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MOD SILVER METALLIZATION FOR PHOTOVOLTAICS

Quarterly Technical Report for the Period March 1—May 31, 1984

By
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R. W. Vest

July 16, 1984

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Purdue Research Foundation
Lafayette, Indiana

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QUARTERLY TECHNICAL REPORT
for the period
3/1/84 through 5/31/84

MOD SILVER METALLIZATION FOR PHOTOVOLTAICS

Purdue Research Foundation

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JPL Flat Plate Solar Array Project

July 16, 1984

"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."

FOREWORD

The research described in this report represents the second three months of effort on Contract No. 956697 with the Jet Propulsion Laboratory, Pasadena, CA, under the technical cognizance of Brian Gallagher. The research was conducted in the Turner Laboratory for Electroceramics, School of Materials Engineering and School of Electrical Engineering, Purdue University, W. Lafayette, IN under the direction of G.M. Vest and R.W. Vest. The research was carried out by Dr. S. Singaram and Mr. C.J. Sabo with assistance from Mr. R.L. Reed.

TABLE OF CONTENTS

1. INTRODUCTION AND OBJECTIVES

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 650-800°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 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 metallo-organic 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 purchase as pure materials or synthesize 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.

MOD silver films have the potential for eliminating most of the present problems with silver conductors. Preliminary results indicate that the MOD silver films can be produced at much lower firing temperatures (e.g. 250°C) and achieve very good adhesion without a glassy phase present. This should eliminate chemical interaction effects as well as deterimental thermal effects on the junction. The specific technological objectives of the current program are to develop screen printable MOD silver inks and suitable processing conditions to produce grid patterns on photovoltaic cells. The metallizations will be evaluated as to their line definition, adhesion, sheet resistance and microstructure. The adhesion and sheet resistance will also be evaluated after thermal aging. Another objective of the program is to develop a model which describes the adhesion between the MOD silver film and the silicon surface.

2. SUMMARY

It was demonstrated that the nature of the initial solvent used to extract the silver neodecanoate during synthesis or to render it into solution for ink formulation has a profound influence on fired film properties. The lower the boiling point of the initial solvent, the more of it was removed during rotary vacuum evaporation, and the less effect it had on fired film properties. Benzene and tetrahydrofuran were superior to xylene and toluene, and inks which used them in their preparation produced fired films with excellent appearance and adhesion if the proper firing sequence was used. The best films also had electrical resistivities very close to that of pure silver, which indicates that near theoretical density was achieved.

Platinum and palladium metallo-organic compounds were investigated so that fired films with good solder leach resistance could be produced. Six metallo-organic compounds were synthesized, four of them were used to make inks, and the properties of films made from these inks were evaluated. The most promising compound evaluated was Pt 2,4 pentane dionate, but additional studies are required.

3. EXPERIMENTAL

3.1 Silver Ink Development

The research efforts with Ag inks during this quarter focused on combining the good to excellent adhesion of films prepared from Inks 21 and 22 with the decent film appearance observed in the much earlier Inks 7, 8, 9. (The properties of films prepared from inks through No. 22 were discussed in the previous quarterly report.) It was noticed that the best film appearances had been obtained from inks not using xylene as the initial solvent; these inks were made by dissolving the silver neodecanoate (AgND) in toluene instead of xylene or they were made by mixing the solid silver neodecanoate directly with a screening agent. It should be noted that films made from Inks 7, 8 and 9 had poor adhesion, but they were not dried at a sufficiently low temperature for a long enough time as more recent results have shown is required. Accordingly, several new inks were formulated using solvents other than xylene or using no high vapor pressure solvent. Table 3.1 describes the general ink formulation methods used. For methods A, B, D and E, the inks still contained a small amount of the high vapor pressure solvent because the last few percent cannot be removed by vacuum distillation at temperatures below where silver neodecanoate begins to decompose. Table 3.2 gives the type and amounts of additives used in the new inks and their preparation method along with the w/o Ag in each ink and the temperature for complete carbon removal (T_D) both determined from thermogravametric analysis (TGA). Also included in Table 3.2 is a column titled "Predicted w/o Ag", which is based on the assumption that the inks contain only AgND and the additive(s). Similar data are included in Table 3.2 for the previous inks for comparison.

Table 3.1 General Ink Formulation Methods.

METHOD A: A xylene solution of silver neodecanoate with known w/o of silver was mixed with the additive, either neat or of known concentration in xylene solution, to give from 25 to 38.7 w/o of Ag in the final ink. The majority of the xylene was stripped off at 40-60°C using rotary vacuum evaporation. The viscous residue still contained some xylene, and had almost the right rheology for screen printing if the proper amount of additive was used.

METHOD B: A toluene solution of silver neodecanoate was used instead of a xylene solution and the additives were added neat, but otherwise the procedure of Method A was followed.

METHOD C: Solid silver neodecanoate was mixed with the additive (neat) to get the correct ink rheology.

METHOD D: A benzene solution of silver neodecanoate was used instead of a toluene solution, but otherwise the procedure of Method B was followed.

METHOD E A tetrahydrofuran solution of silver neodecanoate was used instead of a toluene solution, but otherwise the procedure of Method B was followed.

Table 3.2 Formulation of Silver Inks.

Ink #	Preparation Method	Additive(s)*	Composition AgND: Additive(s)	Predicted w/o Ag	w/o Ag from TGA	T_D (°C)
1	A	α-terp.+BCA	96:2:2	37.0	22	375
2	A	BCA	95:5	36.7	19	275
3	A	Phenyl ether	95:5	36.7	27	360
4	B	BCA	95:5	36.7	19	275
5	B	Dodecane	95:5	36.7	21	275
7	B	BCA	90.7:9.3	35.1(a)	19	275
8	B	Dodecane	72.1:27.9	27.9	21	275
9	C	NDA	not recorded	-	22	240
11	C	BBPE+BCA	64.2:26.8:9.1	24.7(a)	12	212
12	C	Mineral Jelly+BCA	76.9:7.7:15.4	29.8	26	287
13	C	BPDA+BCA	66.6:6.7:26.7	25.8	30	240
20	A	Xylene	not recorded	38.7	28	250
21	A	Triglyme	90:10	34.8	30	244
22	A	Dodecane	92.8:7.2	35.9	30	235
23	C	NDA	not recorded	-	23	257
24	C	BCA	not recorded	-	19	248
25	C	BCA	not recorded	-	20	245
26	B	BCA	63.5:36.5	24.6	21	260
27	D	BCA	80.4:19.6	31.1(a)	26	255
28	E	BCA	69.8:30.2	27.0	24	264
33	B(b)	BCA+NDA	76.6:11.7:11.7	29.6	24	245
35	D	DHN	75.6:24.4	29.2(a)	30	275

*α-terp. = α-terpineol
BCA = butyl carbitol acetate
BBPE = bis-propoxy-boron-2-ethyl butyrate
BPDA = n-propoxy-boron diacetate
NDA = neodecanoic acid
DHN = deca-hydronaphthalene

(a) the TGA was run after the ink had been used for screen printing, and a few extra drops of additive were used when the inks began drying on the screen.

