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MOD SILVER METALLIZATION FOR PHOTOVOLTAICS

Purdue Research Foundation

Principal Investigators:

G.M. Vest (317/494-4110)

R.W. Vest (317/494-7009)

JPL Flat Plate Solar Array Project

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"The JPL Flat Plate 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 flat plate solar arrays. This work was performed by agreement between NASA and DOE."

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1. INTRODUCTION AND OBJECTIVE

Photovoltaic cells require back side metallization and a collector grid system on the front surface. Both front and back surface metallizations should have good adhesion, low contact resistance, low sheet resistance, long term stability, and their deposition methods should not degrade the n-p junction. In addition, the metallization for the collector grid should be capable of producing small grid spacings and grid widths. For the terrestrial flat-plate solar array project, low cost of the metallization is also a very important requirement. One of the dominant systems in use today is screen printed thick film silver conductors. When such conductors are used in hybrid microelectronics they are typically fired at temperatures from 650-850°C for 10-15 minutes, but for solar cells they must be rapidly fired in order to avoid degradation of the junction. This rapid firing compared to the conditions for which the inks were developed often leads to poor adhesion, and porous silver films are always the result. In addition, typical frit bonded thick film silver conductors may present a special problem because the frit dissolves the SiO_2 film on the photovoltaics and sometimes produces a reaction layer down to the junction.

Metallo-organic (MO) compounds are ones in which a metal atom is linked to a long chain carbon ligand through a hetero atom such as O, S, N, P or As. In order that the products of decomposition contain only CO_2, H_2O and perhaps nitrogen compounds, Purdue's Turner Laboratory pioneered the use of a set of MO compounds for ink fabrication where the linking hetero atom was oxygen. Films produced by the metallo-organic decomposition (MOD) process have a number of advantages compared to conventional thick films. The approach followed at Purdue will lead to generic inks because all of the compounds used are either purchased as pure materials or synthesized from commonly available reagents. Even if conventional inks did not contain proprietary additives they still could not be duplicated in the user's laboratory because film properties are dependent on characteristics of the particulates (average particle size, particle size distribution, particle shape, etc.) in addition to their chemical composition. All chemical compounds are in solution in inks for the MOD process, which means the mixing of the constituents is achieved on an atomic scale, and films produced after decomposition of the organic compounds reflect this uniformity. The uniformity of conventional thick films is a strong function of the degree of blending of the particulates in the organic screening agents, and there is always an inherent nonuniformity due to the finite particle sizes of the different constituents in the inks. Films produced by the MOD process are inherently thinner than films produced by conventional thick film technology because the volume change from wet to fired MOD film is typically a factor of 50 compared to a factor of 3 for conventional thick films. This can be a disadvantage if very high conductance is required, but can partially be overcome by deposition of thicker films or multi-layer films.

MOD silver films have the potential for eliminating most of the present problems with silver conductors. The MOD silver films can be produced at much lower firing temperatures (e.g. 300°C), which should reduce chemical interaction effects as well as deterimental thermal effects on the junction. The specific technological objectives of the current program are to identify and characterize suitable MO compounds, develop generic synthesis procedures for the MO compounds, develop generic fabrication procedures for screen printable MOD silver inks, and optimize processing conditions to produce grid patterns on photovoltaic cells. The metallizations will be evaluated as to their appearance, line definition, adhesion, sheet resistance and microstructure. The metallized cells will be evaluated at JPL as to their performance as solar cells, although initial photovoltaic evaluation will be done at Purdue. Once a suitable MOD silver ink or inks have been developed a small weight percent (<5 w/o) of a suitable platinum MO compound will be added to give the ink good solder leach resistance which silver films alone do not possess. The platinum addition will also allow for quantitative adhesion data to be collected. Other additives in the form of MO compounds may also be used should a permanent binding agent be deemed necessary. Once a final ink composition is selected, the metallizations adhesion and sheet resistance will be evaluated after thermal aging. Another objective of the program is to develop a model which describes the adhesion between the fired silver film and the silicon surface.

2. SUMMARY

A firing sequence with approximately the same maximum temperature, but a three times longer firing cycle than standard firing sequence No. 1, appears to eliminate the film cracking and adhesion problems previously occurring in multi-layer films. More work will be done in this area once the ink/film chemistry has been optimized. On-site photovoltaic testing is proving to be very useful in helping evaluate fired films of different composition or which have undergone different processing. It will still be necessary to send fired films to JPL for complete photovoltaic evaluation once suitable progress has been made. The optimization of the bismuth oxide content in the fired films has been completed and it appears that 1 w/o Bi may be adequate for promoting long term adhesion. Thermal spiking of the fired films has proven very useful in improving the photovoltaic performance of the solar cells. Until this technique is optimized, a thermal spiking for 60 seconds at 800°C will be done on all cells metallized by the MOD process. Initial microscopy studies have been useful in showing that at least one additional layer will be needed to provide complete coverage of the cell under the metallized contacts. Microscopy results have also verified the presence of bismuth in the fired films, the approximate 1 μm single layer fired film thickness, and the success of film removal by mercury vapor leaching.

3. REVIEW AND APPROACH

3.1 General

As discussed in the previous quarterly report, metallized solar cell collector grids produced by the metallo-organic decomposition (MOD) process require the presence of a permanent binding agent if consistent initial as well as long term adhesion of the grids to the solar cells is to be obtained. Based on thin film adhesion theory, decomposition temperatures of potential metallo-organic compounds and several other criteria, bismuth oxide produced from bismuth 2-ethylhexanoate was selected as the best available candidate for solving the adhesion problems. Ink SPC2-YZ which contained both platinum and bismuth metallo-organic compounds was suitable for metallizing solar cell collector grids with excellent long term adhesion. Unfortunately, the addition of these compounds, especially the bismuth 2-ethylhexanoate, caused unacceptably large sheet resistances in the fired collector grids.

In order to offset this problem, an attempt was made to produce multi-layer films with only the bottom layer containing bismuth oxide. Regardless of the intermediate and final heat treatments performed on these multi-layer films, cracking always occurred after firing more than two layers and even occurred in some two layer films. The cracking in turn caused poor film adhesion to the solar cell.

