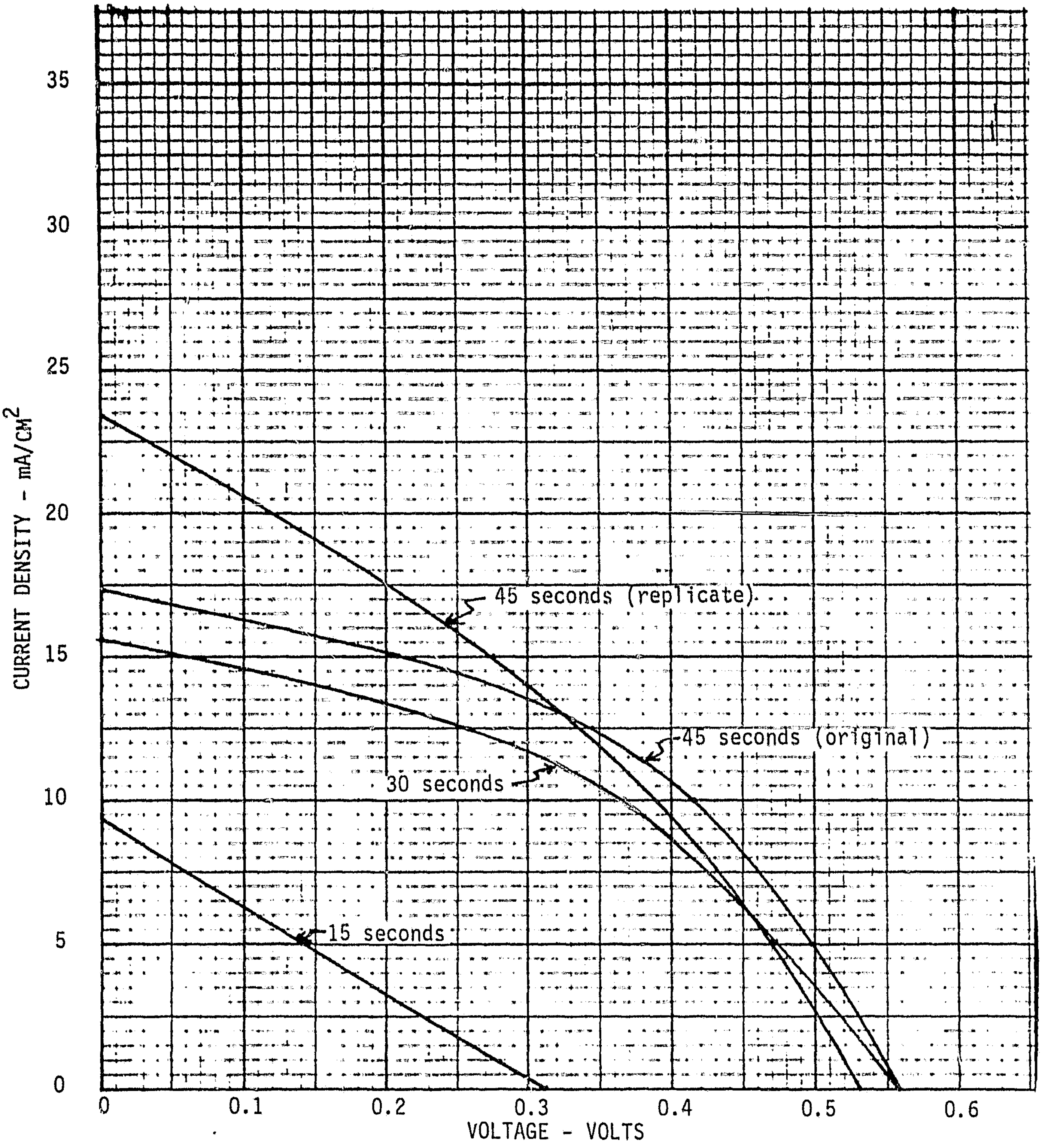

Figure 3.5. Current-voltage curves for TFS 5522 nickel fired at 850^oC on Si_3N_4, not plated.

