NASA CR-159508

(NASA-CR-159508) ALTERNATE METHODS OF APPLYING DIFFUSANTS TO SILICON SOLAR CELLS Final Report, Jan. 1977 - Jan. 1978 (Owens-Illinois, Inc.) 23 p HC A02/MF A01 CSCL 10A G3/44
N79-29603
Unclas
31748

OWENS-ILLINOIS

ALTERNATE METHODS OF APPLYING DIFFUSANTS TO SILICON SOLAR CELLS

Contract NAS3-20579

OWENS-ILLINOIS, INC.

Prepared for
National Aeronautics and Space Administration
NASA Lewis Research Center

August 1979

A REPORT FROM THE TECHNICAL CENTER TOLEDO, OHIO, 43666

NASA CR-159508

ALTERNATE METHODS OF APPLYING DIFFUSANTS TO SILICON SOLAR CELLS

OWENS-ILLINOIS, INC.

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
Contract NAS 3-20579

FOREWARD

This report was prepared by Owens-Illinois, Inc., under Contract Number NAS 3-20579. The sponsoring organization was NASA Lewis Research Center and the contract monitor was John Evans.

The Owens-Illinois Principle Scientist was Marshall B. Field who at the beginning of the contract was an Owens-Illinois employee. During the term of the contract Mr. Field left Owens-Illinois and joined Pantek International Corporation. At this time, Owens-Illinois issued subcontract 99-1472 to Pantek to enable Mr. Field to continue as Principle Scientist.

This is the final report on the project and it covers the technical effort that was conducted during the period of January 1977 to January 1978.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SUMMARY

The objective of the work reported here was to investigate the use of screen printing (thick-film inks) or vapor transport from solid sources to diffuse junctions in silicon wafers. The ultimate goal was the production of n+pp+ cells in a single high temperature excursion. Properties of the doped layers were to be similar to those currently available in space-qualified cells.

Progressing from individual diffusions on n- or p-type silicon wafers, simultaneous diffusions were performed using both screen printing and vapor-phase transport. Both methods can produce good quality n+p junctions; boron and phosphorus cannot be simultaneously codiffused by vapor-phase transport. Sintered aluminum metaphosphate produced good n+ layers at 840°C but could not be reproduced on a second attempt. A low melting point phosphate glass was reliably used to produce shallow junctions of good quality when screen printed and fired at 840°C. An Al alloy thick-film ink performed well as a maskant during codiffusion and as a subsequent ohmic contact. The Al alloy composition did not form a p+ contact.

Allowing for the lack of a back surface field, the best silicon cells were near ten percent in efficiency (AMO). The results of three independent codiffusions showed a large scatter and short circuiting. It is not known how much the application of contacts contributed to this nonuniformity.

INTRODUCTION

The objective of this work was to evaluate the feasibility of new diffusion sources that could be applied uniformly and reproducibly to silicon solar cell wafers. Two methods of applying the dopant materials were considered: screen printing of thick-film paste materials or vapor-phase transport from solid sources. Both n-and p-type sources were investigated. Specific device parameters were defined for this work:

On 10 $\Omega \cdot$cm p-type silicon wafers doped layers with:
$N_d = 10^{19}$-10^{20} donors concentration level
$\rho_{sh} = 100$-$300\ \Omega$/square sheet resistivity
$X_j = 0.1$ to $0.5\ \mu m$ junction depth
were to be produced.

On 0.5 $\Omega \cdot$cm n-type silicon wafers doped layers with:
$N_d = 10^{19}$-10^{20} acceptors concentration level
$\rho_{sh} = 10$-$30\ \Omega$/square sheet resistivity
$X_j = 0.5\ \mu m$ junction depth
were sought.

After the materials and methods were optimized to produce the junctions individually as above, it was desired to investigate codiffusion with a single temperature-time cycle. If successful, a series of three separate experiments with the most-promising method and materials was to be made to evaluate uniformity and reproducibility. Implied in the tasks undertaken was the completion of the solar cell, i.e., the application of ohmic contacts for testing. As will be explained below, this seemingly minor task caused a great deal of confusion in interpretation of results and delays in progress.

The requirements above were determined by the objective of matching or exceeding the performance of space-qualified silicon solar cells which are produced using conventional gaseous diffusion sources. Gaseous diffusion is generally performed in such a way as to produce one junction at a time; that is, an n+pp+ cell would necessitate two gaseous diffusions. A single codiffusion would be much preferable on the bases of cost, convenience and throughput. In the context of this goal the work here must be considered preliminary. Many materials and combinations were to be examined; the methods were to be investigated for single diffusions and then extended to codiffusion. No more than a beginning could be made with the time and resource constraints of this Contract and the report should be read with this in mind.