Research in the current quarter commenced from this point, with the initial approach being to use a slower firing sequence in an attempt to eliminate the film cracking problems. Although this approach showed promise, a decision was made to optimize the ink chemistry first after which multi-layer printing and firing could be further examined. The approach used to optimize the ink chemistry was to remove the platinum compound from the ink and optimize the more critical bismuth compound addition. Once an appropriate level of bismuth compound is found which will produce enough bismuth oxide in the fired films to give adequate long term adhesion, the platinum compound addition can be reinstated so films possessing adequate solder leach resistance can be obtained.

3.2 Evaluation of Progress

In order to aid in the evaluation of fired films produced from inks of varying compositions, it became necessary to expand the evaluation criteria beyond appearance, line definition, electrical sheet resistance and adhesion. From JPL's standpoint the most important criterion has always been how well the metallized solar cells will perform photovoltaically. Since many ink chemistries will be formulated, the use of on-site photovoltaic evaluation will be very helpful. Equipment is available to perform a somewhat incomplete, but nonetheless useful photovoltaic evaluation of solar cells after metallization by the MOD process. This will allow an evaluation of the effect of the level of bismuth oxide, or any other additive, on the operational characteristics of the solar cell itself without the necessity of sending the cells to JPL for evaluation. The complete evaluation available from JPL can be reserved for those cells which show suitable photovoltaic performance based on the on-site evaluation at Purdue.

A second new area of evaluation will involve the use of microscopy and X-ray evaluation of the fired collector grids. By using extensive topographical, cross-sectional and interfacial (after removing the contact by mercury vapor leaching) studies as well as X-ray analysis, it is hoped that both the presence and location of bismuth oxide can be confirmed and its role in promoting adhesion better understood.

4. EXPERIMENTAL

4.1 Ink Formulation for Ink Chemistry Optimization

The ink chemistry optimization studies were initiated in this research quarter by studying the level of bismuth 2-ethylhexanoate added to the ink to produce a certain amount of bismuth (in the form of bismuth oxide) in the fired films for promotion of long term adhesion. In order to do this, the platinum 2-ethylhexanoate addition to the ink was temporarily suspended and a series of inks were formulated containing only silver neodecanoate and bismuth 2-ethylhexanoate with butyl carbitol acetate and neodecanoic acid as screening agents. The amounts of each ingredient material was determined by the weight of silver neodecanoate used in the ink, because all inks contained 30 w/o silver by convention. The amount of bismuth 2-ethylhexanoate used was determined by first determining the weight percent of bismuth oxide in a benzene solution of bismuth 2-ethylhexanoate by thermogravimetric analysis. (It is known from X-ray analysis that bismuth 2-ethylhexanoate decomposes to bismuth oxide.) This was then converted to a weight percent bismuth in bismuth 2-ethylhexanoate. When optimizing the level of bismuth oxide in the fired films, the variable was the ratio of silver to bismuth desired in the fired film assuming the total amount of ink formulated each time did not vary. Three different ratios were studied to optimize the bismuth oxide content. These were 99% Ag/1% Bi, 97% Ag/3% Bi and 95% Ag/5% Bi.

A typical ink formulation procedure for 5 grams of ink (a suitable amount for screen printing a test run of at least 30 solar cells) was as follows (The 99% Ag/1% Bi ink will be used to illustrate the procedure).

NOTE: Ag = silver

Bi = bismuth

AGND = silver neodecanoate

BI2EH = bismuth 2-ethylhexanoate

Bi_2O_3 = bismuth oxide

NDA = neodecanoic acid

BCA = butyl carbitol acetate

1. $(30\%\ \mathrm{Ag}) \times (5\ \mathrm{g\ ink}) = (1.5\ \mathrm{g\ Ag}) \times (\frac{100\ \mathrm{g\ AGND}}{38.68\ \mathrm{g\ Ag}}) = 3.878\ \mathrm{g\ AGND}$

2. Since AGND is a white powder it was necessary to dissolve it in a suitable low boiling point solvent so that a homogeneous ink formulation would be achieved. It has been determined that 2.63 g of benzene (benzene and tetra hydrofuran are considered the best choices of solvent) is required to dissolve each gram of AGND. Therefore, 10.199 g of benzene was used to dissolve 3.878 g of AGND.

3. The amount of BI2EH needed in an ink which will produce fired films of composition 99% Ag/1% Bi was calculated as follows:

$$(3.878\ \mathrm{g\ AGND}) \times (\frac{107.87\ \mathrm{g\ Ag}}{279.13\ \mathrm{g\ AGND}}) \times (\frac{1\ \mathrm{g\ Bi}}{99\ \mathrm{g\ Ag}}) \times (\frac{100\ \mathrm{g\ BI2EH}}{14.4\ \mathrm{g\ Bi_2O_3}}) \times$$

$$(\frac{465.96\ \mathrm{g\ Bi_2O_3}}{417.96\ \mathrm{g\ Bi}}) = 0.3588\ \mathrm{g\ BI2EH\ in\ benzene}$$

4. It has been determined that the amount of screening agents needed does not change when the amount of BI2EH is varied to produce fired films containing between 1 and 5 w/o Bi. These amounts, relative to the amount of AGND in the ink were:

$$\text{Amt. BCA} = (10.0\%) \times (3.878 \text{ g AGND}) = 0.3878 \text{ g}$$

and

$$\text{Amt. NDA} = (20.0\%) \times (3.878 \text{ g AGND}) = 0.7756 \text{ g}$$

The various ingredient materials were combined and thoroughly mixed, and the solution transferred to the rotavac. Upon application of a vacuum and 30-40 °C, the homogeneous solution undergoes solvent exchange (the majority of the benzene was evaporated in favor of the screening agents) and a smooth, homogeneous paste suitable for screen printing resulted.

If both Pt and Bi are used in an ink the only changes in the calculations are in the respective desired ratios of platinum to silver and bismuth to silver in the fired films. Also, the addition of a platinum compound to the ink requires an increase in the amount of screening agents used. The appropriate amounts of NDA and BCA are best determined by a trial and error approach using small batches of ink.

