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for
DEVELOPMENT OF TECHNIQUE FOR AR COATING AND NICKEL AND COPPER METALLIZATION OF SOLAR CELLS
FPS PROJECT
PRODUCT DEVELOPMENT

PERFORMANCE PERIOD
October 1, 1981 to March 31, 1982

JPL CONTRACT NO. 955986
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April 15, 1982

Prepared by:

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"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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PREFACE

The objective of this program is to analyze and evaluate a base metal system for metallizing solar cells. The system to be investigated is printed nickel overplated with copper and applied on top of a predeposited silcon nitride antireflective coating.

1.0 SUMMARY

Further evaluations were made on the ESL D and E paste formulations, and on new formulations F, G, H, and D-1 which were received from ESL during this period. All of these tests replicated the previous results of high series resistance and loss of adhesion during plating. An additional ESL high temperature nickel formulation was tested, but could not be plated.

The ESL nickel thick films after firing were tested for stability in the cleaning and plating solutions used in the Vanguard-Pacific brush plating process. The films were found to be very sensitive to the cleaning and alkaline copper solutions. Less sensitivity was displayed to the neutral copper solution, but even with this solution reduced adhesion was observed after 30 seconds of exposure.

Microscopic and SEM observations showed segregation of frit at the silicon nitride-thick film interface with loose frit residues after lifting off plated grid lines.

Doping of the experimental ESL pastes D and E with silver did not affect any change in performance of the pastes. However doping of Thick Film Systems #5517 nickel with 30% of EMCA #7069 silver paste reduced series resistance without affecting loss of adhesion during plating.

2.0 TECHNICAL PROGRESS

Solar Cell Tests of ESL Paste Formulations

During this period, further investigations were made of the ESL nickel paste D and E formulations and new formulations F, G, H and D-1. The following conditions were observed:

a. High series resistance.

b. Poor mechanical adhesion after brush copper plating.

c. Loss of nickel thick film frit during brush copper plating.

ESL formulated a thick film nickel paste to be fired at high temperatures, 800°C, and in a reducing atmosphere. Cells were produced and printed with this high temperature nickel paste. 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 paste formulation.

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.

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

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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.

Thermal Shock Tests

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

Microscopic and SEM Evaluation

Microscopic and SEM evaluations of ESL thick films (D, E, F & 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 & E formulated pastes. 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 1 for areas studied. Observations are summarized in Table 1.

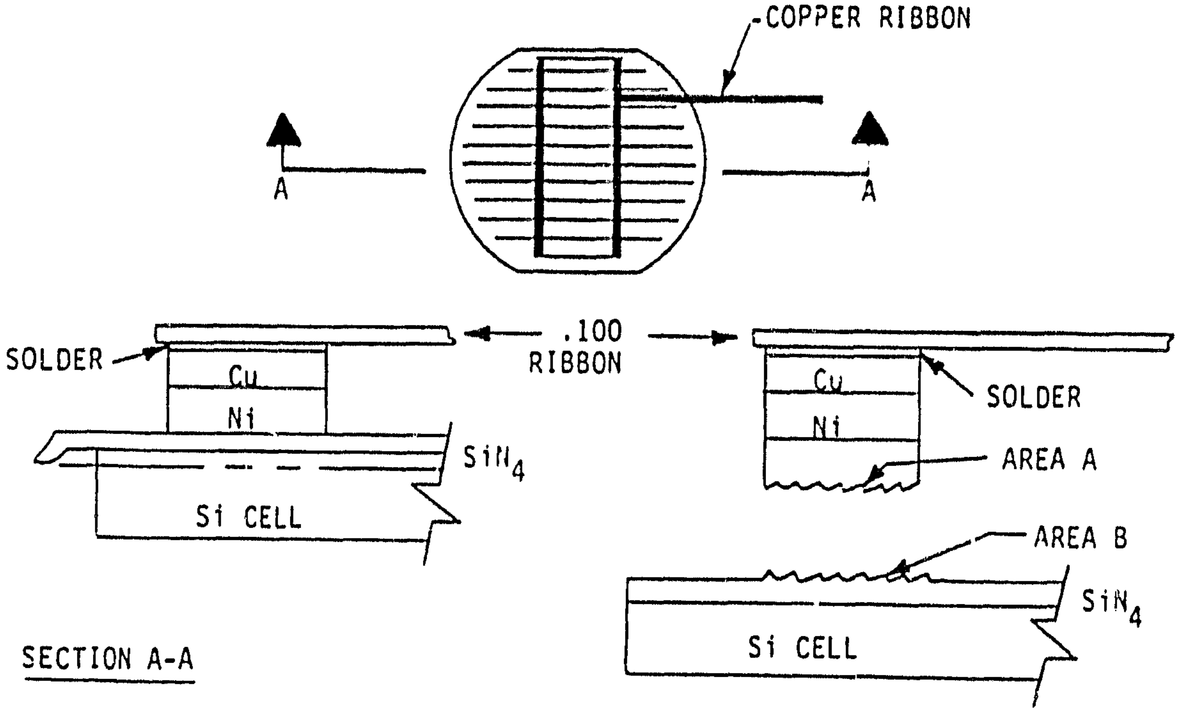

Figure 1. Sample preparation for microscopic and SEM examination.

