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A NEW METHOD OF METALLIZATION FOR SILICON SOLAR CELLS.

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SECOND QUARTERLY REPORT

FOR PERIOD COVERING

1 APRIL 1979 TO 30 JUNE 1979

BY

DR. MILO MACHA

JPL CONTRACT NO. 955318

SOL/LOS INCORPORATED
2231 S. CARMELINA AVENUE
LOS ANGELES, CA. 90064

" THE JPL LOW-COST SILICON SOLAR ARRAY PROJECT IS SPONSORED BY THE UNITED STATES 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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ABSTRACT

THE SECOND QUARTER OF THIS PROGRAM IS CONCERNED WITH THE DETERMINATION OF THE FIRING CYCLE IN A HORIZONTAL TUBE FURNACE FOR MoO_3: SN INK COMPOSITION APPLIED BY SILK SCREENING PROCESS ON P ON N STRUCTURED SOLAR CELLS.

IN COMPARISON WITH THE STRIP HEATER USED IN THE FIRST QUARTER TO DETERMINE THE REACTION MECHANISM, THE REDUCTION OF MoO_3 IN THE TUBE FURNACE PROGRESSES AT A MUCH FASTER RATE AND THE SN:MO ALLOY FORMS AT A MUCH LOWER TEMPERATURE.

THE DEVICE CHARACTERISTICS DETERMINED BY THE V-I CURVE SHOWED A HIGH RESISTANCE (APPROX. 10 OHMS) AT PEAK TEMPERATURES BETWEEN 600°C AND 800°C.

THE HIGH SERIES RESISTANCE CAN BE ATTRIBUTED TO THE LACK OF FORMATION OF $MoSi_2$ WITHIN THE USED TEMPERATURE RANGE AS POINTED OUT IN REFERENCES TO THEORETICAL AND EXPERIMENTAL WORK CONCERNED WITH THE FORMATION OF METAL SILICIDES.

ACCORDING TO THESE REFFRENCES THIS TEMPERATURE RANGE IS RIGHT FOR THE FORMATION OF SILICIDE OF TITANIUM, WHICH, BESIDES HAVING A LOWER RESISTANCE VALUE, FORMS IN THE PRESENCE OF AN OXIDIZED SILICON SURFACE.

THEREFOR THE BASIC MoO_3 INK COMPOSITION WAS MODIFIED BY AN ADDITION OF TITANIUM RESINATE CORRESPONDING TO A TITANIUM CONCENTRATION OF 1-15000 BASED ON THE SOLIDS IN THE MIXTURE.

THE ADDITION OF TITANIUM DECREASED INDEED THE SERIES RESISTANCE TO THE LEVEL OF 1 OHM OR BETTER AND THE DEVICE CHARACTERISTICS WERE COMPARABLE WITH THE DEVICES METALLIZED BY ELECTROLESS NICKEL AND SILK SCREENED SILVER.

1. INTRODUCTION

OHMIC CONTACT TO SILICON PHOTOVOLTAIC CELLS FORMED BY Mo:Sn SYSTEM WAS EVALUATED FOR MECHANICAL AND ELECTRICAL QUALITY AFTER FIRING IN A HORIZONTAL TUBE FURNACE AT VARIOUS TEMPERATURES.

THIS STEP WAS CHOSEN TO SIMILATE FIRING CONDITIONS IN A CONVEYOR BELT FURNACE.

THE INK PREPARED FROM MoO_3:Sn MIXTURE, DISPERSED IN AN ORGANIC BINDER AND SOLVENTS, WAS APPLIED THROUGH SILK SCREENS ON BOTH SIDES OF THE CELL AND, AFTER BURN-OFF OF THE ORGANIC MATERIAL, THE FIRING WAS DONE IN A FORMING GAS ATMOSPHERE.

THE METALLIZATION WAS EVALUATED BY SOLDER TESTS AND V-I CHARACTERISTICS OF THE SOLAR CELL.

THE INK WAS MODIFIED BY ADDITION OF TITANIUM TO LOWER THE SERIES RESISTANCE.

II. ACCOMPLISHMENTS.

II.1 Formulation of a screenable ink from MoO_3:Sn mixture.

Materials used:

Tin powder (Cominco & ROIC) 325 mesh-99.999% purity.

Trichloro ethylene (Los Angeles Chemical Co.)

Ethyl cellulose (Dow Chemical Co.)

Carbitol solvent and

Carbitol Acetate (Orange County Chemical Co.)

Molybdenum Trioxide (Mallinckrodt)

MoO_3 and Sn were mixed in a ratio of 78% Sn and 22% MoO_3.

10 grams of the mixture were used for the formulation of the initial ink composition.

2.2 grams of MoO_3 and 7.8 grams of Sn were dry mixed in a quartz mortar.

The vehicle for the ink consisted of 75% trichloro ethylene, 15% ethyl cellulose, 8% carbitol solvent and 2% carbitol acetate, all amounts are in weight percentages.

10 grams of the MoO_3:Sn mix were blended with 5 grams of the vehicle and homogenized on a glass plate with a spatula.

THE SCREENING TEST WAS DONE USING A 200 MESH SCREEN.