4.2 In-Situ Photovoltaic Evaluation of Metallized Cells

The bottom line in evaluating how well a certain ink composition of proper viscosity will work as a solar cell metallization paste, is how well the metallized solar cell performs photovoltaically. To this point in the research effort on MOD silver metallization for photovoltaics, only 4-5 sets of cells have been sent to JPL for photovoltaic testing. The reason for this is that the bulk of the research has gone into developing a suitable conductor paste which will give front contacts with appropriate materials properties, especially adequate initial and long term adhesion. Now that bismuth 2-ethylhexanoate, which decomposes to bismuth oxide, has been shown to be effective in promoting long term adhesion in the front contacts, the photovoltaic performance of solar cells metallized by the MOD screen printing process becomes a much more important evaluation criterion.

The major thrust of the research in this quarter has been to begin optimizing the ink composition so that the front contacts will continue to have suitable materials properties, as well as allowing for optimum photovoltaic performance of the solar cells. With changes in the ink/metallization chemistry for each set of solar cells produced, it has become important to evaluate the effects of these changes on photovoltaic performance. This is especially important when small changes in chemistry, such as 1 w/o variations in the bismuth content, do not have a significant effect on the fired film materials properties such as appearance, line definition, sheet resistance and adhesion. Also, with so many changes in chemistry the time necessary to continually send the cells to JPL for complete photovoltaic evaluation has become impractical.

With this in mind it became extremely attractive to photovoltaically evaluate the solar cells metallized at Purdue on site. Although a complete evaluation including accurate fill factor and efficiency calculations is not possible with the equipment available (a calibrated illumination source and standard solar cell are necessary), it was possible to create a set-up to give IV curves, both with and without illumination, which can be compared for cells with metallizations of various compositions and/or processing parameters. The set-up consists of a probe station on which the solar cell is placed, an illumination lamp with variable intensity and position and a Tektronix model 576 curve tracer with camera. The probe station consists of an aluminum vacuum pedastal surrounded by four adjustable probes which are connected to the curve tracer. When a vacuum is applied to the pedastal the solar cell being evaluated will be held stationary. One probe is connected to the aluminum pedastal next to the cell forming the p-side connection and a second probe is connected near the center of the bus bar forming the n-side connection. When an alternating current is applied to the cell under an applied voltage of approximately 1.5 V through these connections, a complete IV curve appears on the curve tracer screen. Under illumination this curve represents an IV illumination curve and by completely covering the cell with a photographic cloth, so as to block out all light, an IV dark curve is produced. The IV curve is essentially a closed loop created when the curve continually retraces itself under the alternating current and constant applied voltage.

Provided the illumination intensity and location, cell batch number and probe locations are held constant, the illumination curves can be compared for cells having undergone different processing or metallized with inks of different compositions. The values of V_{oc} (open circuit voltage) and I_{sc} (short circuit current) can be read directly from a photograph of the IV curve where the curve intersects the voltage and current axes respectively. These values can be compared among cells tested under the same conditions. Also, a qualitative evaluation can be made of the cell′s photovoltaic performance from the shape of the curve.

4.3 Thermal Spiking of Metallized Cells

In order to attempt to improve the photovoltaic characteristics of solar cells metallized with bismuth containing inks, a process known as thermal spiking can be performed on the finished, metallized cells. In addition to bismuth oxide's much higher resistivity than silver, its presence may interfere with the charge transfer between the solar cell and the front contact. Thermal spiking, which involves heating the previously fired solar cells to a high temperature (between 600-800 °C) for 30-90 seconds, may be helpful in diminishing this interference without diminishing bismuth oxide's effectiveness as an adhesion promoter. The spiking process hopefully will allow the bismuth atoms to diffuse to positions where they will continue to promote adhesion while minimizing their possible interference with charge transfer. Thermal spiking may also be helpful in improving film adhesion if the diffusion transfers most of the bismuth atoms to the cell/contact interface where they will be most effective in promoting adhesion.

The spiking process itself was done in a batch muffle furnace which was preheated to the desired spiking temperature. The solar cells were quickly loaded into the furnace on a pre-heated setter so that they were exposed to the high temperatures for only the 30-90 seconds normally required for spiking operations. The spiking temperatures used thus far were 600 °C, 700 °C, 750 °C and 800 °C, and the spiking time was held constant at 60 seconds. The solar cells were evaluated for appearance, adhesion, sheet resistance, microstructure and photovoltaic characteristics both before and after the spiking process.

4.4 Microscopy Studies of Fired Films

Microscopy studies were initiated on the metallized contacts from topographical, cross-sectional and interfacial viewpoints. In conjunction with X-Ray analysis it is hoped that such studies can aid in further characterizing the chemistry of the films as well as aid in the formulation of a model describing adhesion of the films to the silicon solar cell surface.

For topographical studies, the metallized solar cells were mounted directly on the face of an aluminum cylinder which was heated to 100°C after wax was applied. Upon cooling, a strong but non-permanent bond existed between the cell and mount. The sample was then coated with aluminum and loaded into the SEM for direct observation. Topographical observation is valuable for observing the density of the film, looking for any defects or inconsistencies in the film, observing the line definition of the film, and for making an elemental analysis of the film using the EDAX attachment on Purdue's Jeol SEM.

For cross-sectional studies, the metallized solar cells were cleaved through the area of interest and mounted on the top of an aluminum block using wax with the edge to be observed overhanging. This edge was then polished smooth using an optically flat glass polishing wheel and water. The sample was then removed from the aluminum block and mounted on a rectangular specimen holder using wax. The sample holder with mounted sample was then placed in an aluminum evaporator and coated with approximately 100 angstroms of aluminum to allow the sample to conduct. After coating, the sample was loaded into the SEM for observation. Cross-sectional examination allows for a view of the cell/film interface although only at one location in the film. This is nonetheless helpful since EDAX analysis can help determine whether or not bismuth is at the interface aiding in adhesion. The cross-sectional viewpoint is also one accurate means of determining film thickness when the proper magnification is used.