EXPERIMENTAL WORK

Choice of Materials

Screen printing: The choice of materials for screen printing on silicon and acting as n- or p-type dopants was based on the following criteria:

1. Dopant type
2. Melting point
3. Compatibility with ink technology
4. Appearance of polished silicon after firing
5. Resistivity/uniformity
6. Junction appearance/performance

Several n-type and p-type materials were selected for screen printing on silicon wafers. The four types of materials were (see Appendix A for a description of these materials:

(1) Low-melting phosphate glasses – 347, 166
(2) Low-melting borate glasses – 621, 013, 619
(3) Crystalline (nonglassy) materials with substantial phosphorus content obtained from MOD process - 166, 585
Boron content - 621, 013, 619
(4) Aluminum and aluminum alloy compositions - 6150 (Lot T-70126), Lot N-70217

The low-melting phosphate and borate glasses were crushed and ball milled for 64 hours in isopropyl alcohol. The dried material of the three borate glasses were analyzed for B_2O_3. Approximately 18% of the original B_2O_3 was lost. A portion of this was due to melting of the glass, but most of it was probably leached from the glass by the alcohol grinding medium. The ground glass of the three low-melting borate glasses was remelted to determine if the 18% loss of the available B_2O_3 significantly affected their flow properties. All three glasses flowed readily at low temperatures and were considered acceptable for evaluation tests.

Each of the n-type and p-type doping materials were mixed with a vehicle and screen printed on opposite type silicon wafers. These wafers were fired at 875°C for 20 minutes in air. The surface condition of each wafer was observed and the resulting sheet resistivities were measured.

These visual observations and data are in Table I.

The sheet resistivities measured on p-type silicon slices doped with the phosphate materials 347 glass, 166 glass, and 166 MOD were all in the 80-150 Ω/sq. range which is close to the desired 100-300 Ω/sq. The sheet resistivities obtained from 585 MOD were above the maximum 300 Ω/sq. The p-n junctions in the Si doped with 166 glass and 166 MOD were shallow ($< 0.5\ \mu$) and could not be readily observed with angle-lapping.

The sheet resistivities measured on n-type silicon slices doped with 013 glass, 013 MOD, 619 glass, and 619 MOD were all above the desired 10-30 Ω/sq. However, the sheet resistivities obtained from these materials were close to the 200-300 Ω/sq. expected from this temperature and time of deposition. A p-n junction measurement was attempted on the silicon doped with 013 MOD. The junction was very shallow and was not observed by the angle lapping technique. Sheet resistivity data could not be obtained on silicon slices doped with 621 glass and 621 MOD. Apparently these two materials did not dope the silicon sufficiently to create a p-n junction.

The most promising n-type dopants for use in screen printing are 166 glass and 166 MOD. The most promising p-type dopants are 013 glass and 013 MOD and possibly 619 glass and 619 MOD. Materials 347 glass, 585 MOD, 621 glass, and 621 MOD appear unacceptable as dopants.

In evaluating aluminum and aluminum alloy materials the appearance of the polished silicon after firing is not important as these materials would not be removed. They would function as electrical contacts as well as diffusion sources. It is important, however, that the materials adhere well to the silicon and fire on with a smooth surface. Both the Al and Al alloy pastes printed reasonably well and adhered to the silicon. The difficulty with pure Al is the tendency to form spheres upon cooling. This leaves a pitted, nonuniform surface which is unacceptable. The junction depth with Al and Al alloy was not measured: the materials diffuse very rapidly and apparently at nonuniform rates.

Junction depths were obtained for the other n- and p-type dopants using a standard angle-lap, etch and stain technique. In the temperature region of interest the junction depths are too small to be measured. In this case the wafers were first diffused at a low temperature (875-925°C) in N_2 and then given a standard 'drive' at higher temperatures in O_2. Table II contains typical data of this type for wafers whose surface condition and sheet resistivity is given in Table I. Notice the scatter in the measurements. It was later determined that an error in etch composition had been made. As a consequence the earlier data were suspect. Upon re-examining the materials it was found that the 585 composition was by far the best in terms of resistivity and junction properties. Table III exhibits this information. Each line represents a separate experiment and measurement. All of the samples showed very uniform junctions as a function of distance from the outside.

Vapor-phase deposition: Owens-Illinois markets a glass-ceramic material to the semiconductor industry under the trade name BORON™. These solid wafers are rugged, reliable, reproducible sources of boron at temperatures 800-1300°C. A companion p-type source was aluminum metaphosphate (AMP) which was pressed and sintered to a high density. AMP is a very satisfactory source of phosphorus as long as the temperature is not too high. It also has a tendency to shatter at moderate cooling rates. The data summarized in Table IV illustrate that the vapor sources yield reasonably reproducible, uniform junctions.

Method of Diffusion: Codiffusion

After qualifying materials individually for either contact or vapor-phase deposition the choice of method hinged on compatibility for codiffusion. The question of compatibility involved basic physical properties such as diffusion rate as well as task-related variables of distribution of vapor, compensation, etc.

An examination of Table IV will show that B and P have much different diffusion rates in silicon. The requirements of sheet resistance and junction depth are such that it is not possible to codiffuse B and P. Phosphorus penetrates silicon much more rapidly than boron at any practical temperature. Non-p cells are thus not achievable within the constraints of 0.1 to 0.5 μm junction depth for both the n and p+ layers. Since B is the slower of the two, it is not a good choice for the p dopant. If the requirement of a shallow back surface were relaxed the pair might make reasonable pnn^+ cells.

