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DEVELOPMENT OF ECONOMICAL IMPROVED THICK FILM SOLAR CELL
CONTACT

Quarterly Report No. 3 for May-July 1979

By
Bernd Ross

August 1979

Work Performed Under Contract No. NAS-7-100-955164

Bernd Ross Associates
San Diego, California

MASTER

U.S. Department of Energy

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Solar Energy

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DEVELOPMENT OF ECONOMICAL
IMPROVED THICK FILM SOLAR
CELL CONTACT

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QUARTERLY REPORT NO. 3

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May - July 1979

August 1979

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Various measurement methods of series resistance and specific contact resistance were considered. Several attempts were made to produce eutectic alloys in air and in neutral (nitrogen) atmospheres, but the resulting product was not considered satisfactory. A commercial source of eutectic aluminum-silicon and aluminum-germanium was located. Fifteen all metal pastes were fabricated during this reporting period including 12 base metal pastes. Silver inks fired in hydrogen were non-adherent. Electrical results of screened solar cell tests were poor, indicating diffused layer penetration. Similar results occurred with titanium-palladium-silver controls. A survey was made of alloys containing nickel and copper. Solubilities of nickel, silver and copper in various low melting metals were calculated from the phase diagrams and plotted. An ink milling procedure was written for all metal inks. Base metal powders were ordered and partially received. A tube furnace was purchased and installed, along with a gas handling system, designed for hydrogen and nitrogen firing.

2.0 INTRODUCTION

The potential for economy and efficiency has been demonstrated for the thick film metallization process using screen printing for solar cell electrodes. However, process reliability and materials economy remain deficient. It is believed that these deficiencies can be removed by the use of ink formulations designed specifically for silicon solar cells, departing from ceramic technology tradition and utilizing all metal systems.

The objectives of this investigation are as follows:

1. Eliminate the glass frit which has been the conventional liquid phase sintering medium and adhesive for metallization inks.
2. Provide an appropriate metal which can serve as the liquid phase sintering medium.
3. Find a chemical constituent which effectively removes the native oxide from the silicon during the firing step, which can be made part of the ink, and which either becomes fugitive or remains an inert part of the matured metallization.
4. Maintain cognizance of the cost objectives of the LSA Project in selecting materials and processes.

The measurement of contact resistance has been somewhat problematical since the work with thick film electrodes began. Several methods have been utilized in the past using either silicon material or solar cells as a point of departure. A relatively simple method uses a silicon rod of simple shape shown in Figure 1. The resistivity of the rod is determined by other means (such as a four point probe). The resistance of the rod and contacts is measured across the two electrodes. The contact resistance is

$$R_C = R - \rho \frac{L}{A}$$

where R = total resistance in Ω

ρ = resistivity of the
silicon material in Ωcm

L = length of rod in cm

A = area of contact in cm^2

While the method has the virtue of analytical simplicity, it is experimentally somewhat cumbersome and requires resistivity determination prior to attaching contacts, with no guarantee that the resistivity remains unchanged as a function of the firing process. In our measurements the series resistance between two adjacent squares of a screened standard pattern was used. The actual current flux pattern in such a configuration is complex and can be handled by using the formalism of source and sink images¹. For our purposes an average current path was estimated, the resistivity of the wafers was in a fairly tight group and only relative measure-

ments were required. Nevertheless, the variation in results and reproducibility problems caused us to lose confidence in the method.

In dealing with diodes or solar cells, contact resistance is a part of the series resistance, including IR drops of semiconductor regions and electrode regions themselves. While some of these can be measured with difficulty, assumptions as to their magnitude are usually made. The series resistance can then be determined from an extended IV curve ($\log I$ versus V) by noting the departure from the exponential diode characteristic². Another method utilizes multiple light levels with series resistance measured by taking incremental currents and noting the shift in corresponding terminal voltage³. (See Figure 2). None of the above methods were considered optimal for this investigation. Therefore, a literature study was undertaken to find a better method.

Fig. 1. Simple Resistance - Contact Resistance Measurement.