II.2 SET-UP AND CALIBRATION OF THE TUBE FURNACE FOR INK FIRING.

A HEAVY DUTY 3-ZONE DIFFUSION FURNACE WITH 3" I.D. QUARTZ TUBE WAS USED FOR THIS PURPOSE. THE INITIAL PEAK TEMPERATURE WAS SET AT 800°C. THE PROFILE OF THE FURNACE WAS MEASURED BY A CHROMEL-ALUMEL THERMOCOUPLE IN ORDER TO ESTABLISH THE TEMPERATURE ZONES CRITICAL FOR FIRING THE MoO_3:Sn MIXTURES.

NITROGEN AND FORMING GAS (60%N-40%H) WERE CONNECTED THROUGH A COMMON FLOWMETER TO ONE END OF THE TUBE.

THE EXPERIMENTS WERE DONE WITH N-TYPE SILICON .5 TO 1.5 OHM/CM RESISTIVITY WITH ONE SIDE POLISHED AND THE OTHER SIDE ETCHED.

AFTER APLLYING THE INK ON BOTH SIDES OF THE WAFER THE SAMPLES WERE AIR-DRIED AND ORGANIC MATERIALS BURNED OUT IN A SMALL CERAMIC MUFFLE KILN (21CM X 16CM X 23CM) ON A QUARTZ BOAT.

THE AIM OF THE FIRST RUNS WAS TO DUPLICATE THE CYCLE PREVIOUSLY ESTABLISHED ON THE GRAPHITE STRIPHEATER IN THE EXPERIMENTAL STATION.

It has been found that in all cases the reduction of MoO_3 to blue MoO_2 took place within the determined temperature range, i.e. between 550°C and 650°C temperature range, put in contrast with the reaction observed on the stripheater, where the metallic tin formed at 800°C, the tin formation in the tube furnace took place shortly after the conversion of MoO_3 into MoO_2.
This was confirmed by a run of MoO_3 coating alone, during which conductive Mo film was obtained between 550°C and 650°C in 5 minutes.
The Mo:Sn layer formed at lower temperatures had a good solderability and in some cases a good bond.
It remained to be determined whether it was important to conduct the heating cycle in such a way to establish if the total conversion of MoO_3 into Mo was necessary before the temperature was raised to 800°C.

II.3 Evaluation of Mo:Sn contact.

The contact formed from a screenable mixture of 78% Sn : 22% MoO_3 was evaluated for mechanical as well as electrical characteristics.
The pattern was screened through 200 mesh silk

SCREENS ON DIFFUSED P ON N SILICON SOLAR CELL STRUCTURES.

AFTER SCREENING, THE TEST SAMPLES WERE DRIED AND ORGANIC MATERIAL BURNED OFF IN A CERAMIC MUFFLE FURNACE.

THE FIRST EXPERIMENTS WERE DONE WITH A PRE-HEAT AT 560°C FOR 5 MINUTES AND A SOAK AT 800°C PEAK FOR 1 MINUTE.

THE ATMOSPHERE WAS 60% NITROGEN AND 40% HYDROGEN, (FORMING GAS, PURCHASED FROM AMWELD INC.)

THE CONTACT HAD A GOOD ADHERENCE, TESTED BY THE X-ACTO KNIFE AND HAD A GOOD SOLDERABILITY.

THE VOLTAGE-CURRENT CHARACTERISTICS DETERMINED ON A X-Y PLOTTER SHOWED A STRAIGHT LINE BETWEEN THE V_{OC} AND I_{SC} VALUES.

THERE WAS NO DEGRADATION IN SHORT CIRCUIT CURRENT NOR IN OPEN CIRCUIT VOLTAGE VALUES, INDICATING THAT THE CONTACT WAS OHMIC, BUT WITH A HIGH RESISTANCE (ABOVE 10 OHMS).

IN ORDER TO ESTABLISH THE EFFECT OF THE PEAK TEMPERATURE ON THIS HIGH SERIES RESISTANCE VALUE, OTHER SAMPLES WERE RUN WITH THE SAME PRE-HEAT CYCLE OF 560°C, BUT WITH PEAK TEMPERATURES OF 700°C AND 900°C RESPECTIVELY.

The results showed that the samples fired at 700°C had the same slope as the samples at 800°C, while the sample fired at 900°C was degraded in open circuit voltage.(Fig.1).

In order to determine whether this degradation was caused by the action of the metallic contact or by the temperature alone, non-metallized cells were subjected to the same cycle.

The results of this test showed also degradation in open circuit voltage, suggesting that the degradation was caused by the heat cycle alone.

II.4 Improvement of the contact series resistance.

In order to explain the reason for the high series resistance Mo/Sn-Si contact, references were searched relating to studies of Mo-Si interface and nature of the contact.

An article published by R.C. Hooper, J.A. Cunningham and J.G. Harper in Solid State Electronics, Vol.8, pp 831-833 (1965), lists contact resistance values of Mo and other metals evaporated on Si of various resistivities.

According to this study the contact resistance of Mo to P-type Si with resistivities of 0.002 and 0.1 ohm/cm is 4.4×10^{-6} ohm/cm^2 and 1.1×10^{-1} ohm/cm^2 respectively.