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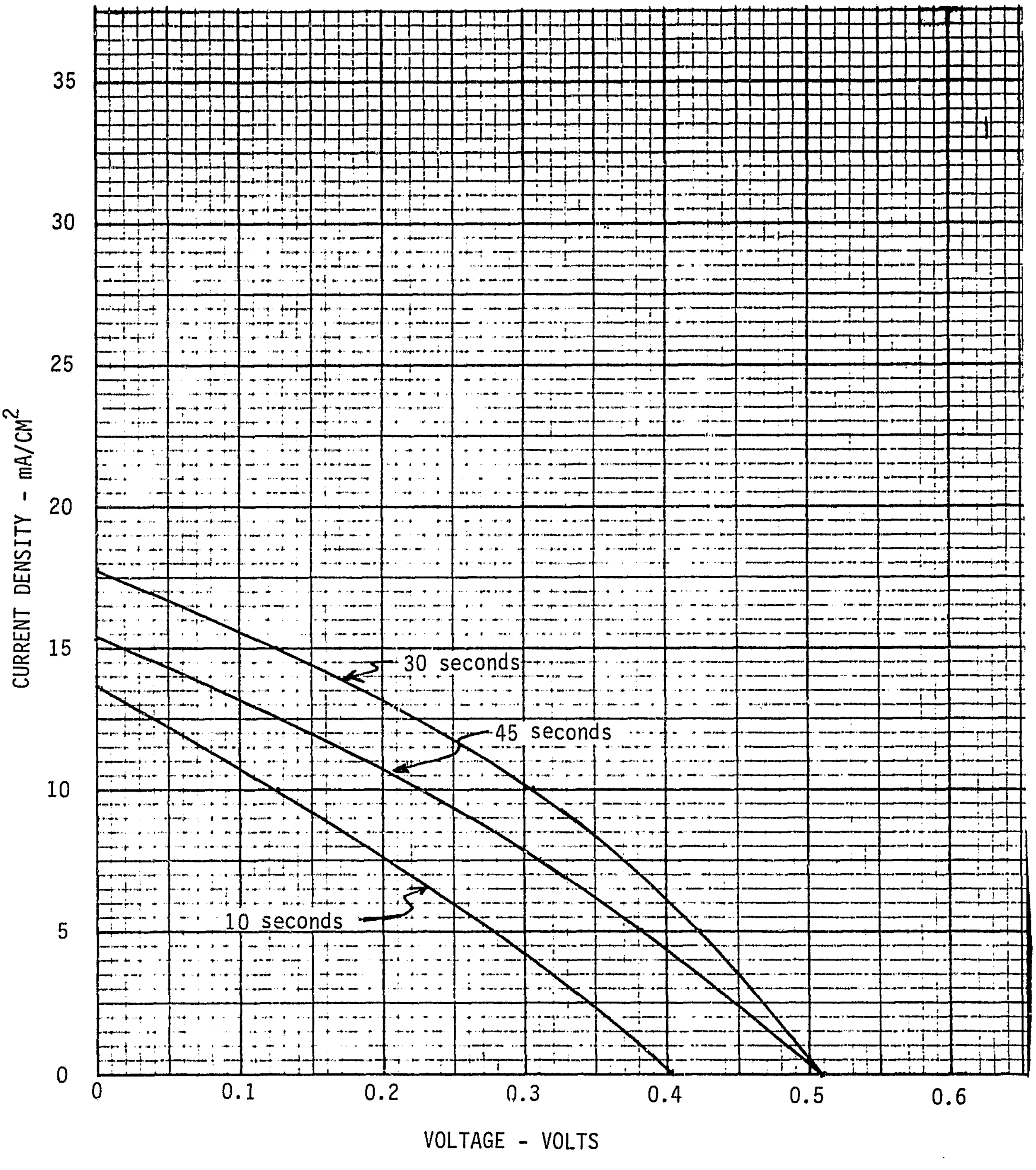

Figure 3.6. Current-voltage curves for TFS 5522 nickel +5% AgF fired at 850°C on Si_3N_4, not plated.