Fig. 2. Series Resistance Measurement by Illumination Level Change (L. D. Swanson's Method)

A reference was found to a contact resistance measurement proposed by W. Shockley. The method was designed to accommodate field effect transistors and was described by Hower et al⁴. The measurement scheme is well-suited to contact resistance evaluation of electrodes or electrode arrays on solar cell material prior to cell processing, pn-junction formation, etc. Since the existence of a conducting sheet on the opposite side of the wafer would severely alter the current flux densities and contours, the test would be less suitable for completed solar cells. While the dimensions of the semiconductor layer and electrodes are quite different in the case of the solar cell experiments from the original FET designs, there are no fundamental reasons why the measurement should not work for our purposes. The method can best be illustrated by Figure 3. Figure 3 (a) shows a contact metal layer on a semiconductor wafer with dimensions x and z (with y dimension arbitrary). The schematic (b) below (a) considers the semiconductor a chain of sheet resistances $R_{\square}$ (in units of ohms per square) connected to the grounded metal contact by contact resistances R_c in ladder network fashion. Since the metal resistance is very small compared to the other resistances involved, it may be neglected in this formulation. The current I flowing through the semiconductor wafer enters the region below the metal contact at $x = 0$. A portion of the current, ΔI enters the electrode through R_c and diminishes the wafer current I . This

results in a potential distribution $V(x)$ given by Figure 3(c).
 The differential equation describing the stated conditions is

$$\frac{R_C}{R_D} \frac{d^2 V(x)}{dx^2} - V(x) dx = 0$$

with solution

$$V(x) = V_0 \exp\left(-\frac{x}{L_T}\right)$$

where $L_T \equiv$ Transfer length

$$= \sqrt{R_C/R_D}$$

All other quantities were previously defined.

The method was reduced to practice by designing masks shown in Figure 4. The current source and drain contacts were squares of 2.5mm edge length spaced to allow potential probe contacts to be placed at equal intervals between them. The small contacts were 0.25mm wide, 0.6mm long and placed on 0.5mm centers. Separate masks were fabricated so that current and voltage contacts could be separately screened.

Figures 5 and 6 show actual photomicrographs of the electrode patterns.

Measurements are performed as follows: A constant current source is connected between the large squares. The potential of the contact lines is probed by connecting one of the current electrodes on the LOW side of a digital voltmeter with good resolution (0.1 mV or better). The HIGH side of the voltmeter is then used to measure the potential on each line electrode. The potential measurements $V(x)$ are then plotted as the ordinate against the dimensionless abscissa x . The transfer length is obtained by extrapolating the straight portion of $V(x)$ beyond $x=0$ to $V(x) = 0$. Physically, the transfer length is the distance that the current must flow under the contact before $0.632I$ is transferred to the contact. The resistance $R_{\square}$ can be calculated from

$$R_{\square} = \frac{\Delta V(x)}{I} \frac{Z}{L}$$

Fig. 3. Metal Semiconductor Contact.

Figure 4. Masks for Contact Resistance Measurement

Fig. 5. S058 screened contact pattern for contact resistance measurement on polished silicon wafer prior to firing (Optical microscope magnification 13X).

Fig. 6. S057 fired at 600°C in air screened on lapped silicon wafer. Scratches on contact pattern indicate probing from previous measurement.

where ΔV = the voltage drop along
in Volts

$L \equiv$ length (in cm) of portion
of the array carrying

$I \equiv$ current in amps

$Z/L \equiv$ number of squares in
interval L (dimension-
less)

The contact resistance R_c (in Ωcm^2) is obtained from the relation

$$R_c = L_T^2 R_{\square}.$$

Initial measurements were plotted to gain familiarity with the method. The best straight line was drawn through the voltage points and the intercept on the x axis gave the transfer length L_T . Subsequently, a program was used to obtain the equation of the line using a regression coefficient to provide a measure of the degree of fit ($K = 1$ is the best obtainable). Data and plots for S057 fired at 550°C and 600°C in nitrogen are given in the appendix. Results for S057, S058, and S059 have given values of contact resistance from the mid $10^{-4} \Omega\text{cm}^2$ to mid $10^{-3} \Omega\text{cm}^2$.