For codiffusion on npp^+ cells we are left with phosphorus for the front surface and Al or Al alloy for the back. Since these materials are both most easily deposited by screen-printing it was obvious to consider screen printing front and back first. The proposed procedure was print, dry one surface and then print, dry, cofire both layers in a continuous-belt furnace. Several difficulties arose in this procedure: the paste printed and dried first had to have excellent green strength to withstand the pressure and handling of the second printing. In conventional thick-film continuous-belt furnaces the parts are fired while laying directly on the high temperature alloy belt. If a similar procedure was tried with the double-printed silicon it is conceivable that the alloy belt would interfere with the sintering of the bottom layer or otherwise contaminate it. Because of the gas flow pattern it is probable that there would be a slight difference of atmosphere between top and bottom. It was found that placing the wafers directly on the belt, Al alloy film down, was not a good idea. The Nichrome belt conducted heat away from the wafer wherever the two were in contact. After cooling a definite pattern of belt marks was noticed in the front surface. Small holders of Al_2O_3 ceramic were fabricated. These fixtures held the wafer 0.025" above the belt surface at three contact points near the edge. This seemed to eliminate the problem.

A number of samples were codiffused using two methods in the thick-film furnace. Both sets had Al alloy back contacts. The wafers with screen-printed 585 MOD front contacts were placed on the Al_2O_3 fixtures as explained above. The wafers to be vapor-coated were placed in silica fixtures between sintered AMP wafers as shown schematically in Figure 1. Vapor-phase diffusion was performed in both a thick-film, endless-belt furnace and a conventional silica tube diffusion furnace. A nitrogen flow of 0.5 to 1.0 liter/minute was maintained in all three cases.

The results of these experiments were somewhat clouded by our difficulty in making ohmic contacts to the cells (see below) but in general the following conclusions were reached:

1. Al alloy films perform the dual function of p^+ contacts and diffusion masks very well.
2. Both printed 585 MOD and vapor-deposited (AMP) sources can be used to produce np junctions on silicon.

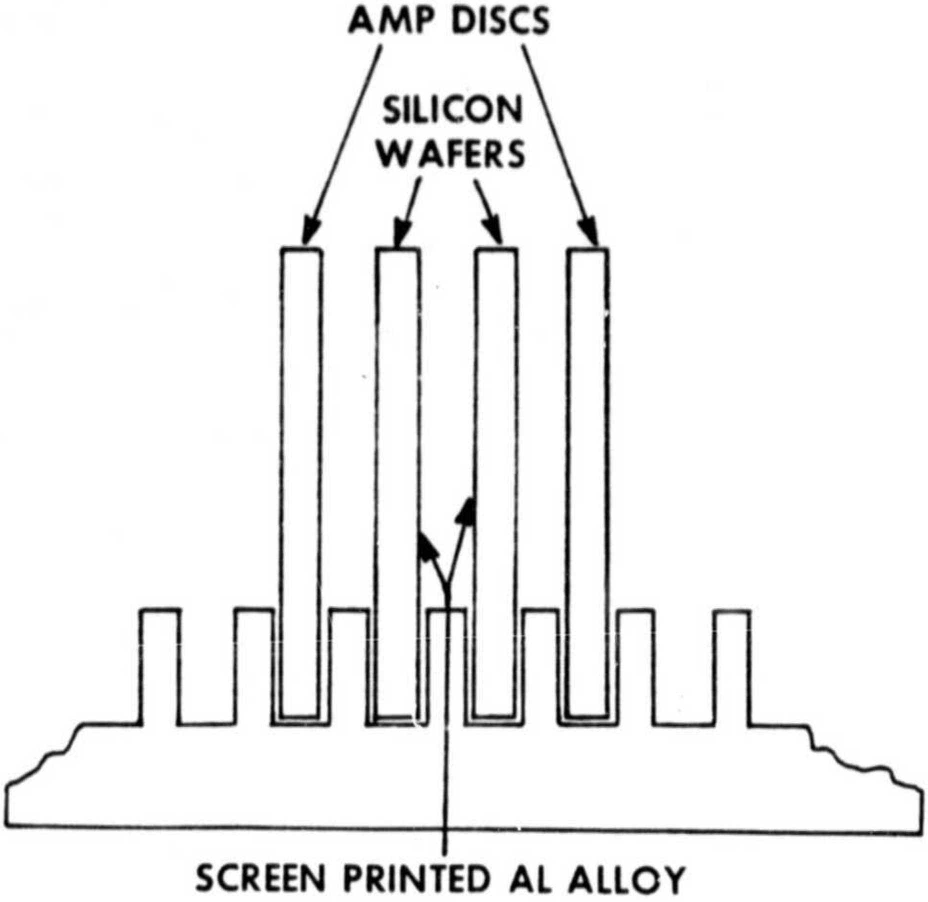


FIGURE 1. Vapor-phase Deposition Fixture and Sample/Source Arrangement

3. Vapor-phase depositions in tube furnaces provide more uniform junctions than those in the thick-film furnace.

The exact procedure used to form junctions and clean up the cells is shown in Table V.

Cell Formation

This contract was aimed at evaluating novel diffusion sources. A part of any evaluation is measurement of photovoltaic operation. This implys that the cells have good ohmic metal contacts. It was this point that proved highly difficult for Owens-Illinois, Inc., to produce. After a long, difficult period of attempting to produce satisfactory contacts by both thick-film and vacuum deposition, an outside contracter was hired to deposit Ti/Ag contacts on three-inch diameter wafers diffused at Owens-Illinois.

Midway through the contract Dr. Evans of NASA-Lewis kindly contacted and measured four wafers for us. Figures 2 through 5 exhibit typical results.