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TABLE 1

Microscopic & SEM Observations

Microscopic and SEM observations of D and E pastes fired at 700° for 3 minutes and brush plated with copper.

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

Effect of Increased Silver Content

Six groups of cells were produced using the Photowatt International, Inc. solar cell process and ESL thick film nickel pastes with silver added. D & E paste 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 electrolyticly copper plated, and again IV curves taken. This experiment was performed to observe the effects of increasing silver and decreasing borosilicate frit on D & E formulated nickel pastes. 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 VOC 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 2 is typical of the curves obtained for all samples. All samples had poor adhesion after plating.

An additional paste (AA) formulated at Photowatt by blending 30% of EMCA Ag 7069 with Thick Film Systems Nickel paste #5517 was tested in a similar series. This formulation produced much better results as shown by the curves in Figure 3. These results were repeated in independent experiments performed at various times over a three month period. This formulation also showed degradation of adhesions during the plating step. SEM examination of the paste/silicon nitride interface after exposure to the copper plating solution again revealed prevalence of frit at the interface, with evidence of loose frit residues.

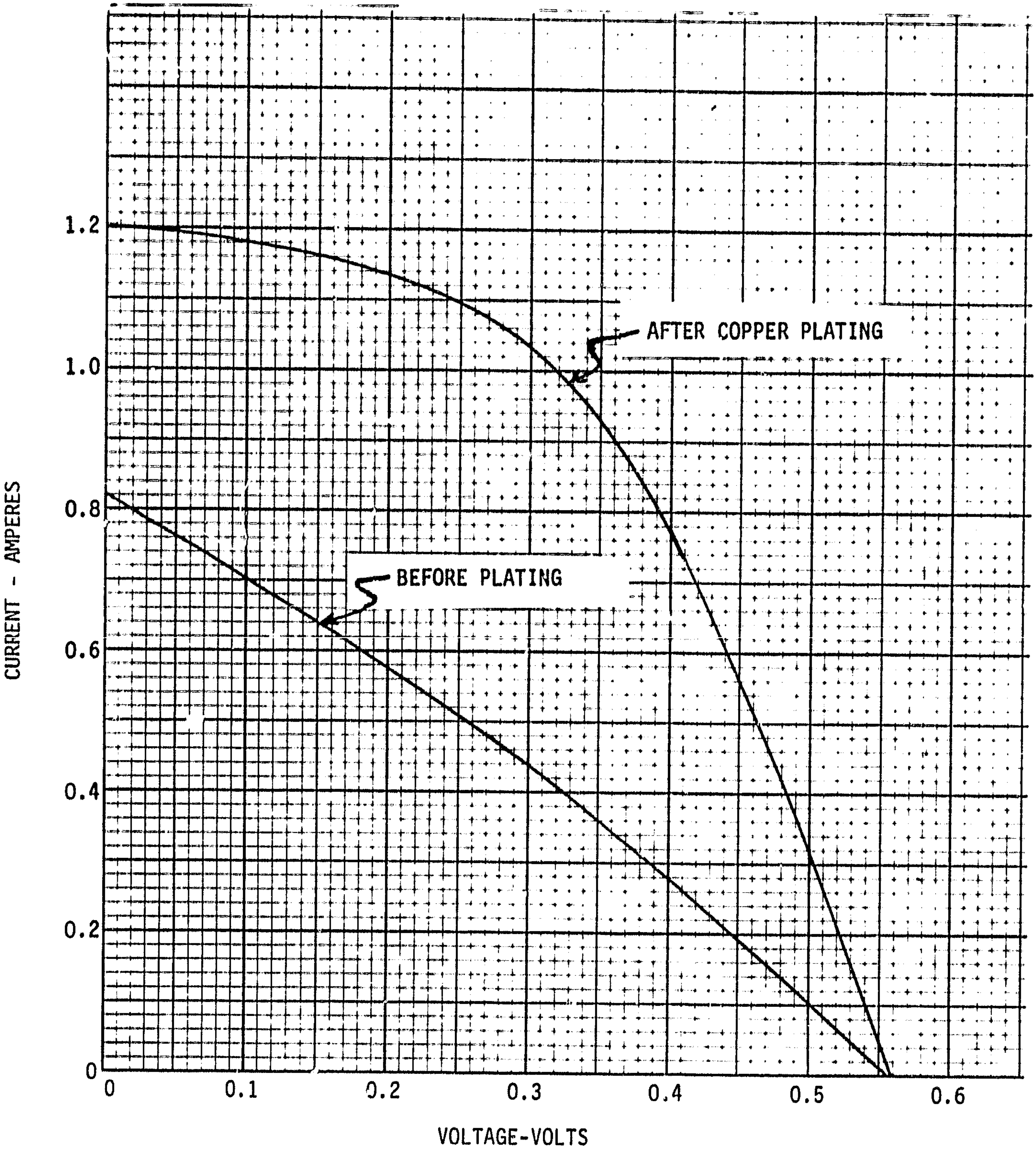

Figure 2. ESL paste E + 5% EMCA Ag 7069 fired at 700°C for 6 minutes.