4.0 METAL SYSTEMS CONSIDERATIONS

4.1 FABRICATION OF GERMANIUM-ANTIMONY EUTECTIC POWDER

Initial attempts to produce eutectic alloys in a nitrogen atmosphere with germanium (Ge) and aluminum (Al) as well as antimony (Sb) powders respectively, were considered unsuccessful because of excessive oxidation. The attempt was repeated using a tube furnace with a hydrogen atmosphere continuously flowing past the sample (courtesy Applied Solar Energy Corp.). The constituents were weighed (11% Ge in Sb), mixed and packed in a Pyrex^R beaker. The beaker was inserted through a flame curtain into the quartz tube of the furnace and placed in a relatively cool position. The beaker remained for five minutes in the warm hydrogen stream ($\sim 0.5 \frac{\text{liter}}{\text{min}}$) to allow purging the powder of a major portion of the entrapped air. Then the beaker was pulled into the center of the furnace which had equilibrated at 624°C and allowed to remain for 15 minutes. After insertion, the powder separated into two equal portions (vertically), with a gas space in between. After two minutes in the hot zone the gas space collapsed and densification was observed. After melting was visible, the process went to completion in two minutes. A black powder dross was found on top of the metal button. The dross was removed and the metal was found to be quite brittle and could easily be reduced to a coarse grained powder with a hammer in a plastic bag. Further reduction in grain size was easily accomplished with a mortar and pestle.

A solar cell experiment was done at the premises of Applied Solar Energy Corporation with the cooperation of P.A. Iles and others. Since the antimony fraction of the inks is highly susceptible to oxidation, the ink firing operations were done in flowing hydrogen (10 minutes). Upon insertion of the cells it was noted that the screened back contact sometimes lifted and curled up. Similarly the adhesion of the front contact was very poor in some cases, coming off while maintaining identity as grid lines or collector busses.

In a previous experiment a similar result was observed with an antimony containing ink (S034). The explanation at that time was thought to be the formation of a eutectic liquid (antimony-silver), melting at 485°C with 44% antimony. It was felt that the surface tension resulting from the additional liquid might overcome the adhesion to the silicon. The quantities involved make this hypothesis weak:

Pb (liquid) 5 wt%

(Sb 0.1 wt% + Ag 0.1 wt%) (liquid).

The additional amount of liquid can only be

$$\frac{0.2 \text{ Ag (+ Sb)}}{5.0 \text{ Pb}} = .04 \text{ or } 4 \text{ wt\% of the liquid.}$$

The other ink utilized S059, contained Ge-Al eutectic and gallium chloride. Print fragments from the lifted electrodes were mounted

and subjected to SEM examination. The results can be seen in the following pages. Figure 7 shows S034 (5% Pb, 2% AgF, 93% Ag, 0.1% Sb) at low magnification (200X). Figures 8, 9 and 10 show increasing magnification, and at least the appearance seems to support the above hypothesis showing a continuous sheet of metal with highly occasional pores. This is quite different from the lacy matrix of sintered silver grains which are typical for these electrodes. At the last two magnifications the rod shaped structures can be seen which were previously identified as the precipitated lead⁵.

The appearance of the other electrodes is different and Figures 11 and 12 show portions from a print of S063 (masterpaste with germanium-antimony eutectic and probably oxides) at increasing magnifications, 510X and 5100X respectively. The color difference could be due to oxide mixtures, bearing in mind that the imaging current of the SEM derives from secondary electron yield rate, which could, in turn, be caused by charging effects. In any case the 'solid sheet' nature of the previous pictures is absent and we have a typical sintered structure. The occasional horizontal raster effect seen in Figure 12 is an artifact of the instrumentation.

The electronmicrographs from S059 (masterpaste + 5% Ge-Al eutectic + 1% gallium chloride) appear to be a combination of the previous pictures. Figures 13, 14 and 15 show magnification of 1000X, 5000X and 10,000X of the subject peeled electrode. The discoloration

Fig. 7. Photomicrograph of peeled electrode print S034 fired in hydrogen at 650°C taken on Cambridge SEM at magnification 200X.