For the final task, an experiment to learn how reproducible the best technique was, screen printing and belt furnace firing was chosen. The materials used were Owens-Illinois glass number 585 on the front, Al alloy on the rear and fired for 45 minutes at 840°C in an atmosphere of nitrogen. Table VI contains the average sheet resistance and V_{OC} and I_{sc} measured in a rather crude simulator. The substrates were nominal 10 Ω.cm p-type silicon.

DISCUSSION

Both methods of codiffusion, vapor phase and screen printing, are feasible for use in the production of silicon solar cells. The vapor-phase transport using BORON+™ sources or aluminum metaphosphate always yields more reproducible sheet resistivities and presumable, more uniform junctions. At the last moment before choosing a technique for codiffusion it was attempted to duplicate a few of the early experiments using AMP and a tube furnace. It was not possible to reproduce the earlier results. Whether this was due to aging of the AMP disc or contamination or whatever, the process was lost.

Screen printing is a convenient method of introducing a dopant onto silicon wafers. It is fast and quite reproducible. The variation in average sheet resistance noted in Table VI is thought to come from the fact that in an eight-foot furnace it is necessary to stop the belt to obtain times on the order of 45 minutes at temperature. This timing is critical and a few seconds one way or the other would change the temperature the wafers were subjected to since the furnace has a temperature gradient along its length. A longer furnace would alleviate this situation.

The materials 585 and Al alloy are inexpensive and can be manufactured reproducibly. Note, though, that the Al alloy did not seem to produce a back surface field at 840°C. This is a consequence of the high frit content of the paste which contains elements that are apparently compensating for the Al. Unfortunately, reducing the frit content leads to a loss of adhesion. It would be extremely interesting to investigate changing the frit content and type and measure the change in performance. An alternative would be to use the more common Al·Ag mixtures as a back contact. These materials are known to produce a BSF and also would serve as a block for the codiffusion of P.

CONCLUSIONS

The methods vapor-phase deposition and thick-film screening can both be used to diffuse silicon and form shallow p·n junctions. The properties of the resultant photovoltaic cell do not seem to be affected by the choice of method.

In vapor-phase deposition BORON^{+TM} solid state sources work very well. The failure to reproduce the early results with aluminum metaphosphate are puzzling and should be thoroughly investigated in order to determine the reason. As pointed out above, simultaneous diffusion of both boron and phosphorus is not feasible: the diffusion coefficients differ too widely. If a second operation is necessary, for example, the vapor deposition of aluminum, screening of aluminum or other dopant, etc., vapor deposition becomes less attractive as a process. It is now questionable whether the advantage of a single high-temperature firing is worth the possible compromise involved in a single time and temperature for both the p·n junction and back surface field. In fact, it is not known if both are achievable with satisfactory results. These remarks should be tempered with the reminder that we are here referring only to the shallow-junction silicon cell for space. Relaxing the requirement of 0.25 μm deep junction makes a difference in how one can proceed. In short, vapor-phase deposition with solid sources can be used very satisfactorily for single diffusions of silicon wafers.

Screen printing silicon cells with a thick-film paste and firing in an endless-belt furnace for simultaneous diffusion and back surface field formation is quite feasible. One material, Owens-Illinois glass 585 or 585 MOD, can be used as a phosphorus source in the area of 840°C. Junctions made with this material are uniform and of good quality. Al alloy paste acts as an effective electrical contact and maskant when cofired with 585. It does not appear to simultaneously form a back-surface field. This is probably due to the high frit content of the paste. Unfortunately, reducing the frit content leads to a loss of adhesion. Mixtures of Al, Ag and frit spall off upon cooling from the high temperature. This is not an insoluble problem and should be investigated in more detail. The thermal expansion coefficient of the paste and resultant film can be controlled by choosing a correct glass frit and solids content.

The results reported above for five supposedly identical lots are not a good representation of the potential of the thick-film method. The short length of the furnace made stopping the belt necessary to achieve a suitable time at temperature. This necessitated timing and estimating position in the hot zone and it is unlikely that this could be done precisely. Endless-belt furnaces are available which can be profiled to accurately treat the samples for the requisite amount of time. This should be done before a final evaluation is completed.

APPENDIX A

SCREEN PRINTING MATERIALS

Owens-Illinois considers the actual chemical composition of these materials to be "proprietary data," as defined in the Rights in Data (March 1976) clause, since these materials were developed at private expense.

The materials are available for purchase from Owens-Illinois and information can be obtained by addressing inquiries to:

T. W. Brock 2-NTC
Owens-Illinois, Inc.
PO Box 1035
Toledo, Ohio 43666

As "form, fit and function" data, we supply the following information:

Glasses 347 and 166 are high P_2O_5 glasses that also contain Al_2O_3 and CaO as major ingredients. Glasses 621, 013 and 169 are high B_2O_3 glasses that also contain Al_2O_3, SiO_2 and MgO as major ingredients.

Crystalline material 585 is a high P_2O_5 material with Al_2O_3 as the other major ingredient.

These materials are made from either the standard raw materials common to the glass industry or from metal-organic-derived (MOD) materials which assure high purity and can affect melt characteristics.

Aluminum composition (Lot N-70217) is mixture of 97 wt.% Al and 3 wt.% G-3196 glass frit.