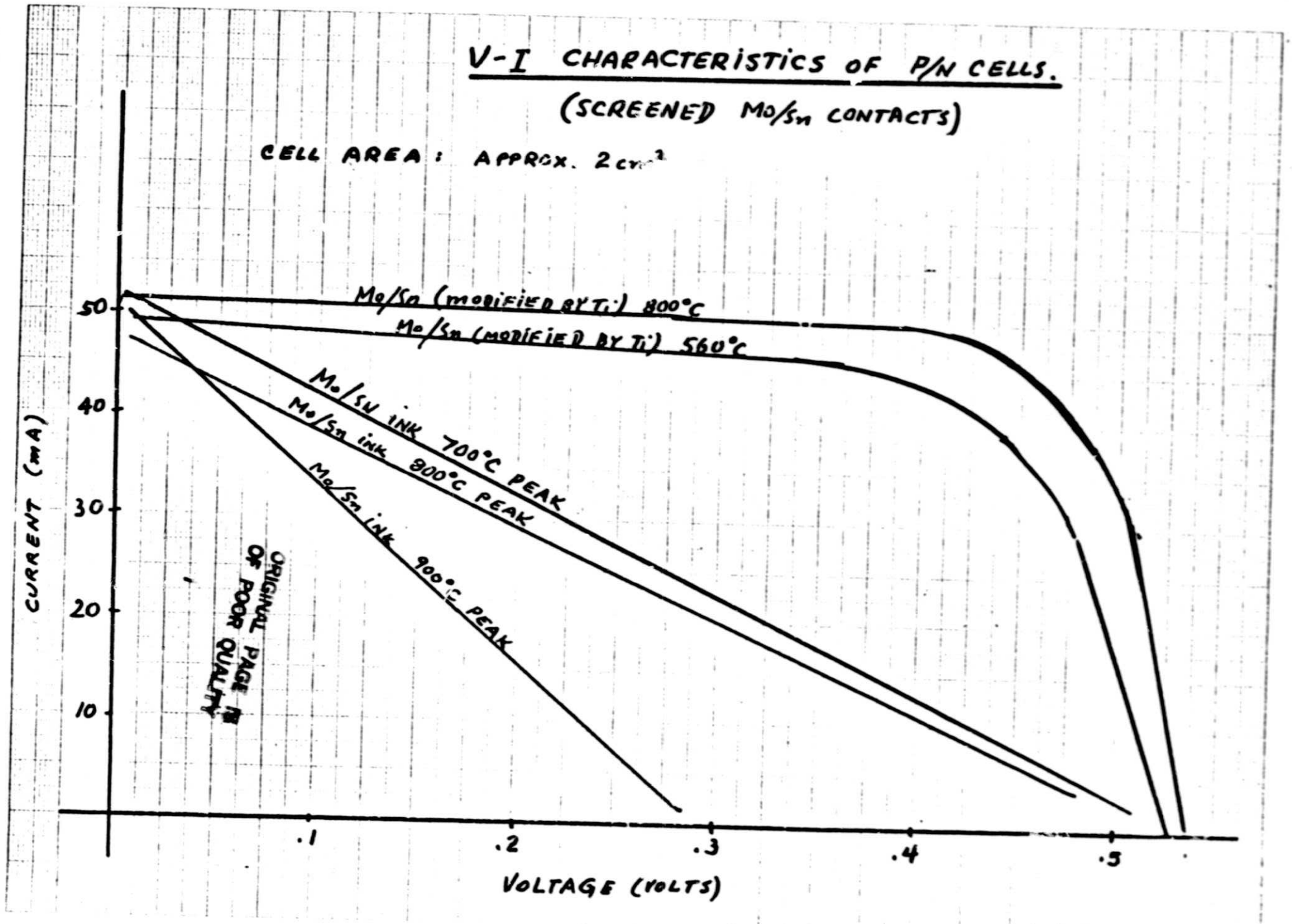

FIG. 1.

MAY 29, 1979

THE CONTACT RESISTANCE OF Mo TO 0.5 OHM/CM P-TYPE Si IS 9.4×10^{-2} OHM/CM^2.

FOR N-TYPE Si OF 0.005 OHM/CM THE CONTACT RESISTANCE IS 7.8×10^{-5} OHM/CM^2, FOR 0.01 OHM/CM 6.1×10^{-1} OHM/CM^2, FOR 0.05 OHM/CM 2.0 OHM/CM^2 AND FOR 0.5 OHM/CM 26 OHM/CM^2.

SINCE THE STARTING SILICON CRYSTAL USED IN OUR SOLAR CELL STRUCTURE IS N-TYPE OF A RESISTIVITY RANGE BETWEEN 0.3 - 0.7 OHM/CM, THE HIGH RESISTANCE OF THE Mo CONTACT COULD BE EXPLAINED BY THE REFERENCED DATA.

ANOTHER ARTICLE PUBLISHED BY R.W. BOWER AND J.W. MAYER IN APPL. PHYS. LETT., VOL.20 - No.9 (MAY 1972) PP. 359-361, IS CONCERNED WITH THE FORMATION OF METAL SILICIDES, SPECIFICALLY Pd, Ti, Cr AND Mo.