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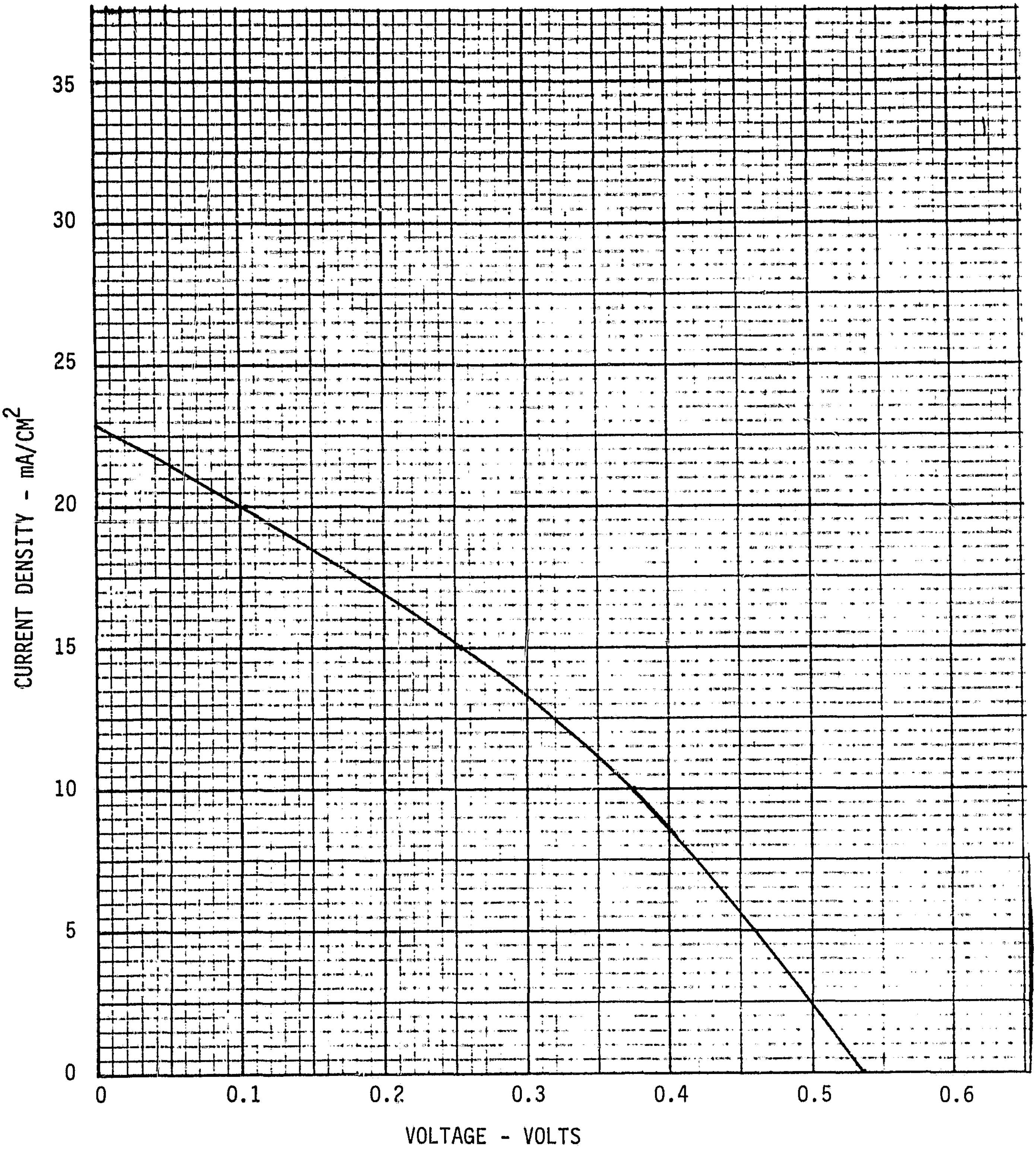

Figure 3.7. Current-voltage curves for TFS 5522 nickel + 0.5% teflon fired 45 seconds at 850°C, not plated.

powder were also tested as nitride penetrants. The formulations tested are given in Table 3.8.