A complete interfacial examination can be accomplished by first removing the film using the mercury vapor leaching apparatus described in previous quarterly report. Once the film is completely removed, the solar cell can be mounted as for topographical examination. Interfacial examinations should be helpful in determining an adhesion model for silver films to silicon solar cells since mercury vapor leaching should only remove atomic species, such as silver, and should not remove bismuth oxide or ionic species which may be present at the interface.

5. RESULTS AND DISCUSSION

5.1 Multi-Layer Films

Although bismuth oxide serves as an effective adhesion promoter in silver films produced by the MOD process, the accompanying increase in sheet resistance makes these films less than optimum conductors. To overcome both this increase in sheet resistance and the inherent thin nature of single layer, screen printed silver MOD films a considerable amount of research has gone into the production of multi-layer films. The increase in thickness obtained with each new layer increases the overall film volume which in turn lowers the sheet resistance. For two layer films the thickness will theoretically be doubled and the sheet resistance reduced by 50% if both layers are of the same composition. Additionally, the adhesion promoting bismuth oxide should be necessary only in the bottom layer so its absence in any additional layers will lead to further decreases in the film sheet resistance.

As documented in the previous quarterly report, multi-layer film production was not as simple as repeating the process for single layer film production. Cracking occurred in all films with three or more layers and even in some two layer films regardless of when standard firing sequence No. 1 was applied (e.g. only once after all layers were printed, after every other layer, or after every layer). Ink SPC2-YZ (containing bismuth) was used to produce the bottom layers and ink SPC1-YZ (no bismuth) was used to produce any additional layers. A batch drying step of 30 min. at 65°C was always used between layers to insure films of suitable line definition would be produced. It should also be mentioned that refiring previously fired films was also eliminated as a cause for the cracking since refiring did not degrade the adhesion or cause cracking of previously fired, excellent adhering films. The difference in composition between the bottom and any additional layers could theoretically be the cause of the cracking due to a difference in thermal coefficient of expansion of the layers of different composition. However, the highly ductile nature of silver which comprises the bulk of all layers should easily overcome any stresses introduced by thermal expansion differences.

In this quarter an attempt was made to eliminate the cracking problem by changing standard firing sequence No. 1 to a firing sequence with a similar maximum firing temperature, but considerably longer firing cycle. The new firing sequence involved a 3 hour firing cycle compared to 70 minutes for standard firing sequence No. 1. This change was made to allow for considerably slower removal of the organics, while allowing for smoother simultaneous formation of the metal film in order to minimize the chance of disrupting the excellent adhering bottom layer.

In order to evaluate the effectiveness of a slower firing cycle two layer films were subjected to standard firing sequence No. 1 while three layer films were subjected to the slower firing cycle. In both cases a 65°C/30 min. batch drying step was performed between intermediate layers. The two layer films showed poor bus bar adhesion, although no visible cracking, while the three layer films showed approximately 95% total adhesion with only slight film removal around the edges of the bus bar.

Although this single test did not insure that slower firing will eliminate film cracking problems, it did provide a direction to take once a more final ink composition has been developed.

5.2 Bismuth Oxide Content Optimization

The initial ink used to evaluate the effectiveness of bismuth oxide as an adhesion promoter produced fired films of theoretical composition 5 w/o bismuth, 4 w/o Pt and 91 w/o Ag. The long term adhesion of solar cell front contacts produced from this ink (SPC2-YZ) was excellent. However, the large sheet resistance of these films requires an optimization of the bismuth oxide content so that the minimum amount of bismuth oxide needed to promote excellent long term adhesion can be determined.

Inks which will produce fired films containing 1 w/o, 3 w/o and 5 w/o bismuth were studied during this quarter in order to optimize the bismuth oxide content. Three batches of ink SPC3-YZ (97% Ag/3% Bi), two batches of ink SPC5-YZ (99% Ag/1% Bi) and one batch of ink SPC4-YZ (95% Ag/5% Bi) were formulated according to the procedure outlined in Section 4.1. The firing study results for all six batches of ink formulated for this study are summarized in Table 5.1 The inks used and fired films produced in tests 1-4 and 9-10, although useful in some respects, were not used in a direct comparison to determine the optimum bismuth oxide addition level. Ink SPC3-1A used in tests 1 and 2 had too little screening agents resulting in the production of somewhat thready quality films. The films used in tests 3 and 4, which were produced from ink SPC3-2A containing the proper amounts of screening agents, could not be used since they were not fired immediately after printing and drying, due to an electrical overload causing the belt furnace used for firing to shut off. The films were eventually fired after 17 hours storage and their adhesion was poor on the bus bar. Since this could have been caused by the delay in firing, a new batch of ink SPC3-YZ was used to make films for the bismuth oxide optimization study. Finally, ink SPC5-1A used in tests 9 and 10 could not be used due to a stability problem. Although printable after considerable stirring, improper storage caused the ink to become brown in color and very dried out. The poor appearance and high sheet resistance of films produced from this ink proved that the ink was not suitable for use in this study.

Table 5.1 Firing Study Results for Bismuth Oxide Content Optimization

Test #	Ink #	Ink(a) Chemistry	# of layers	solar cell(b,c) batch no.	line defin.	sheet resist. (mΩ/sq)	initial adhesion
1	SPC3-1A Age: 1 day	97% Ag 3% Bi	1(d)	346-199	B(e)	not (f) checked	excellent
2	SPC3-1A Age: 1 day	97% Ag 3% Bi	2(g)	346-199	A	69.7	poor on bus bar. Excellent elsewhere.
3	SPC3-2A Age: 9 days	97% Ag 3% Bi	1(h)	346-199	A/B	35.8	Same as test #2
4	SPC3-2A Age: 9 days	97% Ag 3% Bi	2(h)	346-199	B	22.9	Same as test #2
5	SPC4-1A Age: 13 days	95% Ag 5% Bi	1	346-199	A	57.9	excellent
6	SPC4-1A Age: 13 days	95% Ag 5% Bi	2	346-199	A	32.3	one half of bus bar poor. Excellent elsewhere.
7	SPC3-3A Age: 24 days	97% Ag 3% Bi	1	346-208	A	40.3	excellent
8	SPC3-3A Age: 24 days	97% Ag 3% Bi	2	346-208	A/B	24.6	excellent, small piece of bus bar removed.
9	SPC5-1A Age: 44 days(i)	99% Ag 1% Bi	1	346-208	B	106.9	excellent
10	SPC5-1A Age: 44 days(i)	99% Ag 1% Bi	2	346-208	B	67.6	excellent
11	SPC5-2A Age: 2 days	99% Ag 1% Bi	1	346-208	A/B	38.8	excellent
12	SPC5-2A Age: 2 days	99% Ag 1% Bi	2	346-208	B	21.1	one half of bus bar poor. Excellent elsewhere.