ACCORDING TO THE AUTHORS, THE GROWTH RATE OF Pd_2Si AND $TiSi_2$ VARIES LINEARLY AND AT THE SQUARE ROOT OF TIME, WHILE $CrSi_2$ AND $MoSi_2$ GROW LINEARLY WITH TIME.

THE FIRST CASE SUGGESTED DIFFUSION LIMITED RATE GROWTH MECHANISM, WHILE THE SECOND CASE CORRESPONDED TO REACTION LIMITED RATE GROWTH.

THE FORMATION DEPTH OF Pd, Ti SILICIDES IS THERE-

FORE EASIER TO CONTROL THAN THE DEPTH OF Cr AND Mo SILICIDES.

WHILE THE PRESENCE OF AN OXIDE FILM ON Si SURFACE INHIBITS THE FORMATION OF Pd, Cr AND Mo SILICIDES, IT HAS NO DETECTABLE EFFECT FOR THE Si-Ti SYSTEM AND THE $TiSi_2$ FORMS AT RELATIVELY LOW TEMPERATURE (600°C).

BASED ON THESE REFERENCES, EXPERIMENTS WERE PERFORMED TO DETERMINE THE SIGNIFICANCE AND THE EFFECT OF TITANIUM SILICIDES ON THE VALUE OF CONTACT RESISTANCE.

AS THE SOURCE OF TITANIUM, TITANIUM RESINATE WAS USED, PRODUCED BY ENGELHARD, INDUSTRIES DIV., NEWARK, N.J.

THIS ORGANO METALLIC COMPOUND CONTAINS 4.3% SOLIDS AS TITANIUM AND IS IN A SOLUTION FORM WHICH IS COMPATIBLE WITH THE SOLVENTS PRESENT IN THE INK. ONE EYEDROP OF THE RESINATE SOLUTION CORRESPONDING TO APPROX. 0.0013 G OF TITANIUM WAS ADDED TO 30 G OF INK.

THE RATIO OF ADDED TITANIUM TO THIS MIXTURE CORRESPONDED THEN TO APPROX. 1 PART OF Ti TO 15000-16000 PARTS OF MoO_3/Sn SOLID MIXTURE.

THE EXPERIMENTS OF THE INK FIRING DESCRIBED FOR THE

STANDARD Mo:Sn MIXTURE WERE DUPLICATED WITH THE INK MODIFIED BY THE TITANIUM.

THE RESULTS SHOWED A VERY DISTINCT EFFECT ON V-I CHARACTERISTICS.

THE SERIES RESISTANCE HAD A VALUE OF APPROX. 1 OHM AT A CYCLE CONSISTING OF A PRE-HEAT AT 560°C FOR 3 MINUTES, 620°C FOR 3 MINUTES AND A SOAK AT 800°C FOR 1 MINUTE.

SIMILAR VALUES OF THE SERIES RESISTANCE WERE ALSO OBTAINED BY HEATING AT 560°C FOR 9 MINUTES. (FIG. No.1)

THE BONDS ON SAMPLES FIRED AT 560°C WERE WEAKER THAN THE BONDS OBTAINED AT 800°C.

II.5 Optimizing the firing cycle for the Mo:Sn ink modified by Ti.

The objective of this task was to determine the effect of various firing cycles on the combined quality of mechanical adhesion, solderability and electrical performance of solar cells metallized with Mo:Sn ink modified by Ti.

Three firing cycles were employed for evaluation

a) 560°C - 20 minutes and quench

b) 560°C - 3 minutes, 620°C - 3 minutes, 800°C - 1 minute and quench

c) 560°C - 10 minutes, 700°C - 1 minute and quench.

All cycles were donf in a forming gas atmosphere consisting of 60% N and 40% H at a flow rate of 3L/min.

The adhesion was determined by scratch tests (x-acto) and pull tests with soldered leads. The lead attachment was also a measure of solderability.

The electrical characteristics were evaluated by the shape of V-I curves.

The quality of mechanical properties (adhesion

AND SOLDERABILITY) CONFIRMED RESULTS OF TESTS PREVIOUSLY PERFORMED WITH Mo:Sn INK WITHOUT Ti ADDED, I.E. THE BOND WAS WEAKER WITH THE FIRING CYCLE AT 560°C THAN AT CYCLES WITH 700°C AND 800°C PEAK TEMPERATURES.

THE SOLDERABILITY WAS ALSO BETTER FOR LAYERS FORMED AT HIGHER TEMPERATURES.

ELECTRICAL CHARACTERISTICS OF SOLAR CELLS METALLIZED AT THE STATED FIRING CYCLES WERE ON THE OTHER HAND SIGNIFICANTLY BETTER AT THE LOW TEMPERATURE FIRING CYCLE

IN ORDER TO ESTABLISH WHETHER THIS CHARACTERISTIC WAS A RESULT OF THE PEAK TEMPERATURE OF THE FIRING CYCLE ONLY OR OF ADDITIONAL REACTIONS TAKING PLACE DURING LOW TEMPERATURE ANNEALING PROCESS, THE CELLS METALLIZED AT HIGHER TEMPERATURES WERE HEAT TREATED AT LOW TEMPERATURE AFTERWARDS.