Aluminum alloy composition 6150 (Lot T-70126) is a mixture of 75 wt.% of a proprietary Al alloy and 25 wt.% XS-2371 glass frit.

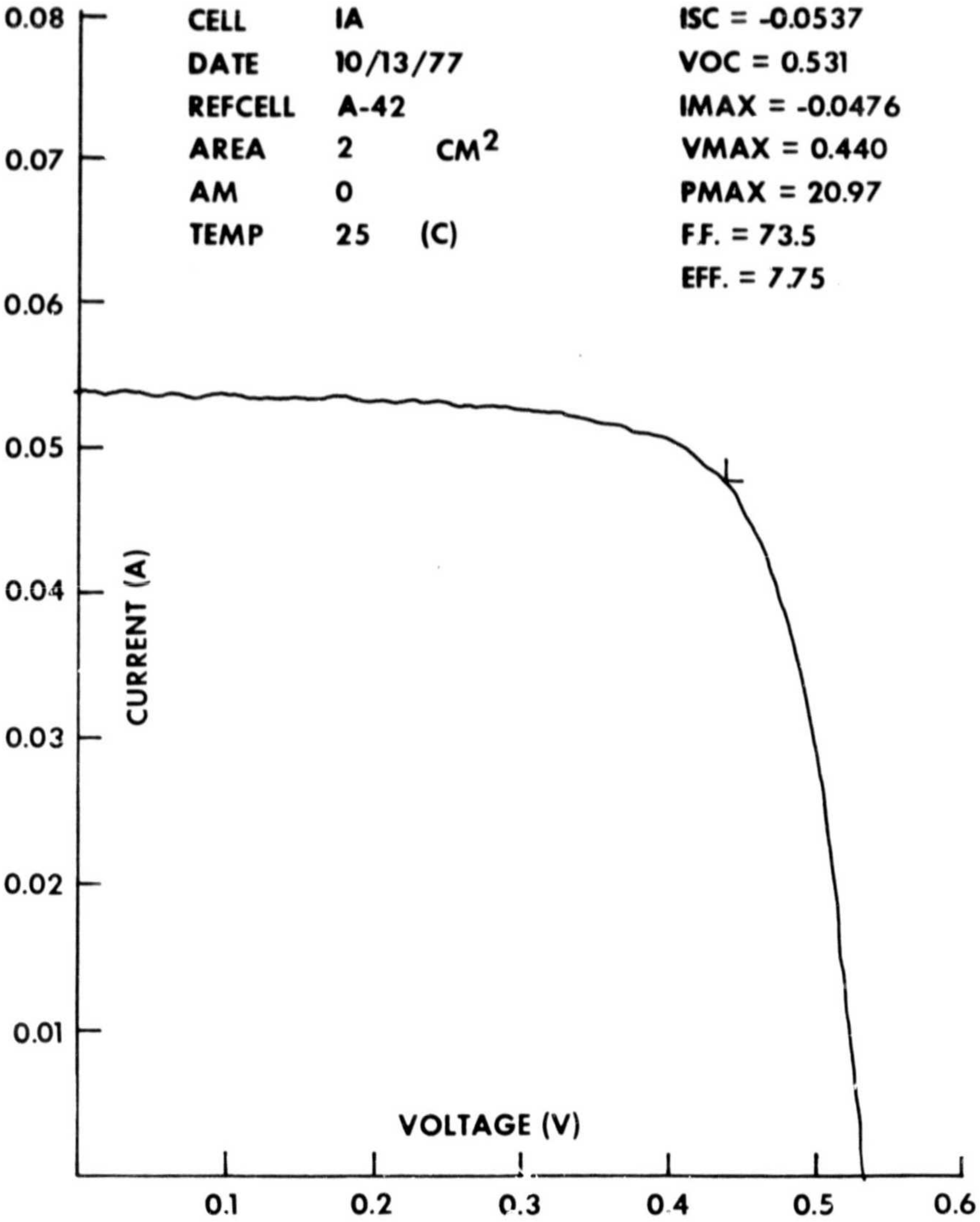


FIGURE 2. SCREEN PRINTED CODIFFUSION. BORON (013) ON FRONT. AL ALLOY ON REAR.