(a) Based on expected theoretical fired film composition which is not verified analytically.

(b) Difference between cell batches 346-199 and 346-208 is that the latter did not receive the aluminum back surface field metallization before back contact deposition. This does not affect the front contact properties, but will influence the cell's photovoltaic characteristics.

(c) All solar cells were cleaned by HF cleaning procedure prior to printing.

(d) Standard firing sequence No. 1 is done on all single layer films.

(e) Films were thready in appearance due to too high of an ink viscosity. This was corrected for second and third batches of ink SPC3-YZ.

(f) Cells sent to JPL immediately for photovoltaic evaluation.

(g) Batch drying at 65°C for 30 mins. done between layers. Std. Firing Sequence No. 1 performed after printing of second layer.

(h) Mechanical failure in belt furnace prevented firing of these films until 17 hours after printing and batch drying.

(i) This ink was stored improperly and did not maintain good stability, although it was screen printable after vigorous stirring. Fired film appearance was very spotty and not silverish.

Inks SPC3-3A, SPC4-1A and SPC5-2A, used in tests 7 and 8, 5 and 6 and 11 and 12 respectively, were the ones used in the direct comparison. These inks contained 3 w/o, 5 w/o and 1 w/o bismuth respectively and were processed under the same conditions. Although the various ink ages differed, no correlation has been found between ink age and film properties when the inks are properly stored. Also, the difference in the cell batch number before and after test No. 7 will not affect the properties of the front side metallization according to JPL.

The single layer initial adhesion, which is the most important property to evaluate as far as bismuth additions are concerned, was excellent for all three levels of bismuth. The fact that it was so, even for the 1 w/o bismuth level (tests 5, 7 and 11), lends further support for not using test No. 3 films in the comparison since they had undergone different processing. A long term adhesion study with the 1 w/o Bi films has revealed continued excellent adhesion for at least three weeks. For two layer films, the continued problems with bus bar adhesion were present in all cases, although test No. 8 films showed only minor film removal. It will be interesting to see whether or not a slower firing sequence, as discussed in Section 5.1, can prevent such problems. This will be investigated once a final bismuth level is selected.

As for the other film properties, the bismuth level affected appearance and sheet resistance also. The line definition did not depend on the bismuth level, but only on the ink's rheological characteristics. With an increase in the amount of bismuth from 1 w/o to 5 w/o the appearance of the films became darker from bright whitish silver for 1 w/o Bi to a copperish silver for 5 w/o Bi. The average sheet resistance for single layer films decreased from 57.9 mΩ/sq to 40.3 mΩ/sq. when the bismuth content was decreased from 5 w/o to 3 w/o. A similarly significant decrease did not occur when the Bi content was lowered to 1 w/o since these films showed a sheet resistance of 38.8 mΩ/sq. This may have been due to a difference in fired film thickness between the 1 w/o and 3 w/o Bi films. The two layer sheet resistances of films containing 1 w/o, 3 w/o, and 5 w/o Bi were all significantly lower than their single layer counterparts as can be seen by comparing tests 5, 6, 7, 8, 11 and 12. However, the decrease in all three cases was not as great as the 50% decrease normally observed when the film thickness is theoretically doubled by the addition of a second layer.

A final note concerning the 38.8 and 35.8 mΩ/sq. sheet resistance values in tests 11 and 3 is that these values are even lower than the 39.1 mΩ/sq. which was documented in the previous quarterly report for pure silver single layer films. Although Although film thickness differences probably account for this discrepency, it is important to realize that the values of sheet resistance obtained, even for films containing 3 w/o Bi, are as low as any which have been obtained throughout the silver MOD photovoltaic metallization research.

At this point it appears that 1 w/o Bi may be suitable as an adhesion promoter in the silver films. However, the results documented in this report will need to be duplicated at least one or two more times before a definitive suitable bismuth level is determined. A set of 1 w/o bismuth films will also need to show continued long term adhesion and the metallized cells will have to show proper photovoltaic characteristics by a JPL evaluation before 1 w/o bismuth is selected as a suitable level. Finally, the successive production of multi-layers, either with or without bismuth, will be necessary in order to minimize the film sheet resistance and improve the overall quality of the metallized contacts.

5.3 Photovoltaic Evaluation of Metallized Solar Cells

Regardless of whatever level of bismuth addition is eventually selected, the final ink composition must be suitable for producing front contacts which will allow transferal of current from the solar cell to the "outside" world without significantly interfering with processes occurring within the cell. The effectiveness of the front contact in the overall solar cell performance depends on many factors such as series resistance within the contact, resistance at the interface between the solar cell and contact (which is directly influenced by how well the contact adheres to the cell) and the line definition of the contact to name a few of the more important. Prior to this quarter of research, photovoltaic evaluation was done only at JPL. Although a sophisticated photovoltaic evaluation set-up which can calculate fill factor and efficiency values is not available at Purdue, a somewhat crude, but very useful set-up has been obtained as described in Section 4.2. This set-up has allowed for an immediate, although limited, evaluation of the effects of bismuth oxide content variations on solar cell performance.

The solar cells produced in tests 1 and 2 (refer to Table 5.1) were sent to JPL for photovoltaic evaluation and the results were very poor.