(b) high purity gold label toluene was used (99 + % purity)

Since the predicted w/o Ag in Table 3.2 was calculated from the assumption that all of the high vapor pressure solvent had been removed, a measure of the amount of high vapor pressure solvent remaining can be obtained by comparing the predicted and measured silver contents. The uncertainties in the measured silver contents is less than 3 w/o, so differences larger than this are significant. The lower boiling point solvents benzene (80°C) and tetrahydrofuran (66°C) used in Methods D and E respectively, produced inks where the predicted and measured silver contents were much closer than was the case for inks starting with the higher boiling point solvents xylene (137°C) and toluene (111°C) used in Methods A and B respectively.

Neodecanoic acid was used as an additive in some of the inks and was used in the synthesis of silver neodecanoate. A commerical sample (prime grade) received as a gift from Exxon was deep yellow in color, and earlier experiments showed that a yellow coating formed on the fired silver films when this acid was added to an ink (Ink 9). This impure acid was also used to synthesize the AgND for Inks 1-11. In order to eliminate this source of impurities, aliquots of the prime grade sample were purified by vacuum distillation prior to use. A 250 ml round bottomed flask containing a magnetic stirring bar was charged with ~100 ml of commercial neodecanoic acid and placed on a heating mantle supported by a magnetic stirrer. This was connected to a two-way distillation head, which held a thermometer and a condenser with circulating cold water. The condenser was in turn connected to a vacuum adapter and a three-way receiver to collect the desired fraction without disrupting the set-up. The system was kept under vacuum (12-14 torr) using the water pump while the acid in the flask was heated with stirring. The initial fraction of ~10 ml, which distilled below 145°C, was collected in one of the flasks and rejected. The main fraction, which distilled in the range 145-147°C, was collected as a colorless oil. (The boiling point of neodecanoic acid is 250-257°C at atmospheric pressure.) The distillation was stopped when ~10 ml of acid was left in the distillation flask. The acid from the main cut of the distillation was used as an additive and in the synthesis of metal neodecanoates for inks numbered 12 and above.

3.2 Synthesis and Characterization of Platinum and Palladium Metallo-Organic Compounds

3.2.1 General

Pure silver is very soluble in tin/lead solders, but good solder leach resistance can be achieved by alloying the silver with platinum or palladium or a combination of the two. The criteria for Pt and Pd compounds to be added to the silver ink to give solder leach resistance in the fired film are listed below:

1. the Pt or Pd metallo-organic compounds should not react with silver neodecanoate (no precipitates should form);

2. the metallo-organic compounds should not contain sulfur or halogens since these will result in the production of toxic vapors during decomposition, nor should they contain any sodium or potassium since these ions may migrate into the silicon and degrade the cell performance. (An optimum compound would contain only platinum or

palladium, hydrogen, oxygen, carbon and perhaps nitrogen);

3. the compounds must decompose at a temperature low enough so that their decomposition does not significantly disrupt the silver film which forms completely by 225°C - 250°C;

4. the compounds must be soluble in at least one organic solvent which also dissolves the solid silver neodecanoate; and

5. after solvent removal the ink should be a smooth homogeneous paste and should not contain particles.

The four platinum and two palladium compounds discussed in the following sub-sections were synthesized so that they could be evaluated as ink constituents according to these five criteria.

3.2.2 Pt (IV) Amine 2-Ethylhexanoate

Reactions:

$$H_2PtCl_6 \cdot 6H_2O + 4C_3H_{10}N_2 \rightarrow Pt(C_3H_{10}N_2)_2Cl_4 + 2C_3H_{10}N_2 \cdot HCl + 6H_2O$$

$$C_7H_{15}COOH + NH_4OH \rightarrow C_7H_{15}COO^-NH_4^+ + H_2O$$

$$Pt(C_3H_{10}N_2)_2Cl_4 + 4C_7H_{15}COO^-NH_4^+ \rightarrow Pt(C_3H_{10}N_2)_2(C_7H_{15}COO)_4 + 4NH_4Cl$$

Chloroplatinic acid hexahydrate (1.54 g = 2.9 mmole) (37% Pt) was dissolved in absolute methanol (8 ml) and cooled in an ice bath. To this solution, 1,2-diaminopropane (1.28 g = 17.4 mmole) was added dropwise with stirring. The reaction was exothermic, and a yellow precipitate separated immediately. The solution was further stirred for 0.5 h, suction filtered, and the precipitate was washed with methanol (5 ml). The solid was then dissolved in water (10 ml).

An ammonium salt of 2-ethylhexanoic acid was prepared by mixing 2-ethylhexanoic acid (2.7 g = 10 mmole), water (5 ml) and ammonium hydroxide (1.25 g = 2 mmole). To this stirred solution, the aqueous platinum solution was added dropwise at room temperature. A cloudy precipitate formed and coagulated immediately into a yellow oil and settled to the bottom. The 2 liquid system was further stirred for 2 h and allowed to stand at room temperature for 3 to 4 h. The clear supernatent liquid was decanted off, and the residue was washed with water (3 X 10 ml), extracted in xylene, and dried over molecular sieves. Evaporation of most of the xylene left a viscous, yellow, oily residue of platinum amine 2-ethylhexanoate giving a 75% yield.

Thermogravimetric analysis showed that the w/o of Pt varied from 9 in dilute xylene solution to 13.5 in a concentrated xylene solution. The pure compound would contain 21.3 w/o platinum. An NMR analysis showed that the compound was similar to the Pt amine octoate purchased from GTE WESGO, and it should be direct replacement for our applications. A chemical analysis of the compound revealed 0.5% chlorine, which indicated that the last reaction did not go to completion.

3.2.3 Diglycine Platinum (II)

Reaction:

$$K_2PtCl_4 + 4C_2H_5O_2N \rightarrow 2KCl + Pt(C_2H_4O_2N)_2 + 2C_2H_5O_2N \cdot HCl$$

An aqueous solution of glycine (0.8862 g = 0.0118 mole in 1 ml water) was warmed with potassium tetrachloroplatinate (II) (0.8862 g = 0.0021 mole) on a water-bath for about an hour. Colorless crystals separated from the hot solution, and on cooling a further crop was obtained. They were recrystallized from hot water giving a 70% yield.

Thermogravimetric analysis of the solid gave 56 w/o of Pt (theoretical w/o 56.85) with final decomposition temperature of 255°C. The main disadvantage of this compound is that it is not soluble in any of the common organic solvents, and in this respect it cannot be used with silver neodecanoate to make a homogeneous solution.