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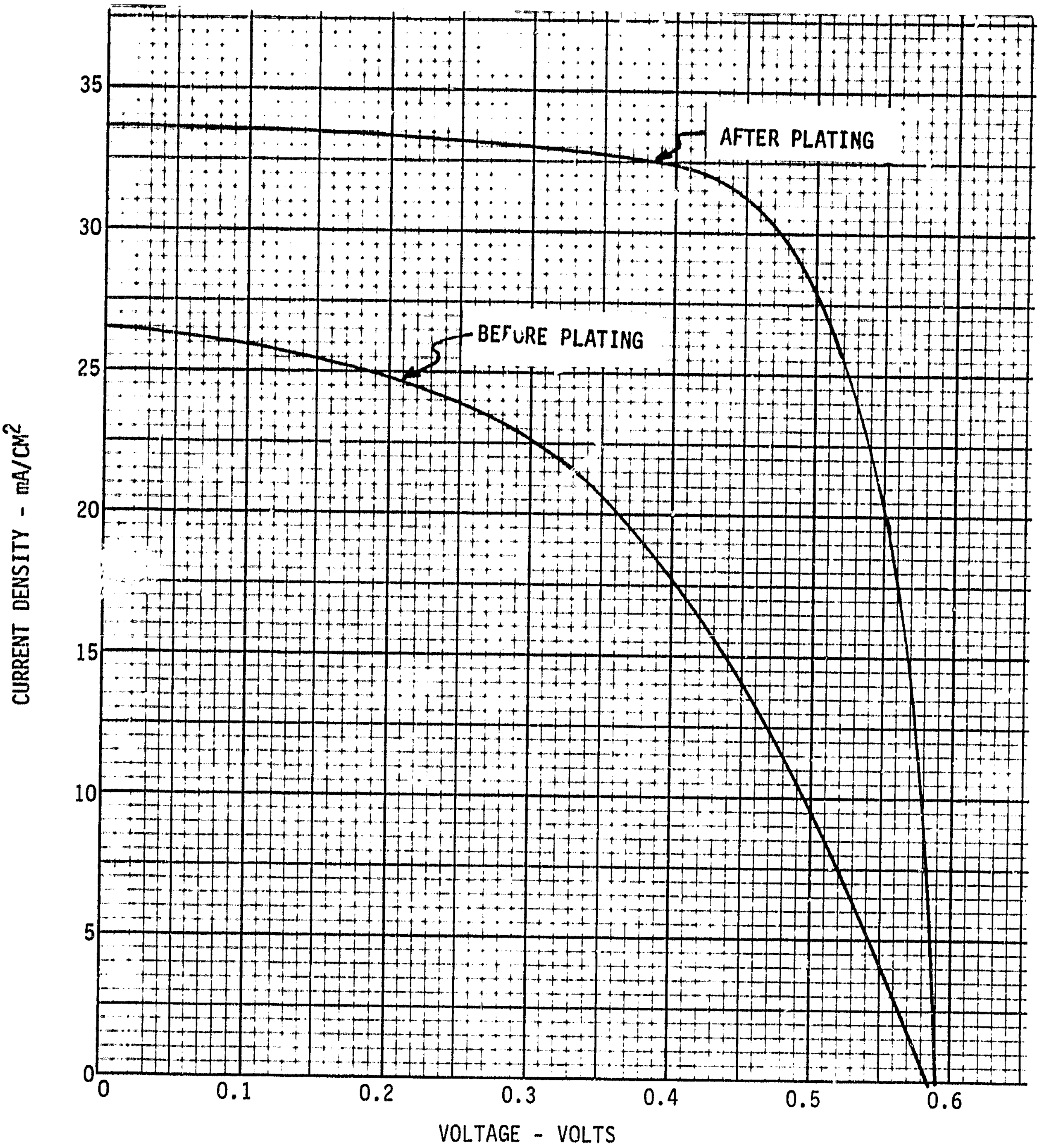

Figure 3. TFS Ni 5517 + 30% EMCA Ag 7069 fired at 700°C for 5 minutes.

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3.0 DISCUSSION

Loss of adhesion during plating is attributed to chemical attack of the frit in the thick film by the plating solution. The frit, being a non-conductor, is also a contributor to the excessive series resistance observed, especially for those formulations in which the frit segregates to the interface. In addition to these deleterious effects, the frit is likely to be reactive with the silver fluoride, reducing the efficacy of the fluoride fluxing activity.

4.0 CONCLUSIONS

Effort on this program should be redirected to investigate fritless printing ink formulations. Additives such as titanium hydride and gold to improve adhesion and reduce contact resistance should be evaluated. Investigation of the role of fluxing agents should be broadened to include phosphates and non-silver bearing agents such as nickel fluoride.

5.0 PLANS

Fritless inks will be procured containing single constituents such as silver phosphate, nickel fluoride, tin-titanium hydride, nickel and molybdenum. These inks will be blended to produce samples for evaluation of the effectiveness of the various constituents. Evaluation procedures will be extended to include determination of contact resistance and heavier reliance on SEM observations.