The current-voltage (IV) illumination curves for these cells were linear between the open circuit voltage (V_{oc}) and the short circuit current (I_{sc}). This type of curve is characteristic of a highly resistive response and vety poor solar cell performance. An ideal response is a rectangular curve where V_{oc}, I_{sc} and $V = 0$, $I = 0$ origin form three of the four corners. The better the IV curve fills this ideal rectangle, the better the solar cell efficiency will be. As tootnoted in Table 5.1, the front contacts of the cells sent to JPL were thready in appearance, which may have greatly contributed to the poor cell performance.

All three sets of cells used to optimize bismuth oxide content in the contacts were subjected to on-site photovoltaic testing. In each case 9 cells were tested and an IV curve generated for each under constant light intensity. Before discussing these curves in detail several important factors which influence on-site testing need to be mentioned. First of all, one of the sets of cells (those with contacts containing 5 w/o Bi) was different from the other two. These cells had a back surface field applied during fabrication at JPL whereas the other two sets of cells did not. Although this does not effect the front contact in any way, it does affect the photovoltaic performance of the cells. According to JPL, the absence of a back surface field results in a decrease in open-circuit voltage by approximately 10%. This fact should be kept in mind if unexplained differences result during on-site testing of metallizations on the two types of cells. Secondly, the major drawback to the on-site testing procedure which has surfaced deals with the top side probe used to connect the solar cell to the curve tracer. It has been noticed that the IV curves are very sensitive to how and where this probe is placed on the bus bar of the front side contact. Since the contacts are so thin (approximately 1.5 μm for single layers) and the probes are sharp metal pins it is possible to pierce the contact down to the silicon surface unless extreme caution is used. If this occurs, the IV curve is usually either resistive in nature or cannot be generated at all. For this reason the probe is placed at several different locations on the bus bar to generate as accurate an IV curve as possible.

The on-site evaluation of solar cells with silver metallizations containing 1,3 and 5 w/o bismuth produced some useful information. In general, the IV curves for the 5 w/o bismuth metallized cells were linear, which is characteristic of resistive, poorly performing cells. The cells metallized with contacts containing both 1 w/o and 3 w/o bismuth were generally better performing with some curvature in the IV curves although these curves were not characteristic of very good solar cells. A closer comparison of these latter two sets showed slightly better performance for cells with contacts containing 3 w/o bismuth. Although the V_{oc} and I_{sc} values were similar for the majority of cells in both groups, the 3 w/o bismuth metallized cells produced several IV curves with clearly better visual fill factors than any of the 1 w/o Bi metallized cells. This may be the result of higher contact resistance in the cells metallized with 1 w/o Bi since the average sheet resistances for the contacts of the two sets of cells were similar (see Table 5.1, tests 7 and 11). However, more photovoltaic testing will need to be done on-site as well as at JPL before a determination can be made as to whether either one or the other is superior from a photovoltaic standpoint.

Regardless of which may eventually be deemed better, very few cells metallized with single layer contacts by the MOD process have shown even reasonable photovoltaic performance when compared to the ideal IV curve. Limited evaluation of several cells with two layer films showed similarly poor performance. When this is combined with the results obtained at JPL (even though these cells had somewhat thready contacts), it becomes obvious that something needs to be done to enhance cell performance. Although a change in chemistry or an increase in film thickness may be helpful, the relatively simple process of thermal spiking introduced in Section 4.3 may be helpful in improving the photovoltaic response of cells metallized by the MOD process.

5.4 Effects of Thermal Spiking on Fired Film Properties

The thermal spiking process of solar cells was described in Section 4.3. It should be pointed out that spiking is currently part of the standard processing for solar cells metallized with conventional silver conductors. The difference between that and the spiking procedure to be used on cells metallized by MOD processing is that in the former the spiking serves as the firing step in the process. For MOD films, the spiking is an additional heat treatment to be used on finished, working solar cells in an attempt to improve their performance.

Each of the sets of cells used to evaluate the optimum bismuth oxide content (1, 3 or 5 w/o Bi) were subjected to thermal spiking after photovoltaic evaluation. For each set, four spiking temperatures were used for 60 seconds on two cells each. These temperatures were 600°C, 700°C, 750°C and 800°C all of which are below the melting points of the two constituents in the front contacts, silver (960.5°C) and bismuth oxide (820°C). The results of these spiking tests are summarized in Table 5.2. The most important result of these spiking tests was the general improvement which resulted in solar cell photovoltaic performance after spiking. This was especially true for the higher spiking temperatures of 750 and 800°C. In addition, materials properties improvements occurred for sheet resistances, adhesion and overall film appearance. It can not be determined at this point why these improvements occur until considerable microscopy studies are performed on both spiked and unspiked films.

As documented in Table 5.2, the average sheet resistance decrease was between 31.2 and 51.9% with the amount of the decrease increasing as the amount of bismuth oxide in the films increased. Also, the sheet resistances after spiking were very similar (ranging from 21.4 - 28.6 mΩ/sq.) regardless of the bismuth level (Note that prior to spiking sheet resistances ranged from 35.2 to 61.0 mΩ/sq.). The sheet resistance decreases were usually slightly less for the two highest spiking temperatures compared to the two lower temperatures used. The adhesion of films was checked by the Scotch tape test on a typical film before spiking and on one film spiked at each of the various temperatures. For two sets of films (SPC4-1A and SPC3-2A) the adhesion improved with spiking as it was excellent after spiking at all temperatures compared to bus bar adhesion problems prior to spiking. For the other two sets of films (SPC3-3A and SPC5-2A) the adhesion was excellent both before and