3.2.4 Platinum (II) 2,4-Pentanedionate

Reaction:

$$K_2PtCl_4 + 2C_5H_8O_2 + 2KOH \rightarrow Pt(C_5H_7O_2)_2 + 4KCl + 2H_2O.$$

The compound was prepared by dissolving potassium tetrachloroplatinate (II) (1.377 g = 0.0033 mole) in hot water (8 ml), stirring in KOH (0.600 g = 0.010 mole) dissolved in water (2 ml) and warmed slightly until the solution became yellow, then finally adding acetylacetone (1.2 ml = 0.0115 mole). The mixture was heated to 50°C with frequent shaking. The amount of the pale yellow precipitate which began to form gradually increased. The temperature was held at 50°C for 1 to 1.5 h, after which precipitation was usually completed. The mixture was cooled and the crystalline residue was filtered off. A solution of KOH (0.2 g in 1 ml water) and acetylacetone (0.6 ml) was added to the mother liquor then reheated for an hour. The second crop of salt was removed and combined with the first crop of crystals and washed with water and dried in a desiccator. The yield was only 35% (≃ 0.5 g).

Thermogravimetric analysis of the solid in air at a heating rate of 10°C/min. gave 27 w/o Pt with a decomposition temperature of 215°C. The theoretical w/o was 49.6. The lower value of Pt indicated that the compound tends to evaporate before it fully decomposes. On looking into the TGA unit after cooling the system it was observed that the inside quartz beam was Pt coated.

3.2.5 Bis-Dimethylglyoxime Platinum (II)

Reaction:

$$K_2PtCl_4 + C_4H_8N_2O_2 \rightarrow 2KCl + Pt(C_4H_7N_2O_2)_2 + 2HCl$$

An aqueous solution of potassium tetrachloroplatinate (0.5466 g = 0.0013 mole in 3 ml water) was mixed with a solution of dimethylglyoxime (0.3 g = 0.0026 mole) in 50% ethanol (60 ml). The resulting reddish orange clear solution was stirred at room temperature for 30 min. No visible reaction took place. It was then refluxed for 2 hours when a dark grey-blue precipitate separated. The solid was filtered under suction, washed with water and 50% alcohol, and dried. A TGA of the solid gave 37 w/o of Pt (theoretical w/o 45.8) with final decomposition temperature of 375°C.

The two main drawbacks of using this compound in silver-platinum inks is that the compound is insoluble in solvents used for silver neodecanoate and has a relatively high decomposition temperature.

3.2.6 Palladium (II) 2-Ethylhexanoate

Reaction:

$$Pd(CH_3COO)_2 + 2C_7H_{15}COOH \xrightarrow[\text{steam bath}]{\text{benzene}} Pd(C_7H_{15}COO)_2 + 2CH_3COOH$$

The 2-ethylhexanoic acid (1.3968 g = 0.0097 mole) was added to a solution of palladium acetate (1 g = 0.0044 mole) in benzene (20 ml). The solution was stirred at room temperature for 30 min. and then transferred into a china dish and concentrated in a steam bath for 2 to 3 hours. When all the solvent and the by product acetic acid were evaporated, the honey colored viscous liquid was dissolved in toluene ($\simeq$ 4 ml).

A few drops of the toluene solution were spread on a glass slide and dried at 60°C for 30 min, then fired at 200°C for 30 min. + 250°C for 20 min. X-ray analysis of the resulting grey powder run immediately after decomposition showed peaks corresponding to Pd only and not PdO. A TGA of the toluene solution yielded 14 w/o Pd and showed that all carbon was removed by 260°C.

3.2.7 Palladium (II) Neodecanoate

Reaction:

$$Pd(CH_3COO)_2 + 2C_9H_{19}COOH \xrightarrow[\text{steam bath}]{\text{benzene}} Pd(C_9H_{19}COO)_2 + 2CH_3COOH.$$

Neodecanoic acid (1,66 g = 0.0097 mole) was mixed with a benzene solution (20 ml) of palladium acetate (1 g = 0.0044 mole). After stirring for 30 min. the honey colored solution was transferred into a china dish and warmed on a steam bath for 2 to 3 hours until all the solvent and acetic acid had evaporated. The viscous honey colored liquid was dissolved in toluene (4 ml), and a TGA showed that 16 w/o Pd was produced after all carbon had been removed by 250°C.

3.2.8 Summary

All Pt or Pd metallo-organic compounds were subjected to TGA analysis at a heating rate of 10°C/min in air and the results are listed in Table 3.3.

Table 3.3 TGA Analysis of Pt and Pd Compounds in Air at 10°C/min.

Compound	Form	w/o Prod.	T_D (°C)	Comments
Pt (IV) amine 2-ethylhexanoate	xylene solution	13.5	430	high T_D
Diglycine platinum (II)	solid	56	255	insoluble in common solvents
Pt (II) 2,4-pentane dionate	solid	27	215	partial evaporation before decomposition
Pt bis-dimethylglyoxime	solid	37	375	insoluble in

				common solvents
Pd (II) 2-ethylhexanoate	toluene solution	14	260	promising
Pd (II) neodecanoate	toluene solution	16	250	promising

The diglycine platinum and Pt bis-dimethylglyoxime were not considered further because they were not soluble in any of the solvents used for Ag neodecanoate. The other 4 compounds were evaluated as ink constituents because it was possible that the decomposition of Ag neodecanoate would trigger the decomposition of Pt amine 2-ethylhexanoate at a lower temperature, and it was also possible that Pt 2,4-pentane dionate would not vaporize before decomposing when it was a constituent in an ink.

3.3 Silver/Platinum Ink Development

3.3.1 General Approach

It was decided to apply the knowledge gained to date to inks with platinum additions. The rationale was that the platinum is necessary in the final inks to give good solder leach resistance, and even small additions (1-4 w/o) may cause film quality problems. Therefore, it was logical to optimize the inks after platinum was added. The initial inks were made to produce fired films with 4 w/o Pt since a previous study revealed that 1 w/o was inadequate but 4 w/o was sufficient to give good solder leach resistance (intermediate amounts were not investigated). Once a suitable platinum metallo-organic compound is selected, studies will be conducted to optimize and minimize the amount of platinum added since it adversely affects the resistivity of silver films. The synthesis of all of the Ag/Pt inks involved mixing a benzene solution of silver neodecanoate and the additive(s) neat along with a benzene solution of the Pt metallo-organic compound. The majority of the benzene was stripped off at 40-60°C using rotary vacuum evaporation.

Table 3.4 gives the additive(s) used and their amounts relative to the combined weights of Ag and Pt compounds. The predicted w/o Ag + Pt was calculated by assuming that all benzene had been removed from the inks. Thermogravimetrical analysis giving the w/o Ag + Pt and the temperature of complete carbon removal (T_D) are also listed. The good agreement between predicted and measured amounts of Ag + Pt can be attributed to the use of low boiling point benzene as the initial solvent. The sections below discuss the inks made with the two Pt additives.