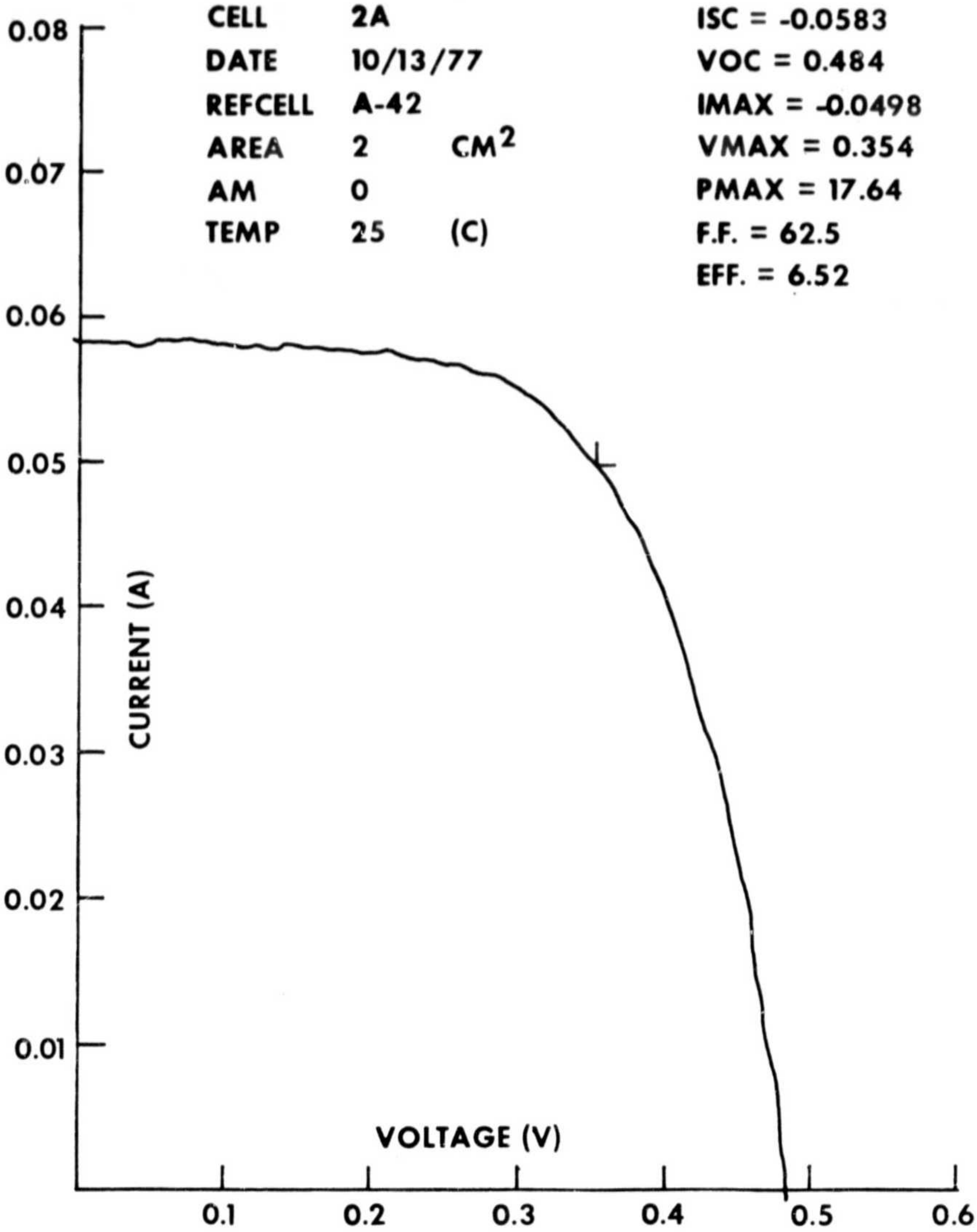


FIGURE 3. SCREEN PRINTED CELL. PHOSPHORUS ON FRONT, BORON ON BACK.