Fig. 8. Same as Fig. 7 at magnification 1000X.

Fig. 9. Same as Fig. 7 at magnification 5000X.

Fig. 10. Same as Fig. 7 at magnification 10,000X.

effect is the same as in the case of S063, supporting the contention of oxide mixture, but the electrode appears oversintered with few voids. At this point we do not have an adequate explanation of the observed phenomenon.

Fig. 11. Photomicrographs of peeled electrode print S063 fired in hydrogen at 650°C taken on Cambridge SEM at magnification 510X.

Fig. 12. Same as Fig. 11 at magnification 5,100X.

Fig. 13. Photomicrograph of peeled electrode of print S059 fired in hydrogen at 650°C taken on Cambridge SEM at magnification 1000X.

Fig. 14. Same as Fig. 13 with magnification 5,000X.

Fig. 15. Same as Fig. 13 with magnification 10,000X.

Cells tested consisted of four controls with titanium-palladium-silver (Ti-Pd-Ag) evaporated front and back contacts sintered at 600°C and 650°C respectively, three textured front surface cells and three cells with regular polished front surfaces. All of the surviving cells had Ti-Pd-Ag evaporated back contacts and were fired at 600°C or 650°C in hydrogen. The original curve traces are reproduced in the Appendix 2.

Of the four control cells, two showed sharp decreases in open circuit voltage, which was an even more serious problem in the experimental cells. This might be due to a junction processing problem resulting in spotty low shunt resistance. The restricted number of cells is due to a cell availability problem at the time the experiment was run.

All the experimental cells had poor open circuit voltages. The cells fired at 650°C showed open circuit voltages about half of those fired at 600°C, indicating more severe shunting at the higher temperature. Likewise, the ink containing the hydrogen-reacted Ge-Sb eutectic gave much higher open circuit voltage than the nitrogen-air reacted material (See Table 1).

Five percent of this material was combined with masterpaste S032 (93% Ag - 5% Pb and 2% AgF) to result in S064 for use on the phosphorous diffused layer. Other inks tried in this experiment were S063 (composition similar to S064 but with the eutectic alloyed in air) and S059, a P type ink with a 5% germanium-aluminum eutectic and 1% gallium chloride. The Ge-Al eutectic is also suspect since it was reacted in a nitrogen atmosphere containing unknown amounts of room air.

Table 1. Electrical Results

PASTES	TEMPERATURES			
	600°C		650°C	
	Isc (A)	Voc (V)	Isc (A)	Voc (V)
S063	--	--	.3	.06
S064	.41	.26	.3	.13
Controls	.58	.56	.49	.52
Controls	.58	.27	.47	.12

The silver-lead and silver-tin systems have been investigated previously⁶ with good results in the case of silver-lead, leading to low temperature liquid phase sintering. In view of the above it is useful to review the phase diagram⁷ of this system, Fig. 16, and plot the solubility curve, Fig. 17.

Fig. 16. Equilibrium Phase Diagram of Silver-Lead System.

The solubility of silver in the lead rich melt can be obtained from the locus of the intersections of isotherms with the liquidus curve.

SILVER DISSOLVED
IN LIQUID LEAD

Fig. 17. Solubility Curve of Silver-Lead System.

The solubility of silver in liquid lead is quite large.

Figure 18 shows the phase diagram of the nickel tin system and Fig. 19 the corresponding solubility plot. It can be seen that the solubility of silver in lead at 400°C is almost exactly one order of magnitude higher than the nickel solubility in tin at 400°C. On the basis of solubility only, the nickel tin system does not have a high probability of success.

Fig. 18. Equilibrium Phase Diagram of Nickel-Tin System.

NICKEL DISSOLVED
IN LIQUID TIN

Fig. 19. Solubility Curve of Nickel-Tin System.

The phase diagram of nickel-lead is shown in Figure 20. It can be seen that a considerable miscibility gap exists. The solubility of nickel in the lead melt is given in Fig. 21 and is relatively low up to quite high temperatures.