Table 3.4 Formulation for Ag/Pt Inks*

Ink #	Pt Compound (PtMO)	Additive(s)*	Composition AgND+PtMO :Additive(s)	Predict. Ag+Pt	w/o Ag+Pt from TGA
30	Pt amine 2-ethylhexanoate	BCA	66.5:33.5	24.9	23
31	Pt 2,4-pentanedionate (a)	BCA	65.9:34.1	25.9	22
34	Pt 2,4-pendanedionate (b)	BCA + NDA	73.2:17.9:8.9	28.7	26
36	Pt 2,4-pendanedionate (c)	BCA + NDA	73.2:17.9:8.9	28.8	28

a) recrystallized from commercial Alfa sample

b) synthesized at Turner Laboratory

c) fresh Johnson-Matthey commercial sample

*BCA = butyl carbitol acetate

NDA = neodecanoic acid

3.3.2 Ink 30 with Pt Amine 2-Ethylhexanoate Additive

Pt amine 2-ethlyhexanoate was synthesized as described in Section 3.2.2. The pure compound was found to decompose at ≃ 430°C, but when added to a silver ink the decomposition was almost completed by 250°C. However, complete carbon removal from the ink did not occur until above 500°C. Additionally, the Pt amine 2-ethylhexanoate in benzene formed a precipitate upon mixing with a benzene solution of silver neodecanoate. This precipitate may have been some type of Pt-Ag complex along with some AgCl which may form due to the presence of 0.5% Cl in the Pt compound.

3.3.3 Inks 31, 34, and 36 with Pt 2,4-Pentane Dionate Additive

The first compound investigated was purchased from Alfa Inorganics. When mixed with the silver neodecanoate the solution completely decomposed by 275°C. However, the commercial Pt compound was approximately 1 year old and further evaluation using a fresh generic sample of Pt 2,4-pentane dionate was required.

This compound was then synthesized, as described in Section 3.2.4, but a TGA showed that only ≃ 50% of the theoretical amount of platinum was produced after decomposition. This behavior was verified by running a TGA on a fresh commercial sample of Pt 2,4-pentanedionate which was purchased from Johnson Matthey, Inc. This compound was analyzed by Johnson-Matthey and found to contain 49.16 w/o Pt. However, a TGA revealed only slightly more than 28 w/o Pt after decomposition. Additionally, there was some evidence of Pt deposition on interior parts of the thermobalance. These results proved that pure Pt 2,4-pentane dionate vaporizes to some extent before it decomposes.

In order to study the behavior of Pt 2,4-pentane dionate when it is a constituent in a thick film ink, Inks 34 and 36 were formulated to give a fired composition of 96% Ag and 4% Pt. The platinum additions to the inks were based on TGA analysis of synthesized Pt 2,4-pentanedionate which decomposed to 27 w/o Pt. These inks proved to be very screen printable on both alumina substrates and solar cells. Several samples were fired through the belt furnace in an open-ended, glass tube to see if a film would form on the tube interior due to platinum vaporization prior to decomposition. No film formation was observed, which suggests that the platinum compound does not sublime before decomposing when it is part of an ink as a small weight percentage; thus, these fired films contained more than 4 w/o Pt. Therefore, Pt 2,4-pentane dionate was considered to be a candidate material for the Ag/Pt inks, but future Pt additions to inks will be based on a platinum analysis of the as-synthesized compound rather than on a TGA analysis.

3.4 Silver/Palladium Ink Development

Palladium is not as attractive as Pt as an additive to Ag inks because considerably more ($\approx$ 20 w/o Pd) is required to give good solder leach resistance. However, Pd compounds were synthesized and formulated into Ag/Pd inks because it was possible that a suitable Pt compound could not be developed. Initially, inks were formulated to give a fired composition of 4 w/o Pd-96 w/o Ag in order to compare adhesion and film appearance with Ag/Pt films. Both Pd compounds were in toluene solution, and were added to a benzene solution of Ag neodecanoate with the appropriate additives. The majority of the benzene and toluene solvents were stripped off at 40-60°C using rotary vacuum evaporation to give a screen printable ink. The additives along with the TGA results obtained on one ink are summarized in Table 3.5.

Table 3.5 Formulation for Ag/Pd Inks

Ink	Pd Compound	Additive(s)*	w/o Ag + Pd in ink	T_D (°C)
501	Pd 2-ethylhexanoate	EC+NDA	23.5	350
502	Pd 2-ethylhexanoate	NDA	-	-
503	Pd 2-ethylhexanoate	NDA+BCA	-	-
504	Pd neodecanoate	NDA+BCA	-	-

*EC = ethyl caprate

NDA = neodecanoic acid

BCA = butyl carbitol acetate

The T_D of 350°C for ink 501 was surprising because the highest T_D of any of the 4 constituents was 260°C for the palladium compound.

3.5 Firing

An important consideration in the firing of the silver metallo-organic thick films for photovolatics is the maximum firing temperature, because the p-n junction is less than 0.5 μm below the surface to be metallized. If the semiconductor is exposed to too high of a temperature, diffusion of the dopant atoms can occur and the p-n junction can be degraded. Therefore, a maximum firing temperature of 350°C was chosen for the processing of the silver MOD films. This relatively low maximum firing temperature is one of the major reasons for the use of the silver MODS rather than conventional silver inks. Since there are no suspended particles in MOD inks, there is no need for high temperature sintering to obtain a good conducting film with good adhesion. With the MOD inks the maximum firing temperature needs to be only higher than the temperature at which complete decomposition of the ink occurs such that a continuous silver film results with good adhesion, resistivity and line definition. Of course, many parameters, besides the maximum firing temperature but connected with firing and other processing steps, have some influence over these film characteristics.

Another important firing consideration which relates to film quality and adhesion is that all solvents and screening agents must be removed prior to the beginning of silver film formation. If not, the silver film will be disrupted as the organic screening agents and solvent decompose mainly as volatile hydrocarbons, CO and CO_2. In order for this to be accomplished, an adequate drying step must proceed any firing step. During the early stages of this study it was believed that the silver film formation began at $\simeq 220^{\circ}C$ and suitable firing sequences were chosen with this in mind. However, more detailed TGA analysis of the silver neodecanoate revealed that the compound may begin to decompose to silver at temperatures as low as $75^{\circ}C$ even though the majority of the decomposition occurs between $150-225^{\circ}C$, as discussed in the preceeding quarterly report. Therefore, some significant adjustments were made in the firing sequences used so that most, if not all, of the solvents and/or screening agents would be removed prior to any silver film formation.

Four types of firing have been used to date in the silver MOD study. They were:

1. muffle furnace at constant temperature and still air;
2. muffle furnace with time-temperature programming and controlled air flow;
3. belt furnace with variable time-temperature profiles and natural convection; and
4. combinations of No. 1 and No. 3.