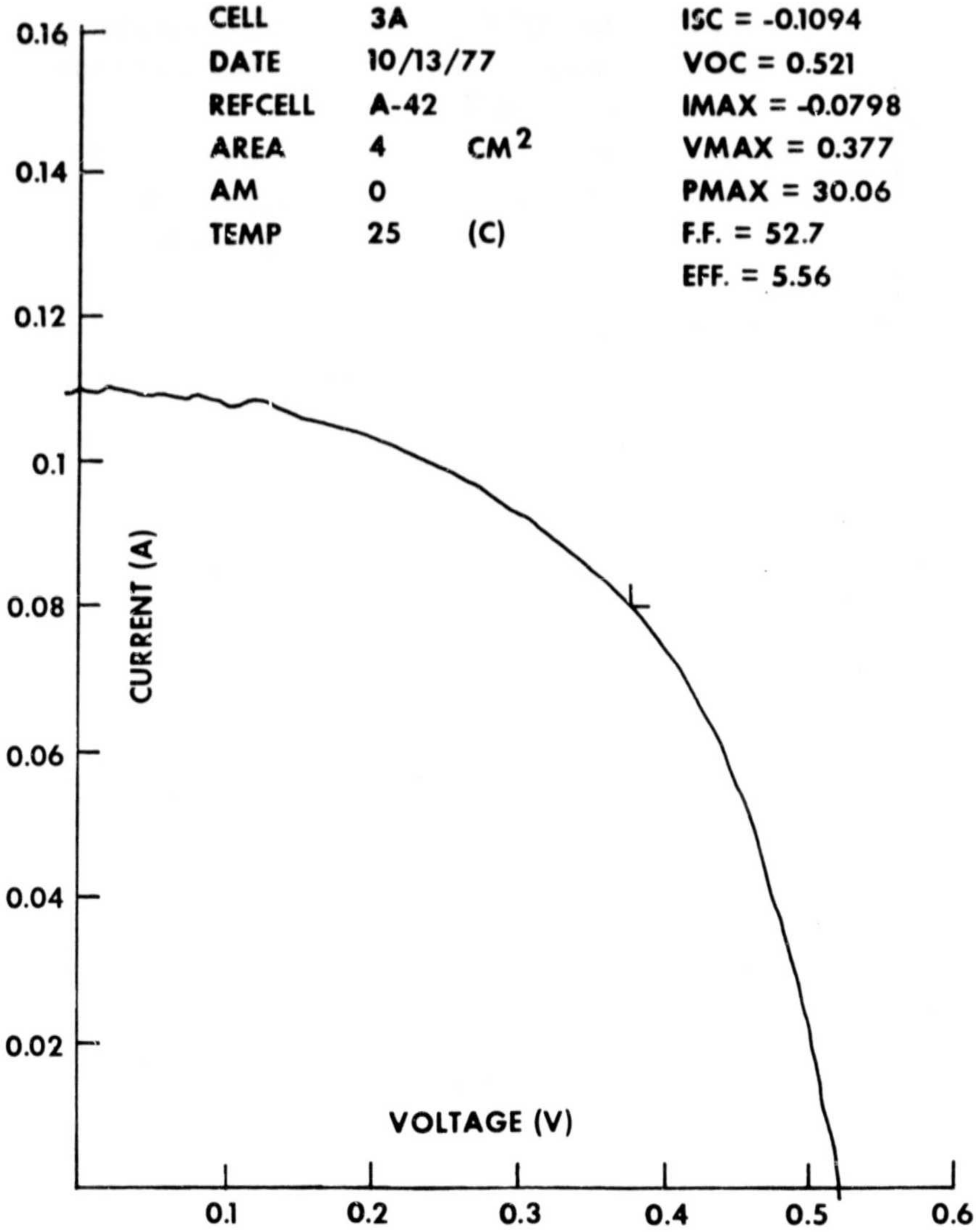
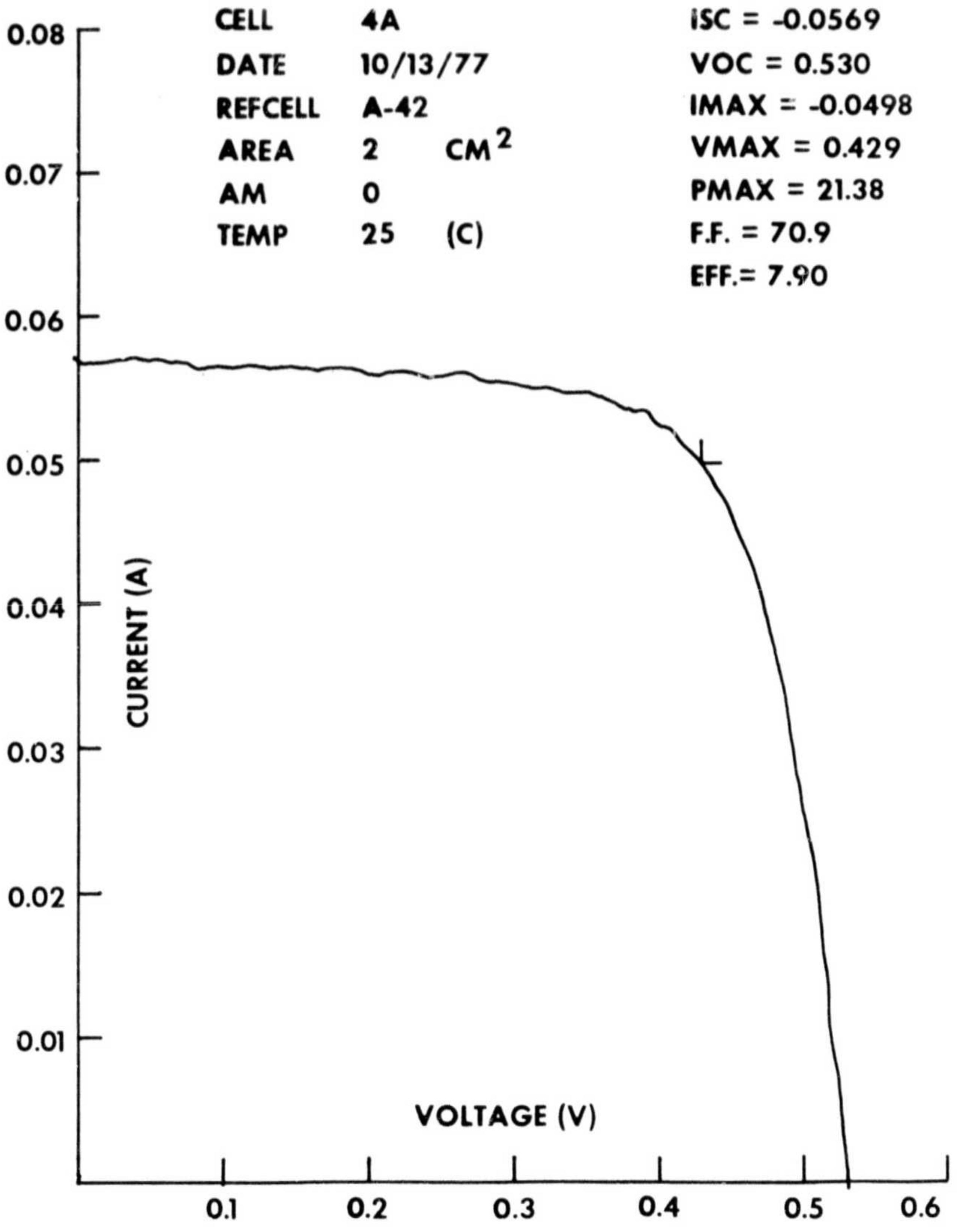


FIGURE 4. SCREEN PRINTED CELL. PHOSPHORUS ON FRONT, BORON BACK.