THE RESULT OBTAINED FROM THIS TEST ESTABLISHED THAT THE V-I CHARACTERISTICS IMPROVED TO THE QUALITY OF THE CELLS METALLIZED AT LOW TEMPERATURE ONLY. (FIG. II)

FROM THESE RESULTS OTHER SETS OF EXPERIMENTS WERE PLANNED TO DETERMINE WHETHER THIS HEAT

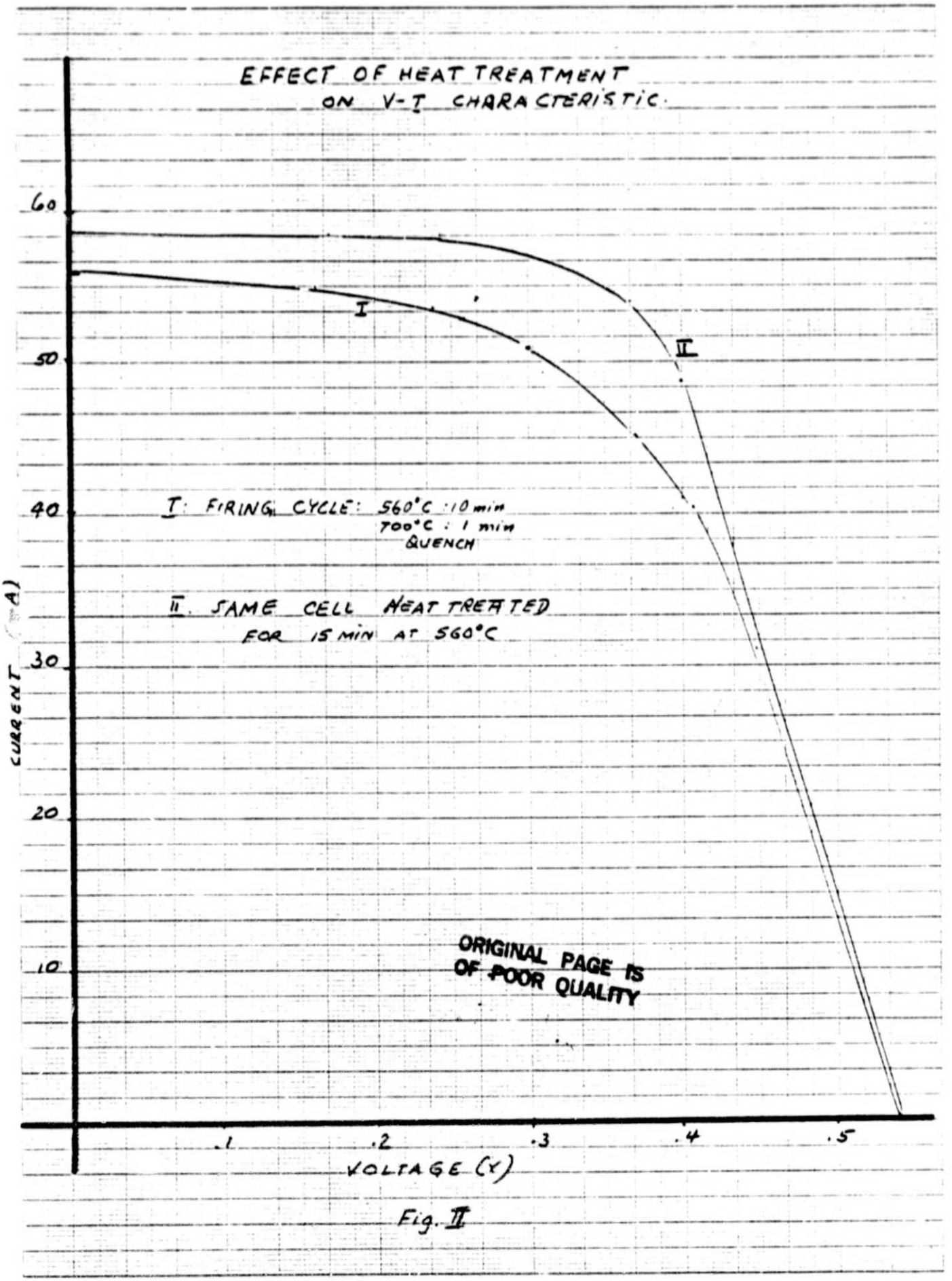

Fig. II

TREATMENT CAN BE DONE AS A PART OF THE FIRING CYCLE OR MUST BE PERFORMED AS A POST HEAT TREATMENT STEP. ALSO IT WAS NECESSARY TO DETERMINE WHETHER 550°C IS THE OPTIMUM HEAT TREATMENT TEMPERATURE OR WHETHER THE TREATMENT HAD ANOTHER PEAK.

THE RESULTS OBTAINED FROM THESE TESTS POINTED OUT THAT THE HEAT TREATMENT CAN BE INCORPORATED IN THE FIRING CYCLE AND THE OPTIMUM EFFECT LIED AT 450°C FOR 15 MINUTES. (FIG. III)

II.6 COMPARISON OF Mo:Sn CONTACT WITH NICKEL PLATED AND SILVER PLATED CONTACT.