Electrical properties of solar cell structures having tin base printed contacts fired on silicon nitride are given in Table 3.9. All of these structures had poor curve shapes reflecting high series resistance. Best results were observed with tin containing 1% silver fluoride fired in a carbon monoxide atmosphere (Figure 3.8). As previously reported, (Table 3.5) mechanical adhesion of these contacts degraded during plating.

Zinc chloride was the most aggressive additive used to penetrate the silicon nitride but resulted in powdery friable deposits and caused plating across the entire surface of the cell.

.05% teflon powder as an additive to tin and fired at 600°C resulted in extensive browning of the silicon nitride.

TABLE 3.8

Fritless Tin Base Printing Inks

98 Sn 2 TiH_3
99 Sn 1 AgF
90 Sn 10 Ag
89 Sn 10 Ag 1 AgF
80 Sn 18 Mo 2 TiH_3
98 ($Sn/Mo/TiH_3$) 2 AgF
90 ($Sn/Mo/TiH_3$) 10 Ag
80 ($Sn/Mo/TiH_3$) 20 Ag
10 Sn 90 Ni + $ZnCl_3$

TABLE 3.9

ELECTRICAL PROPERTIES OF SOLAR CELL STRUCTURE HAVING TIN BASE PRINTED CONTACTS FIRED ON SILICON NITRIDE.

COMPOSITION	TIME MIN.	TEMP °C	ATM.	BEFORE PLATING		AFTER PLATING	
				I_{sc} mA.Cm2	V_{oc} mV	I_{sc} mA/Cm2	V_{oc} mV
80 Sn 18 Mo 2 TiH_3	5	650	N_2	0.8	550	11.5	560
80 Sn 18 Mo 2 TiH_3	3	800	N_2	1.3	550	13.0	560
	5	800	N_2	2.4	545	17.5	560
	10	800	N_2	1.9	550	13.4	500
(Sn/Mo TiH_3)+2% AgF	1 - 3	700	N_2	0.3-0.8	540-550	3.5 - 7.9	480-550
(Sn/Mo/TiH_3)+10% Ag	3 & 10	600	N_2	0.3-0.4	480-544	5.5 - 6.6	480
	3 & 10	700	N_2	0.8	515-530	10.1 - 16.7	514-550
(Sn/Mo/TiH_3)+20% Ag	5	700	N_2	0.9	540	14.3	515
	3	800	N_2	2.9	540	18.4	550
	5	800	N_2	2.1	547	15.5	540
Sn + 2% TiH_3	3	800	N_2	9.6	540	19.8	540
Sn + 1% AgF	10 & 15	700	N_2	0.2-1.4	550-565	13.4 - 15.1	550-564
	20	700	N_2	0.5	575	6.6	535
	2 - 5	800	N_2	2.7-3.8	533-575	18.0 - 20.8	548-575
	10	800	N_2	1.6	570	2.9	570
Sn + 10% Ag	15	750	N_2	1.8	564	8.8	560
	10	800	N_2	2.3	560	18.2	560
Sn + 10% Ag	10	800	CO	3.3	537-555	7.3	544
Sn + 1% AgF	5	800	CO	0	520-548	22.6	540
Sn + 10% + 1% AgF	5	800	CO	6.0-7.7	538-546	22.8	520