Fig. 20. Equilibrium Phase Diagram of Nickel-Lead System.

NICKEL DISSOLVED
IN LIQUID LEAD

Fig. 21. Solubility Curve of Nickel-Lead System.

The dashed portion of the curve is estimated since no data was found in the literature.

A number of nickel systems have more favorable solubility factors, however they are often associated with metals having fairly high vapor pressures. Some of these are nickel-antimony, nickel-zinc and nickel bismuth. The phase diagrams of these systems are reproduced in the appendix⁹.

A phase diagram of nickel-silicon is shown in Figure 22.

Figure 22. The nickel silicon system

Aside from its complexity, it shows the temperature of the lowest melting eutectics between silicon and nickel, which should not be approached in any firing cycles. While this is an absolute temperature limit, melting may occur at lower temperatures depending upon other additives to the paste composition such as aluminum and germanium.

The copper systems were also examined. The copper-lead phase diagram is given in Figure 23.

Figure 23. The equilibrium phase diagram for the copper-lead system.

The copper solubility curve in liquid lead is shown in Figure 24. Again the solubility is quite low until considerable temperatures are reached.

COPPER DISSOLVED
IN LIQUID LEAD

Figure 24. Copper solubility in a lead melt

Other systems again showing a higher solubility of copper can be found in the appendix. The copper aluminum system may be singled out as an interesting one, as it combines a relatively high melt solubility with a metal commonly used as doping metal in p-type silicon. However the combination of the metals tends to have severe corrosion problems in wet atmospheres.

The figure is a temperature-composition phase diagram for the Cu-Si system. The main diagram plots Temperature in degrees Celsius (300 to 1500) against Atomic Per Cent Silicon (0 to 100). It shows the liquidus, solidus, and solvus lines, with phase regions labeled α (Cu), β, γ, δ, and ε. Key temperatures include 1083°C (melting of Cu), 858°C (peritectic), and 358°C (eutectic). An inset diagram shows a magnified view of the 30-35% Si region, highlighting the β, γ, and δ phases and their solubility limits.

In the use of copper in contact with silicon further comments are appropriate. Copper was suspected early in semiconductor technology as the major recombination center in germanium and silicon (Collins et al⁸). Work by the present author in 1957 indicated that silicon with a high initial copper concentration introduced at high temperatures, but undergoing slow cooling suffered no minority carrier lifetime degradation⁹. Nevertheless copper in silicon devices has remained suspect for a

quarter century. A recent study of the severity of various impurities in silicon material¹⁰ has corroborated the author's experience. Another degradation mechanism attributable to copper is its tendency to diffuse rapidly through the lattice and precipitate in clusters on defects or dislocations, leading to decoration of defects (Dash¹¹). Therefore a copper spike can be driven through the space charge region of a p-n junction by allowing copper to diffuse and aggregate on an edge dislocation perpendicular to the wafer and junction. This can lead to severe junction shunting, particularly when an array of dislocations exists. Since copper is a particularly rapid diffuser, direct contact between silicon and copper should be avoided. The role of barrier metals is presently being investigated by several researchers. In any case, processing steps and structures must be carefully planned in the presence of copper metallization.

5.0 METAL PASTE PREPARATIONS

Although the phase diagrams and solubility curves did not look very favorable, it was decided to do experiments with nickel-lead and nickel-tin, copper-lead and copper-tin due to the immediate availability of materials, and the benign character of lead (chemical resistance, oxidation resistance) in our experience with the lead silver system and others.

Table 2 shows the constitution of all metal inks compounded during this period.

Table 2.
All Metal Pastes Fabricated
During Current Quarter

PASTE CODE	MASTER PASTE	METAL	SILVER FLUORIDE	METAL FRIT	DOPANT
S062	S032	Silver	2%	--	10% Ge-Al [*] , Ga
63	S032	Silver	2%	--	5% Ge-Sb [*]
64	S032	Silver	2%	--	5% Ge-Sb
65	"	Nickel	5%	Lead 5	0
66	"	"	"	" 10	0
67	"	"	"	" 20	0
68	"	"	"	Tin 5	0
69	"	"	"	" 10	0
70	"	"	"	" 20	0
71	"	Copper	"	Lead 5	0
72	"	"	"	" 10	0
73	"	"	"	" 20	0
74	"	"	"	Tin 5	0
75	"	"	"	" 10	0
76	"	"	"	" 20	0

* eutectic not satisfactory

Firing of these inks awaits operational status of the tube furnace recently purchased and the gas handling system being installed.