Since the research to date has focused on developing an ink chemistry which will yield films of suitable quality in terms of appearance and adhesion, extensive firing tests with any one ink have not been conducted. However, a variety of firing sequences were used for each ink printed. In some cases a variety of furnaces and firing times and temperatures were used while in others firing at one temperature and time only was performed. The firing steps served only to aid in making a quick evaluation of the ink's potential and no attempt was made with any of the inks to optimize the firing sequence. However, a careful examination of the results will reveal some general patterns in the firing sequences used. Some type of drying step was usually used since, as was mentioned previously, it was recognized that the solvents and screening agents had to be driven off before the silver began to form. Once the low (approx. 75°C) silver neodecanoate beginning decomposition temperature was discovered a drying step was introduced in the 60-70°C temperature range for much longer times than had been used previously. The drying step was usually omitted for a few samples from each ink to observe the effects of immediate firing after printing. However, it appears that the drying step for solvent and screening agent removal is essential if adequate film adhesion is to be obtained.

Following the drying step, a very wide range of firing sequences were used, but the maximum firing temperature was always limited to 350°C or less. The length of various firing steps ranged from 10-60 minutes, with most in the 15-30 minute range. Firing rates also varied depending on the furnace used. For batch firing (system 1) the furnaces were capable of heating rates up to 30°C/minute, and batch fired samples were both fired at single temperatures and over a range of temperatures. For belt furnace firing (system 3), a wide variety of time-temperature profiles were possible, but were very time consuming to adjust. The small programmable muffle furnace (system 2) provided the widest controlled range of firing sequences.

4. RESULTS AND DISCUSSION

4.1 Silver Inks

Eight silver inks (23, 24, 25, 26, 27, 28, 33, 35) were fabricated and their method of preparation, chemistry and the TGA results were discussed in Section 3.1. The inks were screen printed using a modified Aremco 3100 Screen Printer through a stainless steel screen onto substrates and fired to produce silver films. The substrates used were alumina (AlSiMag 838), glass (soda line silica) microscope slides, polished Si wafers from Monsanto, and Si solar cell substrates supplied by JPL. The alternate substrates were used because the number of Si solar cells was inadequate for the number of experiments conducted; from 4 to 9 samples were printed for each different firing sequence for each different ink. Two screen patterns were available: the 200 mesh Turner Laboratory Conductor Pattern with a 102 square pattern for measuring sheet resistance and lines spaced 4, 8, 12, 16 and 20 mils apart for line definition determination, and the cell metallization pattern supplied by JPL that was developed on a 325 mesh screen.

The films were evaluated in terms of film quality (surface appearance), sheet resistance and adhesion using the methods described in the previous quarterly report. Line definition was also evaluated, but since the narrowest separation of lines in the JPL solar cell pattern is .023" it is not very accurate to report line definitions as a quantitative number (in inches as is done for the Turner Pattern). Instead, the following rating system was used for reporting line definitions of fired films of the JPL pattern:

A - Excellent

B - Acceptable with room for improvement

C - Unacceptable

Three photographs are shown in Fig. 4.1 which illustrate the three line definition ratings. Two major types of unacceptable line definitions are: (1) thready films usually resulting from too thick of an ink during printing; and (2) poorly defined films resulting from bleed-out during firing.

A summary of the results along with the type of furnace, the firing sequence used, the substrate type and which conductor pattern was used for each ink is given in Table 4.1.

Results using inks 23, 24 and 25 suggested that the film appearance problem may be due to the solvent. These inks were all made by directly mixing the solid silver neodecanoate with a screening agent, namely neodecanoic acid or butyl carbitol acetate. Proper firing resulted in films of nice whitish silver appearance with good to excellent adhesion. Unfortunately, with the available equipment it is impractical to mix the silver neodecanoate powdery solid directly with screening agent on anything but a very small scale. The reason for this is that homogeneous mixing becomes very difficult since the solid does not readily dissolve in the screening agent. Therefore, Inks 26, 27 and 28 used toluene, benzene and tetrahydrofuran, respectively, in an attempt to

Table 4.1 Properties of Fired Silver Films.

	Firing Sequence						Sheet	
Ink#	Temp. (°C)	Time (min)	Type of Furnace	Substrate* Pattern	Surface Appearance	Line Defin.	Resist. (Ω/□)	Adhesion
1	25	10	1	Al_2O_3 T	dark green	fair to good	∞	-
	120	10						
	200-350	10°/min.						
	350	8						
2	100	20	1	Al_2O_3 T	light brownish yellow	fair to good	0.89-2.68	-
	220	5						
	220-350	10°/min						
	350	17						
2	25-75	5°/min	3	Al_2O_3 T	grey silver	fair to good	0.259-0.817	-
	75-285	8.4°/min						
	285	5 min						
3	25-75	5°/min	3	Al_2O_3 T	dark brownish grey	fair to good	2.19-6.00	-
	75-310	8.4°/min						
	335	5						
4	25-75	5°/min	3	Al_2O_3 T	greyish silver	fair to good	>9.7	fair
	75-310	8.4°/min						
	310	5						
5	25-75	5°/min	3	Al_2O_3 T	greyish silver with brown tint	fair to good	3.07-5.37	fair to good
	75-310	8.4°/min						
	310	5						
7	25-75	12.5°/min	3	Al_2O_3 T	greyish silver	fair to good	0.394-0.411	fair to good
	75-310	21°/min						
	310	2						
8	25	15	1	Al_2O_3 T	yellowish silver with brown residue around fired pattern	poor	0.161-0.234	poor
	200-350	30°/min						
	350	20						
9	200-350	10°/min	1	Al_2O_3 T	silvery surface with yellow tint	poor	0.113-0.112	poor
	350	20						
11	200-350	10°/min	1	Al_2O_3 T	brownish black with oily texture	excellent	∞	poor to fair
	250	30						
12	100	15	1	Al_2O_3 T	brownish grey	poor	not measured	poor
	200-350	10°/min						
	350	45						
12	100	15	1	Glass T	brownish grey	good to excellent	not measured	good to excellent
	200-350	10°/min						
	350	45						
20	70	15	1	Al_2O_3 T	brownish grey	good 0.008"-0.012"	0.460-5.36	good to excellent
	200	10						
	200-250	10°/min						
	250	10						
	350	30						
21	60	30	1	Al_2O_3 T	dull yellowish silver	fair 0.020"	0.189	good
	200	20						
	225	20						
	350	30						