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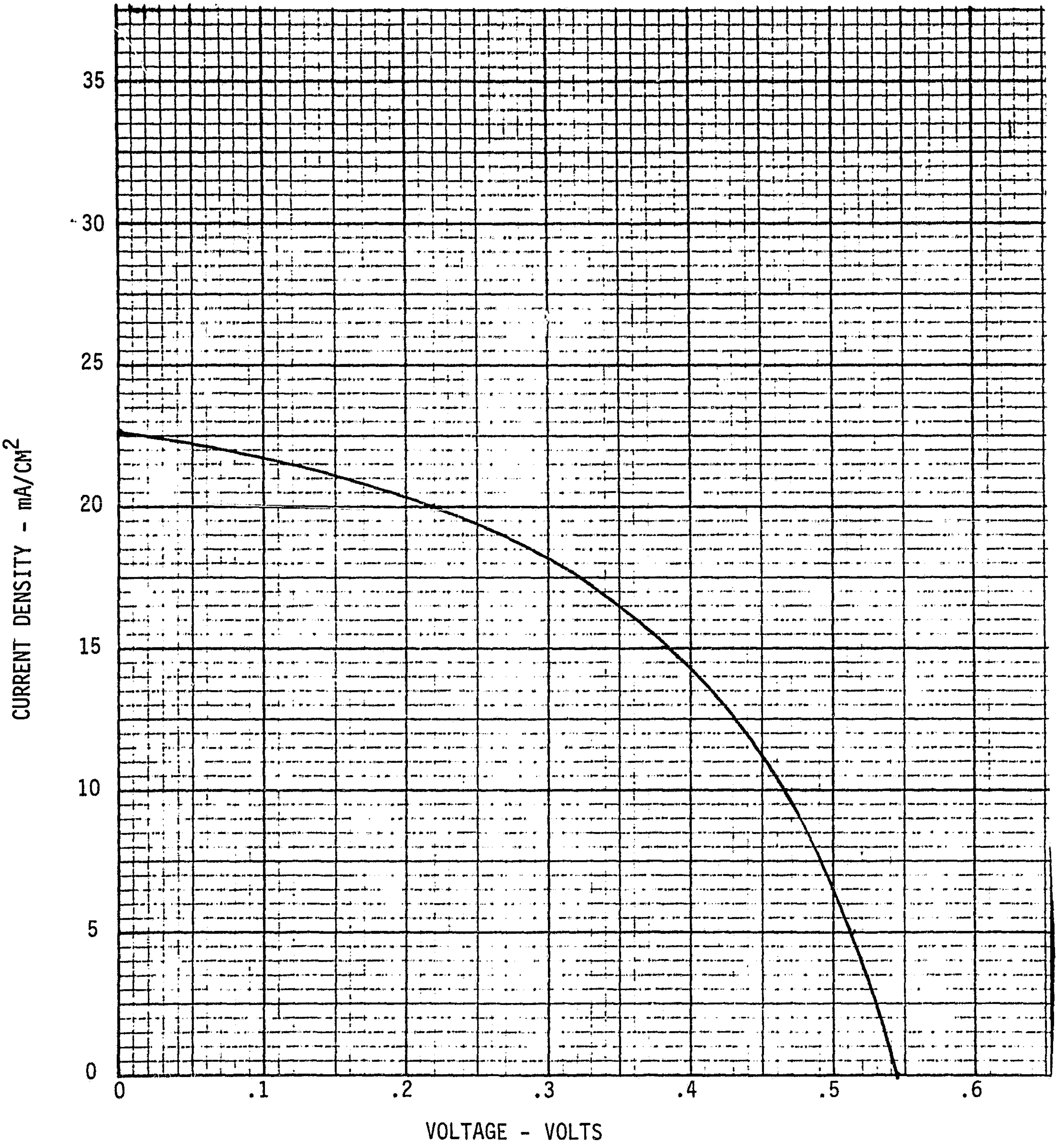

Figure 3.8. IV curve for Sn + 1% AgF fired for 5 minutes at 800°C in N_2 + CO atmosphere. Silver plated.

4.0 CONCLUSION

Fritted nickel printing inks, which showed the best electrical performance, were unstable with respect to the plating solutions used.

Fritless nickel printing fired for 10 minutes at 650°C showed good resistance to plating solutions but this was lost when agents such as silver fluoride and teflon were added to the ink to promote penetration of the silicon nitride. Under these firing conditions the junctions were shorted. With other firing conditions where electrical performance was promising, resistance to plating solution was poor.

Fritless tin based printing inks were very susceptible to oxidation during firing. When fired in reducing atmosphere containing hydrogen they had poor adhesion as fired. Adhesion was obtained by firing in pure nitrogen or reducing atmospheres containing carbon monoxide, but these films had poor curve shapes, were difficult to plate and tended to lose adhesion in plating.