Table 5.2 Summary of the Effects of Thermal Spiking

Ink #(a)	Bismuth Content (wt. %)(b)	Spiking Temp (°C)(c)	Initial Sheet Resist. (mΩ/sq)	Final Sheet Resist. (mΩ/sq)	Δ Sheet Resist. (mΩ/sq)	Adhesion Effects	Photovoltaic Response Improvement (d)	Comments
SPC3-2A Age: 22 days(e)	3	600	35.6	21.7	13.9	1/2 bus bar removed prior to spiking, but Excellent after spiking for all temps.	none	Overall there were no dramatic changes in photovoltaic response after spiking. Avg. sheet resistance decrease for all spiking temps. was 38.6%.
SPC3-2A Age: 22 days	3	700	35.3	21.4	13.9		none	
SPC3-2A Age: 22 days	3	750	35.2	21.9	13.3	same as above	slight positive	
SPC3-2A Age: 22 days	3	800	35.3	22.6	12.7	same as above	slight positive	
SPC4-1A Age: 32 days	5	600	57.8	27.1	30.7	same as above	slight negative	8 of 9 cells before spiking had resistive photovoltaic response. Only 1 cell did not improve with spiking. Ave. sheet resistance decrease of 53.9% after spiking.
SPC4-1A Age: 32 days	5	700	61.0	26.9	34.1	same as above	very positive	
SPC4-1A Age: 32 days	5	750	59.2	27.1	32.1	same as above	very positive	
SPC4-1A Age: 32 days	5	800	53.6	25.7	27.9	same as above	very positive	
SPC3-3A Age: 17 days	3	600	41.4	27.5	13.9	Excellent before and after spiking	none	The 2 cells which had a resistive photovoltaic response had IV curves with some curvature after spiking. Higher spiking temps. clearly better. Ave. sheet resistance decrease of 35.0% with spiking.
SPC3-3A Age: 17 days	3	700	39.6	26.0	13.6	same as above	slight negative	
SPC3-3A Age: 17 days	3	750	37.7	26.5	11.2	same as above	positive	
SPC3-3A Age: 17 days	3	800	37.3	24.9	12.4	same as above	positive	
SPC5-2A Age: 17 days	1	600	37.4	26.1	11.3	Excellent before and after spiking	slight positive	This set of films showed best response to spiking. Two cells with resistive response improved with spiking. Overall sheet resistance decrease of 31.2% after spiking.
SPC5-2A Age: 17 days	1	700	37.8	24.2	13.6	same as above	positive	
SPC5-2A Age: 17 days	1	750	38.0	27.9	10.1	same as above	very positive	
SPC5-2A Age: 17 days	1	800	36.4	28.6	7.8	same as above	very positive	

(a) See Table 5.1 for additional information about fired films produced from these inks (tests 3, 5, 7 and 11). All spiking was done on single layer films.

(b) Based on theoretical fired film elemental composition. Balance of 100% is silver.

(c) Spiking done in batch muffle furnace for 60 seconds in all cases.

(d) Based on visual examination of shape and V_{oc}, I_{sc} values of IV curves.

(e) Age in this table refers to the time elasped between original film firing and thermal spiking.

after spiking. In no cases did the film adhesion degrade upon spiking. As for the film appearance, spiking in all cases resulted in brighter, more silvery appearing films with the best improvements occurring with the higher spiking temperatures. This improvement may be due to oxide removal or possibly residual organic removal since the initial low temperature standard firing may not be completely and cleanly removing all the organics from the printed films. This appearance improvement may be directly related to the improved sheet resistances after spiking.

As can be seen in Table 5.2, thermal spiking have a significant effect on the photovoltaic response of the solar cells in many cases. In fact, it had a positive effect on every cell tested when the spiking temperature was either 750° or 800°C. The effects on photovoltaic response at spiking temperatures of 600°C and 700°C were more mixed with some cases of spiking having a slightly negative effect. Of the 12 solar cells tested (with contacts of various compositions) which showed a resistive response prior to spiking, all but one showed some degree of photovoltaic response after spiking. The best results of spiking occurred at 700, 750 and 800°C for films printed from ink SPC4-1A (5 w/o Bi) and at 750 and 800°C for films printed from ink SPC5-2A (1 w/o Bi). In the former case, the rating of very positive improvement was given because the cells went from resistive response (linear connection between V_{oc} and I_{sc}) to fairly good photovoltaic response. In the latter case, the cells were already performing, although poorly, before spiking; after spiking their IV curves improved considerably such that they were better than any previous IV curves recorded during on-site testing.

Due to the drawbacks associated with the on-site testing procedure, especially with regard to the sensitivity of probe location, more spiking studies will need to be done in order to find the best spiking temperature and time. However, a 60 sec. thermal spiking at 800^{o}C seems to be the best process at this time for improving film properties and solar cell photovoltaic response. Once the bismuth content, spiking temperatures and film microstructure are further studied, the role of thermal spiking will be better understood. For now it does appear that thermal spiking is very useful and it will therefore continue to be used as standard processing on all films deposited by the MOD process on solar cells.

5.5 Microscopy Studies

Topographical studies of single layer fired films (SPC4-1A) containing silver and 5% Bi as bismuth oxide revealed very dense films although complete coverage of the solar cell by the fingers of the contact was not observed in single layer films. This coverage problem apparently occurs because the solar cell surface is dimpled, and the single layer films are too thin to cover the dimple ridges. In SEM photographs at 1600 X the metallized film has regions where the silver forms tiny "islands", presumably on the elevated ridges in the solar cell surface. The bulk of the film appears as large very dense areas of silver, presumably where there are dimples and level areas in the solar cell surface. EDAX analysis confirmed that these large areas and the islands are indeed mostly silver, whereas the areas surrounding the islands were analysed as nearly 100% silicon. The films continue to perform as conductors since there is a continuous connection both among the silver "islands" and between the islands and the bulk deposits of silver film. Limited studies with two layer films have shown almost complete film coverage. EDAX analysis on the top surface of the film was used to confirm the presence of bismuth (presumably in the form of bismuth oxide) in the films. Although the analysis reveals mostly silver and silicon (due to the thin nature of the films), bismuth was detected even though an accurate quantitative analysis was not possible. Continued studies in this area will focus on the effects of spiking effects on microstructure and, hopefully, a correlation between bismuth content, spiking temperature and film microstructure can be found.

The first sample prepared for cross-sectional studies using the technique described in Section 4.4 was observed in the SEM. A photomicrograph of the sample provides another method of measuring fired film thickness. The primary use for cross-sectional studies is to aid in determining what, if anything, is different at the cell/film interface, in films containing bismuth oxide to promote adhesion in the films. An EDAX analysis of the entire cross-sectioned area will be done in the near future to determine if any differences exist. There were no visual differences in the cross-section of the one sample studied, and the film appeared very dense and homogeneous.