Table 4.1 Continued

Ink#	Firing Sequence Temp. (°C)	Time (min)	Type of Furnace	Substrate* Pattern	Surface Appearance	Line Defin.	Sheet Resist. (Ω/□)	Adhesion
21	60	30	1	Al_2O_3 T	whitish silver	fair	0.062	poor to fair
	200	20						
	225	20						
	350	30						
	350-500	30°/min						
	500	12						
21	60	40	1	Si Wafer T	brownish grey yellow	fair	0.280-0.626	good
	200	20						
	350	30						
22	65	30	1	Al_2O_3 T	grey with gold tint	fair 0.016"	0.078-0.121	good to excellent
	200	20						
	200-300	10°/min						
	300	25						
22	65	20	2	Al_2O_3 T	yellowish grey silver	fair 0.012-0.016"	0.083-0.103	fair to good
	25-70	5°/min						
	70	15						
	70-200	5°/min						
	200	20						
	200-300	5°/min						
23	55	30	1	Al_2O_3 JPL	whitish silver	B	.105	good
	200	30						
	325	30						
23	55	30	1	Si Wafer JPL	whitish silver	B	.074	good
	200	30						
	325	30						
23	25-70	1°/min	2	Al_2O_3 JPL	whitish silver	B	fired films not continuous	excellent
	70	30						
	70-150	1°/min						
	150	15						
	150-225	5°/min						
	225	15						
	225-325	5°/min						
	325-147	34.1°/min						
	147-69	10°/min						
	69-30	1.8°/min						
23	25-70	1°/min	2	Si Wafer JPL	whitish silver	B	fired films not continuous	excellent
	70	30						
	70-150	1°/min						
	150	15						
	150-225	5°/min						
	225	15						
	225-325	5°/min						
	325-147	34.1°/min						
	147-69	10°/min						
	69-30	1.8°/min						
24	25-70	1°/min	2	Al_2O_3 JPL	whitish silver outlined by brown burn-off residue	B	.179	fair
	70	30						
	70-150	1°/min						
	150	15						
	150-225	5°/min						
	225	15						
	225-325	5°/min						
	325-247	34.1°/min						
	147-69	10°/min						
	69-30	1.8°/min						

Table 4.1 Continued

	Firing Sequence							
Ink#	Temp. (°C)	Time (min)	Type of Furance	Substrate* Pattern	Surface Appearance	Line Defin.	Sheet Resist. (Ω/□)	Adhesion
24	25-70 70 70-150 150 150-225 225 225-325 325-147 147-69 69-30	1°/min 30 1°/min 15 5°/min 15 5°/min 34.1°/min 10°/min 1.8°/min	2	Si Wafer JPL	whitish silver	B	fired films not continuous	fair to good
24	65 200 325	45 20 20	1	Al_2O_3 JPL	whitish silver	B	.093	excellent
24	65 200 325	45 20 20	1	Si Wafer JPL	whitish silver	B	.063	data not taken
25	60 200 325	45 30 20	1	cell JPL	whitish silver	B	.352	fair to good
26	45 200 275	45 30 20	1	Al_2O_3 T	brownish gold	>.020"	.079	poor
26	45 200 275 275-500 500	45 30 20 30°/min 7.5	1	Al_2O_3 T	spotty silverish	>.020"	not checked	not checked
26	45 200 275	45 30 20	1	Si Wafer T	brownish gold	.008"	.111	poor
26	45 25-80 80-290 290 290-65 65-34	45 13.75°/min 21°/min 2 34.6°/min 3.4°/min	4	Al_2O_3 T	spotty silverish	>.020"	.062	poor
26	45 35-290 80-290 290 290-65 65-34	45 13.75°/min 21°/min 2 34.6°/min 3.4°/min	4	Si Wafer T	spotty silverish	.016"	.097	poor
27	45 200 275	45 30 20	1	Al_2O_3 T	silver	.016"	.017	poor
27	45 200 275	45 30 20	1	Si Wafer T	silver	.016"	.018	poor to fair

Table 4.1 Continued

	Firing Sequence						Sheet	
Ink#	Temp. (°C)	Time (min)	Type of Furnace	Substrate* Pattern	Surface Appearance	Line Defin.	Resist. (Ω/□)	Adhesion
27	45 25-80 80-290 290 290-65 65-34	45 13.75°/min 21°/min 2 34.6°/min 3.4°/min	4	Al_2O_3 T	silver	.016"	.017	fair
27	45 25-80 80-290 290 290-65 65-34	45 13.75°/min 21°/min 2 34.6°/min 3.4°/min	4	Si Wafer T	silver	.016"	.017	excellent
27	25 65 200 325	44 hrs. 30 30 20	1	Al_2O_3 T	silver	.010"	.0172	excellent
28	65 200 325	30 35 20	1	Al_2O_3 T	silver	.016"	.0192	excellent
28	65 25-80 80-290 290 290-65 65-34	30 13.75°/min 21°/min 2 34.6°/min 3.4°/min	4	Al_2O_3 T	silver	.020"	.017	fair to good
33	65 200 335	30 30 20	1	Al_2O_3 JPL	silvery	C	fired films too thready	good
35	60 25-249 249-313 313-334 334 334-294 294-67 67-31	20 26.7°/min 22.5°/min 8.75°/min 2.5 14.5°/min 47.8°/min 3.8°/min	4	Al_2O_3 JPL	silvery	C	fired films too thready	good

*Substrate: Al_2O_3 = AlSiMag 838

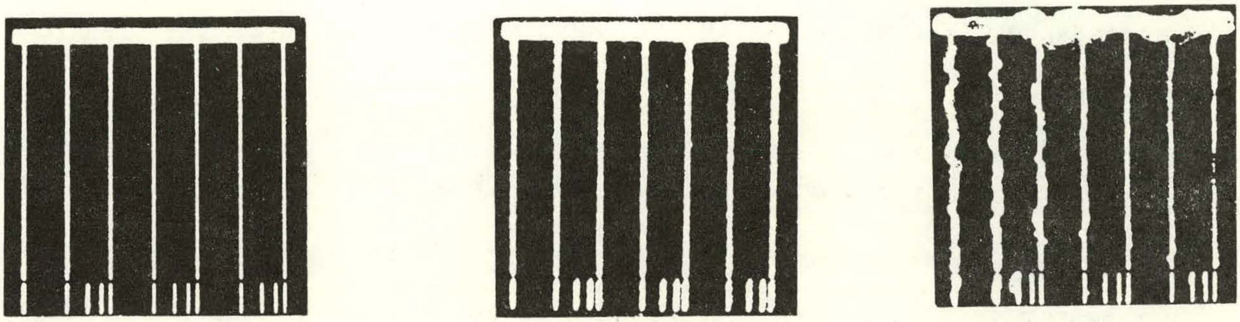
glass = Soda lime silica microscope slide

Si Wafer = Commercial polished Si Wafer from Monsanto

cell = JPL supplied Solar Cell substrate

Pattern: T = Turner Laboratory Standard Pattern with 103 squares printed through a 200 mesh screen.

JPL = JPL Supplied Pattern printed through a 325 mesh screen.



A. Excellent B. Acceptable C. Unacceptable

Figure 4.1 Rating System for Reporting Line Definition of Fired Films using the JPL Patten.

obtain inks which gave good fired appearance with good line definition, adhesion and resistivities. All three of these solvents have boiling points lower than xylene. Ink 26, made with toluene as a solvent, proved to give fired films similar to those made with inks that used xylene. The films were a spotted (shiny & dull areas) brownish gold color. Therefore, xylene and toluene will be avoided for the time being until the effect on the poor silver film appearance can be evaluated more completely. Both benzene and tetrahydrofuran (Inks, 27 and 28) proved to be suitable initial solvents for giving fired films with good appearance. The proper firing sequence also produced films with excellent adhesion.