NICKEL PLATED CELLS USED FOR THE COMPARATIVE TESTS WERE PRODUCTS OF THREE MANUFACTURERS.
THE SCREENED SILVER CELLS WERE FROM ANOTHER SOURCE.

THE MECHANICAL CONTACT OF THE Mo:Sn CELLS WAS EQUAL TO THE BEST NICKEL PLATED CONTACT AND SUPERIOR TO THE SCREENED SILVER CONTACT.
ACTUALLY THE SILVER SCREENED CONTACT WAS INFERIOR SINCE THE PATTERN AS WELL AS THE BACK METALLIZATION COULD BE PEELED OFF WITHOUT ANY EFFORT.

V-I CHARACTERISTICS OF CELLS :
LOW TEMP. METALLIZATION : I (560°C)
HIGH TEMP. + 450°C HEAT TREATMENT.

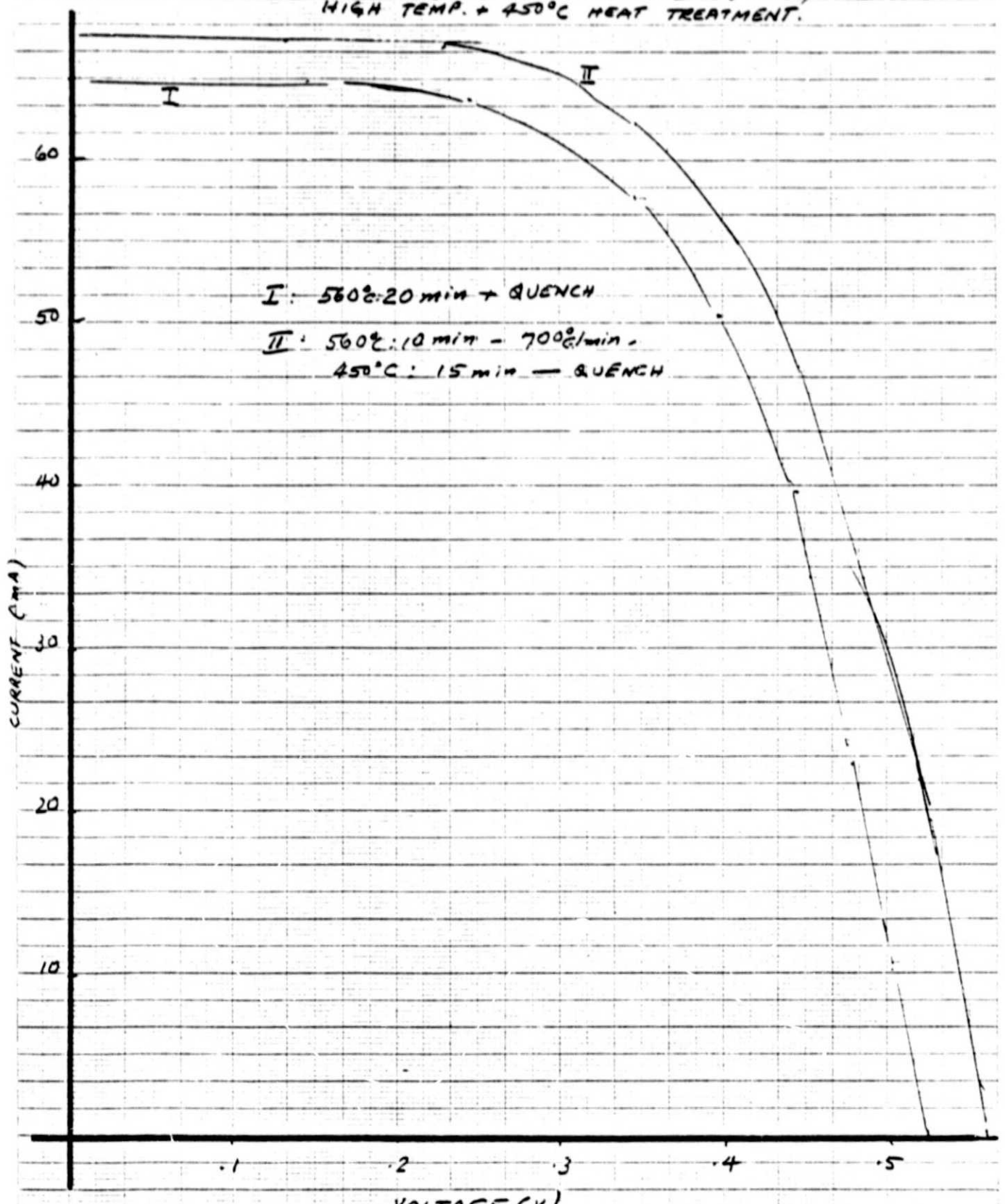

FIG. III

Electrical characteristics displayed by the V-I curves is shown in Fig. IV-2.
It was comparable with the characteristics of other metallization. Only in cases when the test samples were scribed to size, the shunt resistance and series resistance showed some degradation caused by the mechanical damage. Generally the series resistance of all cells tested was 1 Ω in average.