CELL 4A
DATE 10/13/77
REFCELL A-42
AREA 2 CM^2
AM 0
TEMP 25 (C)

ISC = -0.0569
VOC = 0.530
IMAX = -0.0498
VMAX = 0.429
PMAX = 21.38
F.F. = 70.9
EFF.= 7.90

FIGURE 5. VAPOR DEPOSITED CELL. AMPON FRONT, BORON$^+$ ON BACK.

TABLE I. Visual Observations on Doped Wafers

Low-melting Phosphate Materials	Printed Material after 875°C for 20 minutes in air	Silicon surface condition	ρ, Ω/square near solid solubility	ρ/σ,%	ρ/σ,%
347 ground glass	flaked off	pitting/crazing	80-150	102/9	75/16
166 ground glass	flaked off	slight pitting/crazing		73/5	72/9
166 MOD batch	good	good		144/6	153/8
585 MOD batch	good	good		473/7	669/9
Low-melting Borate Materials					
621 ground glass	very good	good	200-300	-	-
621 MOD batch	good	good		-	-
013 ground glass	good	good/slight staining		391/5	347/10
013 MOD batch	very good	good/slight staining		256/10	268/7
619 ground glass	blistering	pitting/crazing		293/4	326/5
619 MOD batch	good	good		256/5	561/10

TABLE II. Junction Depth and Variation after Diffusion at 875°C in N_2 for 20 Minutes and 'Driven' in O_2.

Composition	Temp. -	Time	Junction Depth	Spread
013 MOD	1150°C	30 mins.	2.57 μm	0.25 μm
			2.0	0.25
013 Glass	1150°C	30 mins.	2.63	0.20
			3.21	0.10
			1.29	0.25
619 Glass	1150°C	30 mins.	1.4	0.3
			2.36	0.25
			3.0	0.4
619 MOD	1150°C	30 mins.	1.71	0.3
			1.50	0.3
			1.29	-
			0.86	0.3
166 Glass	1150°C	30 mins.	2.14	0.25
			1.93	0.25
166 MOD	1150°C	30 mins.	2.14	0.25
			2.36	0.40

TABLE III. Resistivity and Junction Depth of 585 MOD Material as a Function of Temperature and Time. Nitrogen Atm.

Temp. (°C)	Time (mins.)	Ps (Ω/sq.)	Junction Depth (μm)
840	45	121	
	45	173	
	45	78	
	45	148	
875	60	-	0.86
	120	-	1.29
	120	-	0.86
	120	-	0.64
900	60	-	0.64
	60	-	0.43
	60	-	0.64
	60	33	0.86
	20	40	1.82
	20	73	0.54
	20	33	0.54
	20	33	0.86

TABLE IV. Vapor-Phase Deposition Sources.

Source	Temp.	Time	Ps(Ω/sq.)	Junction Depth (µm)
AMP	900°C	60 mins.	137	1.1
AMP	900	60	138	1.9
AMP	900 &	60		
	925	60	17	1.2
AMP	900	60	18.5	0.71
	925	60		
AMP	900	60	138	0.7
AMP	900	60	91	0.86
AMP	900	20	523	-
BORON+™	975 &	20		1.93
	1150	30		
	900 &	60		2.14
	1150	30		
	900 &	60		2.36
	1150	30		
	925	60	59.06	0.64

TABLE V. Experimental Procedure.

1. Wash wafers in 3% HF acid, deionized H_2O and alcohol.
2. Screen print back Al alloy contact. Full coverage to within 0.050" of edge.
3. Dry at 110° for 15 minutes.
4. Reprint using 585 MOD, dry, fire if thick-film diffusant, diffuse if AMP source.
5. Remove P_2O_5 glass from top surface: 30% HF acid for 30 seconds. Rinse in H_2O.
6. Contact front surface and back, if desired.

TABLE VI. Average Sheet Resistance and V_{oc} and I_{sc} Measurements of Large Round Solar Cells.

		I_{sc}	V_{oc}	Temp.(°C)	Sheet Resistance
No. 1	1	540	.575	28	78 Ω/square
	2	520	.559	28	
	3	520	.556	28	
	4	510	.540	28	
	5	500	.531	29	
No. 2	1	100	.062	28	174 Ω/square
	2	200	.203	25	
	3	420	.552	28	
	4	410	.519	29	
	5	465	.549	28	
	6	440	.548	28	
	7	480	.547	27.6	
	8	320	.434	29	
	9	490	.530	29	
	10	420	.500	29	
No. 3	1	90	.341	29	113 Ω/square
	2	40	.054	29	
	3	100	.071	28	
	4	35	.017	29	
	5	420	.543	29	
	6	380	.550	29	
	7	440	.549	28.4	
	8	340	.479	28	
	9	340	.499	29	
No. 4	1	480	.500	28.6	120 Ω/square
	2	440	.531	29	
	3	40	.024	29	
	4	60	.036	29	
	5	220	.221	29	
	6	100	.061	28.6	
	7	40	.023	28	
	8	50	.170	28	
(Broke)	9	140	.513	26	
No. 6	1	140	.538	26	149 Ω/square
(Broke)	2	160 Lg.	.515	25	
(Broke)	3	90 Sm.	.521	25	