The sheet resistances of films made from Inks 27 and 28 were lower than any others reported in Table 4.1. In order to compare the resistivity of these films to that of pure silver, it is necessary to multiply the film thickness times the sheet resistance. However, the thicknesses of the fired conductor test pattern lines were too thin to be measured directly with equipment available in the Turner Laboratory. However, the dried film thickness (film dired 15-30 minutes at 60-65^{o}C) could be measured using a light section microscope. Using the procedure outlined below, this dried film thickness value and the sheet resistance were used to calculate the resistivity of the fired film. In order to make this calculation it was assumed that: (1) the dried film was 100% silver neodecanoate; (2) the fired film was 100% silver; and (3) significant spreading did not occur during printing or drying. Using assumptions 1 and 2, the ratio of the volume of silver (V_{Ag}) in the fired film to the volume of silver neodecanoate (V_{AgND}) in the dried film is given by:

$$\frac{V_{Ag}}{V_{AgND}} = F_{Ag}\,\frac{d_{AgND}}{d_{Ag}} = 0.387\,\frac{1.22}{10.50} = 0.0450 \tag{1}$$

where F_{Ag} is the weight fraction of silver in silver neodecanoate (0.387), d_{AgND} is the density of silver neodecanoate (1.22 g/cm^3), and d_{Ag} is the density of silver (10.50 g/cm^3). These volumes can also be written as

$$V_{Ag} = A_{Ag}\ell \tag{2}$$

$$V_{AgND} = t_{AgND}w\ell \tag{3}$$

where A_{Ag} is the cross sectional area of the fired film, t_{AgND} is the measured thickness of the dired film, w is the width of the dried film and according to assumption 3 can be obtained from the screen pattern, and ℓ is the film length which is the same for dried and fired films. Combining Eqs. 1, 2 and 3 gives

$$A_{Ag} = 0.0450\ t_{AgND}w \tag{4}$$

The resistivity (ρ) of any material is related to the measured resistance (R) by

$$\rho = R\,\frac{A}{\ell} \tag{5}$$

Combining Eqs. 4 and 5 gives

$$\rho = R \frac{0.0450\, t_{AgND} w}{\ell} = 0.0450\, t_{AgND}\, R \left(\frac{w}{\ell}\right) \qquad (6)$$

$$\rho = 0.0450\, t_{AgND}\, R_s . \qquad (7)$$

where $R_s = R\ (w/\ell)$ is the sheet resistance. Equation 7 was then used to calculate the resistivity of the fired films made from Inks 27 and 28 from the measured values of sheet resistance and dried film thickness. The films from Table 4.1 which had excellent adhesion on Al_2O_3 substrates were used for this calculation, and the results are compared with pure silver in the Table 4.2. The values for films from Inks 27 and 28 suggest that these films are near theoretical density.

Table 4.2 Film Resistivity Compared to Pure Silver

Ink #	t_{AgND} (cm)	R_s (μΩ/sq)	ρ (μΩ-cm)
pure Ag	-	-	1.59
27	23.5×10^{-4}	1.72×10^{4}	1.82
28	25×10^{-4}	1.92×10^{4}	2.16

A high grade toluene was used in Ink 33 with NDA and BCA as screening agents; however, the ink gave thready prints that indicated that there was not a sufficient amount of screening agent or not an optimum combination of additives. In Ink 35, decahydronaphthalene was used as a screening agent in an attempt to replace the BCA and NDA; however, only partial prints were observed.

4.2 Ag/Pt and Ag/Pd Inks

Four Ag/Pt inks as described in Table 3.4 were investigated, and the properties of the fired films similiar to those described for Ag inks are summarized in Table 4.3. The poor surface appearance, high sheet resistance, and fair adhesion of films made from Ink. No. 30 can all be blamed on the high T_D value for this ink (see Section 3.3.2 and Table 3.4). The three inks using Pt 2,4 pentane dionate (Ink Nos. 31, 34 and 36) showed promising results. When the proper drying and firing sequence was used the fired films had good appearance and line definition, excellent adhesion, and relatively low sheet resistance.

The four Ag/Pd inks described in Table 3.5 were investigated, and the properties of the fired films similar to those described for Ag inks are summarized in Table 4.4. All of the fired films had reasonably good appearance and line definition, but the adhesion was only fair and sheet resistances were higher than films made from the Ag/Pt inks. The fair adhesion is probably due to the fact that T_D values for all four inks were higher than desired, which meant that some carbon remained when the film was completely formed. However, the T_D values were below the maximum firing temperature of 292°C so all of the carbon would be removed to give the silvery gray surface appearance. The high sheet resistance values were even more discouraging because the Pd content would have to be increased 5 fold to give good solder leach resistance, which would lead to a significant increase in the already high sheet resistance. Therefore, so further studies are contemplated with Ag/Pd inks unless it is convincingly demonstrated that a suitable Ag/Pt ink cannot be developed.

Table 4.3 Properties of Ag-Pt Inks.

	Firing Sequence							
Ink#	Temp. (°C)	Time (min)	Type of Furnace	Substrate* Pattern	Surface Appearance	Line Defin.	Sheet Resist. (Ω/□)	Adhesion
30	65 25-249 240-313 313-334 334 334-294 294-67 67-31	30 26.7°/min 22.5°/min 8.75°/min 2.5 14.5°/min 47.8°/min 3.8°/min	4	Al_2O_3 T	copperish gold	.016"	.687	fair
31	25 60 25-249 249-313 313-334 334 334-294 394-67 67-31	20 30 26.7°/min 22.5°/min 8.75°/min 2.5 14.5°/min 47.8°/min 3.8°/min	4	Al_2O_3 T	greyish silver	.016"	.120	excellent
31	25 60 200 325	20 20 35 30	1	Al_2O_3 T	black/silver	>.020"	.134	poor
34	6 25-249 249-313 313-334 334 334-294 294-67 67-31	40 26.7°/min 22.5°/min 8.75°/min 2.5 14.5°/min 47.8°/min 3.8°/min	4	cell JPL	whitish silver	B	.035	excellent (poor for connecting bar)
34	65 25-249 249-313 313-334 334 334-294 294-67 67-31	30 26.7°/min 22.5°/min 8.75°/min 2.5 14.5°/min 47.8°/min 3.8°/min	4	Al_2O_3 JPL	whitish silver	B	.039	excellent
34	65 200 350	40 25 25	1	cell JPL	whitish silver	A	.028	excellent
36	60 25-249 249-313 313-334 334 334-294 294-67 67-31	30 26.7°/min 22.5°/min 8.75°/min 2.5 14.5°/min 47.8°/min 3.8°/min	4	cell JPL	whitish silver	B	.042	fair to good
36	60 25-249 249-313 303-334 334 334-294 294-67 67-31	30 26.7°/min 22.5°/min 8.75°/min 2.5 14.5°/min 47.8°/min 3.8°/min	4	Al_2O_3 JPL	whitish silver	B	.078	excellent

Substrate: Al_2O_3 = AlSiMag 838

glass = Soda lime silica microscope slide

Si Wafer = Commercial polished Si Wafer from Monsanto

cell = JPL supplied Solar Cell substrate

Pattern: T = Turner Laboratory Standard Pattern with 203 squares printed through a 200 mesh screen

JPL = JPL Supplied Patterns printed through a 325 mesh screen.