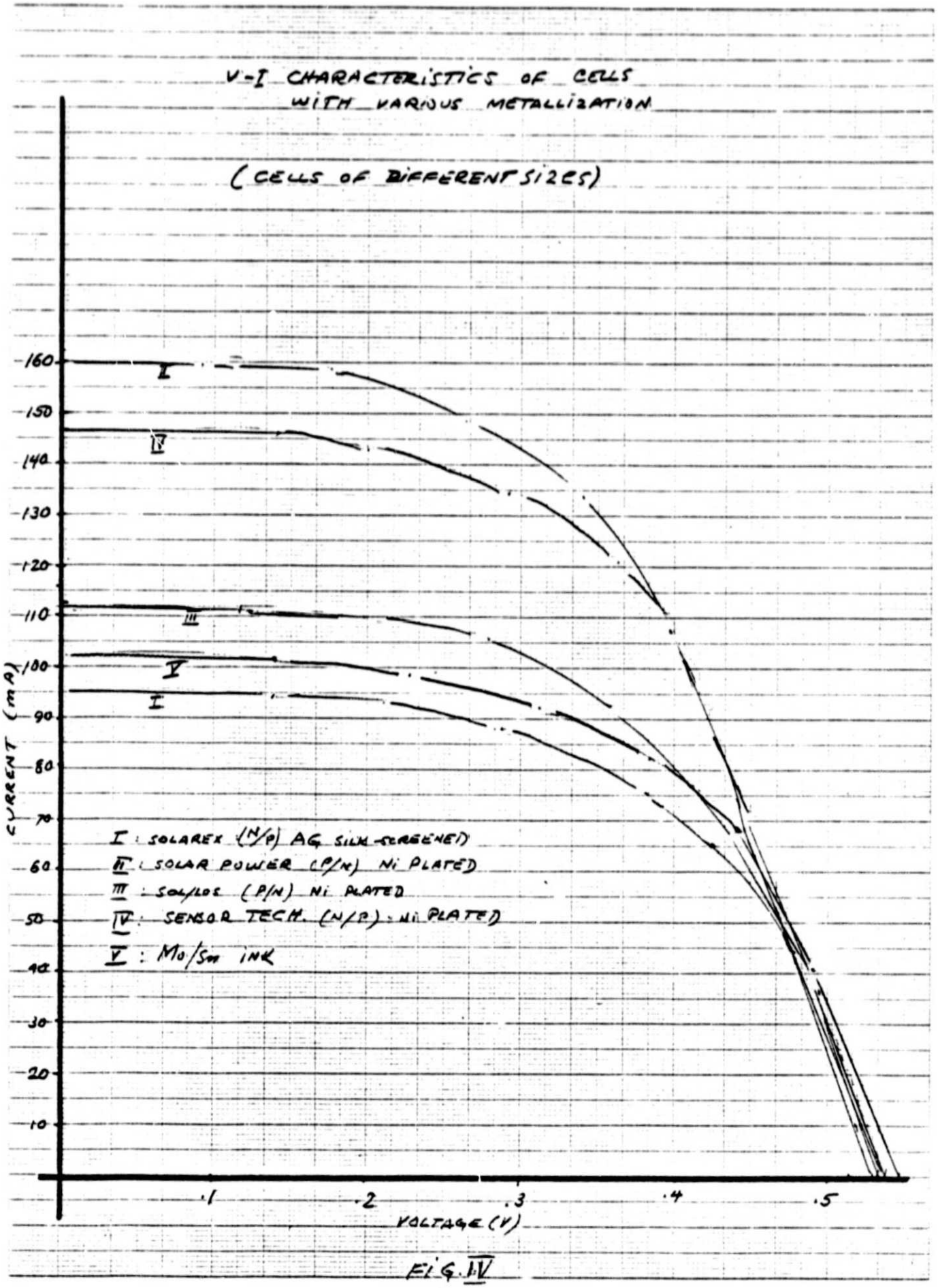

FIG. IV

III. CONCLUSION

EXPERIMENTAL WORK COMPLETED IN THE SECOND QUARTER RESULTED IN THE FOLLOWING CONCLUSIONS:

1. METALLIC COATINGS FROM MoO_3:SN SCREENABLE INK ARE OBTAINED IN A HORIZONTAL TUBE FURNACE AT $560^{\circ}C$, IN FORMING GAS ATMOSPHERE (60% N- 40% H) IN 5 MINUTES.

2. THE CONTACTS OF THE MO:SN SYSTEM TO P ON N STRUCTURED SOLAR CELLS ARE OHMIC, BUT HAVE A HIGH SERIES RESISTANCE (APPROX. 10 OHMS).

   THIS HIGH SERIES RESISTANCE IS IMPROVED BY AN ADDITION OF TITANIUM RESINATE TO THE BASIC INK COMPOSITION, WHICH CAN BE ATTRIBUTED TO A FORMATION OF TiS_2 OF HIGH CONDUCTIVITY VALUE AT THE SI METAL INTERFACE.

IV. PROJECTED WORK FOR THE NEXT QUARTER.

THE WORK TO BE PERFORMED IN THE NEX QUARTER WILL BE CONCERNED WITH THE FOLLOWING TASKS.