The interfacial microscopy studies are used to study to cell/film interface after mercury vapor leaching. The initial observations on a interface region showed only silicon and mercury after leaching away a silver/platinum fired film. This result showed that the mercury vapor leaching process is successful at completely removing the film. In the future, the excess mercury will be removed after leaching by cleaning the surface with dry ice. The next leached film will have contained bismuth oxide. Since any bismuth oxide at the interface should not be removed by mercury vapor leaching, a study of the interface should reveal some clues to the reasons behind bismuth oxide's effectiveness as an adhesion promoter in silver MOD films.

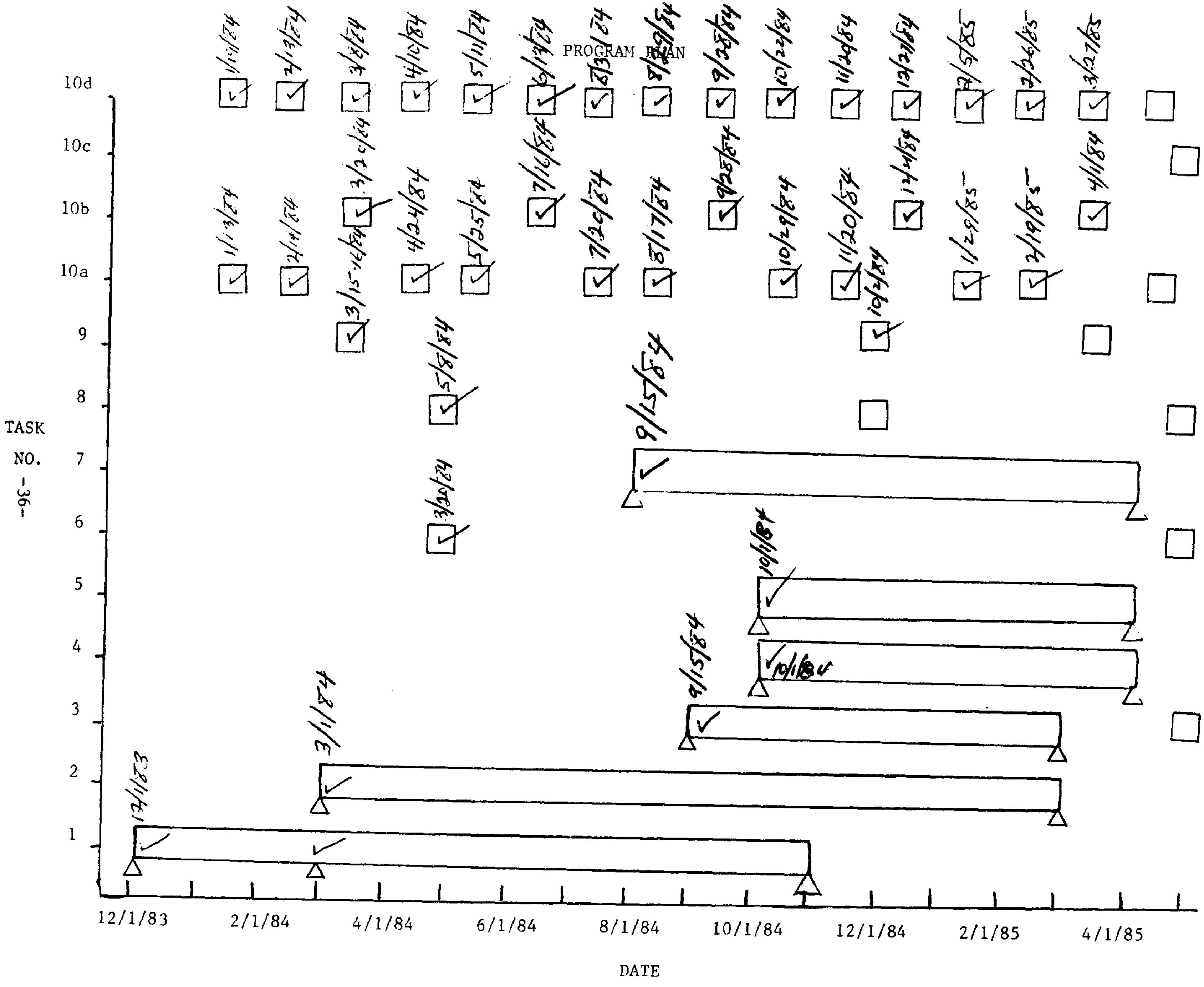
6. FUTURE PLANS

The remaining quarter of the MOD silver metallization for photovoltaics research will be spent mainly on continued ink chemistry optimization, microstructure correlation to film chemistry and properties, and determination of an adhesion model describing the adhesion mechanisms of silver films to silicon solar cells. At this point it appears 1 w/o bismuth may be sufficient to promote long term adhesion provided the films are spiked after normal belt furnace firing. A complete photovoltaic evaluation will be performed at JPL during the next month on solar cells metallized with 1 % bismuth films. Also, multi-layer films will be fabricated using slow firing methods in order to insure complete coverage of the silicon with an excellent adhering contact. Provided reasonable solar cell performance is observed at JPL, the platinum addition can be reinstated and quickly optimized. Once a final composition is selected, a large batch of fabricated solar cells can be sent to JPL for final evaluation of the MOD silver metallization by screen printing process for photovoltaics.

7. SCHEDULE

The list of tasks and updated program plan are attached.

Task No.	Description
1	Ink Development
2	Processing Studies
3	Fabricating Cells
4	Characterizing the Cells
5	Environmental and Operational Testing on Fabricated Units
6	Specifications
7	Adhesion Model
8	Data for Economic Evaluation
9	Personnel for Meetings
10a	Monthly Technical Reports
10b	Quarterly Technical Reports
10c	Final Technical Report
10d	Monthly Financial Management Reports



PROGRAM PLAN