Table 4.4 . Properties of Ag-Pd Inks.

	Firing Sequence							
Ink#	Temp. (°C)	Time (min)	Type of Furnace	Substrate* Pattern	Surface Appearance	Line Defin.	Sheet Resist. (Ω/□)	Adhesion
501	25	30	4	Al_2O_3	silvery grey	B	.110	fair
	60	20						
	29-263	6.7°/min		JPL				
	263-292	4.6°/min						
	292	113						
	292-245	7.0°/min						
	245-62	18.3°/min						
	62-25	1.1°/min						
502	65	30	4	Al_2O_3	silvery grey	B	.097	fair
	29-263	6.7°/min						
	263-292	4.6°/min		JPL				
	292	11.3						
	292-245	7.0°/min						
	245-62	18.3°/min						
	62-25	1.1°/min						
503	65	30	4	Al_2O_3	silvery grey	B	.114	fair
	29-263	6.7°/min						
	263-292	4.6°/min		JPL				
	292	11.3						
	292-245	7.0°/min						
	245-62	18.3°/min						
	62-25	1.1°/min						
504	25	10	3	Al_2O_3	silvery grey	B	.103	fair
	29-263	6.7°/min						
	263-292	4.6°/min		JPL				
	292	11.3						
	292-245	7.0°/min						
	245-62	18.3°/min						
	62-25	1.1°/min						

Substrate: Al_2O_3 = AlSiMag 838

glass = Soda lime silica microscope slide

Si Wafer = Commercial polished Si Wafer from Monsanto

cell = JPL supplied Solar Cell substrate

Pattern: T = Turner Laboratory Standard Pattern with 103 squares printed through a 200 mesh screen.

JPL = JPL Supplied Pattern printed through a 325 mesh screen.

5. FUTURE PLANS

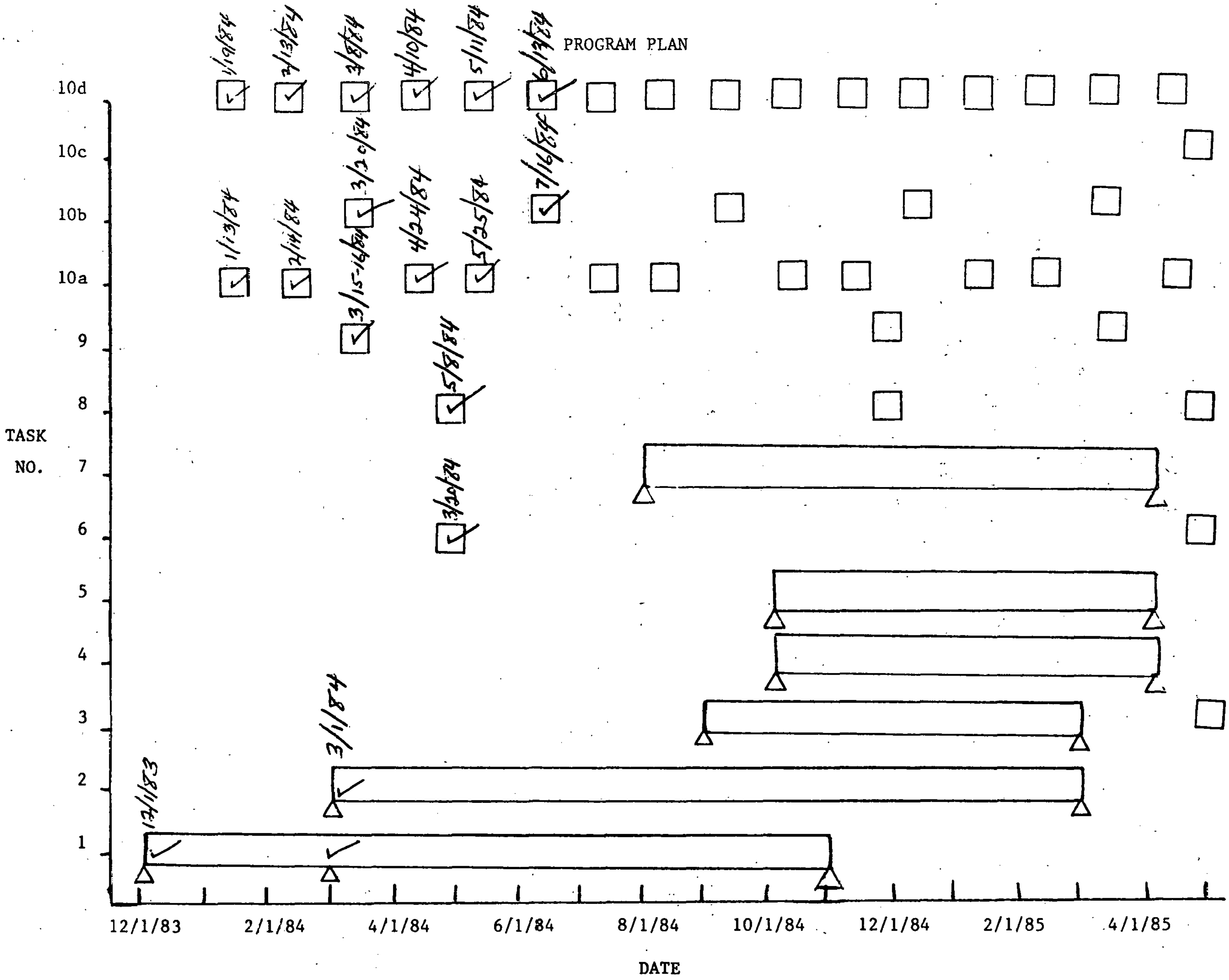
The immediate future work will concentrate on optimizing the chemistry of the Ag/Pt ink. Ink 34, which gave the best films discussed in this report, will be further evaluated (e.g. shelf life, long term adhesion of fired films, etc.). The search for an appropriate platinum compound will continue because of the potential partial sublimation problem of the Pt 2,4 pentane dionate used in Ink 34. Promising compounds will be formulated into inks, with Ink 34 used as a basis for comparison. If an ink made with a superior Pt compound proves to be as good as Ink 34, the ink composition will be frozen and the firing sequence optimized. At this point, studies with multilayer films will be initiated in order to reduce the series resistance presented to the solar cells.

Studies of the mechanism of adhesion between the films and the Si solar cells will be initiated during the next quarter. This research will also require studies of film microstructure. The adhesion model to be developed must include the effects of time and environment on adhesion.

6. SCHEDULE

The list of tasks and the updated program plan are attached. All milestones have been reached as scheduled, except for the distribution of this report which was delayed due to the vacation schedule of the co-principal investigators.

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



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