1. APPLICATION AND EVALUATION OF THE CONTACT APPLIED ON N ON P STRUCTURED SOLAR CELLS PROVIDED BY JPL.
2. EVALUATION OF THE NEW METALLIZATION PROCESS BY ENVIRONMENTAL TESTS.
3. FINALIZING THE PROCESS IN A WRITTEN REPORT INCLUDING PROCESS SPECIFICATIONS.

CONTRACT No: 955318

PROGRAM PLAN

FOR

A NEW METHOD OF METALLIZATION FOR SILICON SOLAR CELLS

SOL/LOS INCORPORATED
2231 S. CARMELINA AVE.
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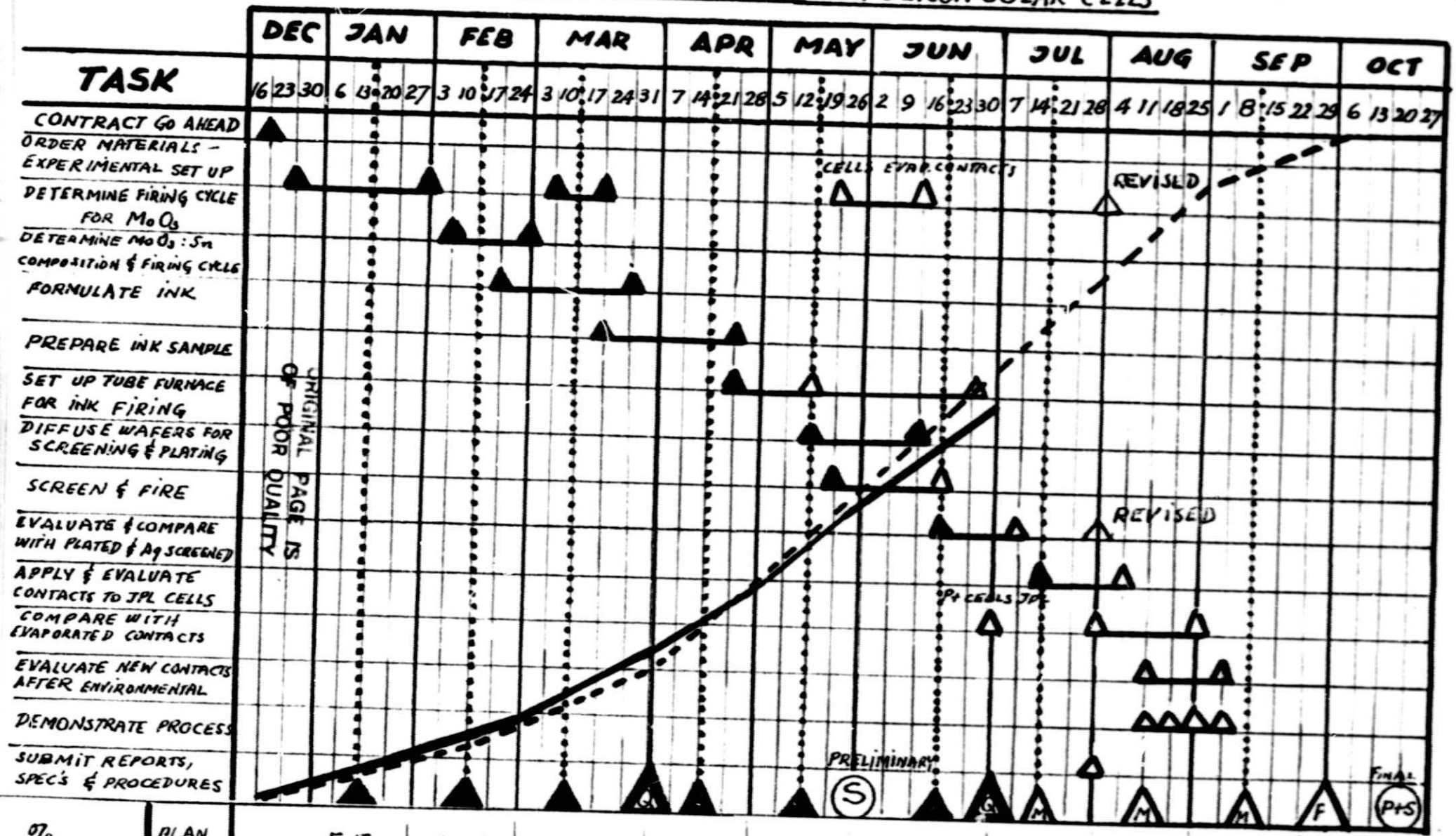
(213) 820-5181

12/27/'78



% COMPLETE													
	PLAN	5.5	14.2	23.0	37.0	50.0	66.5						
	ACTUAL	6.0	15.0	25.0	35.0	44.0	55.0						

V. NEW TECHNOLOGY

NEW PROCESSES HAVE NOT BEEN SUFFICIENTLY DEVELOPED TO BE REPORTED AS NEW TECHNOLOGY. ALL NEW DEVELOPMENTS WILL BE SPECIFIED AT COMPLETION OF THE CONTRACT.