Masks were fabricated adapting the Shockley method for contact resistance measurement to thick film technology. A series of measurements were made on pastes with eutectic additives screened onto modest resistivity p-type silicon. Results were good, but must be viewed with caution until the measurements can be verified by independent means. Problems with measurement reproducibility were experienced and were due to the digital voltmeter.

Early pastes made with eutectic additions for doping purposes have been suspect due to the likelihood of oxidation of the powder constituents prior to eutectic alloying.

Hydrogen firing has produced adhesion problems, possibly relating to increased powder wetting, or interference with the etching action of the silver fluoride fluxing agent. In the case of base-metal inks the situation may change and the experimental evidence must be assessed at that time.

A detailed analysis of solubilities of copper and nickel in various liquid metals was made and compared with silver solubilities in the systems in which experience was acquired. Results of solar cell tests to date have been disappointing. This may be partially due to inadequate eutectic powders.

In order to allow increased flexibility in experimentation a tube furnace was purchased. A gas-handling system, gases to allow use of reducing atmospheres, as well as clean inert atmospheres will be acquired at the facility of Bernd Ross Associates.

The furnace and associated equipment will be installed and calibrated. Additional nickel and copper sources will be sought to establish a range of physical powder parameters.

Further eutectic and doping experiments will be done after the furnace installation is operational.

Pastes will be prepared from available stock of nickel and copper powder with tin and lead. Solar cell tests will be done with base metal inks doped with eutectic powders, assuming the metallurgical problems are surmountable.

8.0 PROGRESS ON PROGRAM PLAN

ACTIVITY

MONTHS AFTER AWARD

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16

LITERATURE SEARCH AND
BACKGROUND WORK

ORDER MATERIALS

PERFORM EXPERIMENTS

PERFORM SEM ANALYSIS

REPORTS AND DATA
PREPARATION

REVIEW MEETINGS

X X X X X X X X X X

PLANNED X

ACTUAL .

8.0 PROGRESS ON PROGRAM PLANT (continued)

PROGRAM ACTIVITY	MONTHS AFTER AWARD							
	1	2	3	4	5	6	7	8
PHASE I 1.0								
PHASE II 2.0								
1.1 Ohmic Contact Optimization	▽			Δ				
2.1	▽					Δ		
1.2 Contact Conductance		▽Δ						
2.2				▽Δ				
1.3 Pull Test			▽Δ					
2.3				▽Δ				
1.4 Temperature-Humidity Cycle			▽Δ					
2.4						▽Δ		
1.5 Solder Leach Resistance				▽Δ				
2.5						▽Δ		
1.6 Firing Temperature-Time Optimization	▽		Δ					
2.6					▽	Δ		
1.7 Vehicle Percent Solids Optimization			▽Δ					
2.7					▽Δ			
1.8 Reports and Documentation	▽							Δ
1.9 Review Meetings	X	X	X	X	X			

9.0 APPENDIX

APPENDIX A.1

→ 50 μm

$$R_{\square} = \frac{0.173 \text{ V}}{0.005} \cdot 0.10 = 3.46 \Omega/\square \quad (\text{Eqn. (11) p 10})$$

$$R_c = L_r^2 R_{\square} = (3.2 \cdot 50 \cdot 10^{-4} \text{ cm})^2 \cdot 3.46 \Omega/\square$$

$$= 8.86 \cdot 10^{-3} \Omega \text{ cm}^2$$

SAMPLE PLOT + CONTACT RESISTANCE CALCULATION

$$R_{\square} = \frac{0.276}{0.005} \cdot 0.1 = 5.4 \Omega/\square$$

$$R_c = 7.2 \cdot 10^{-4} \Omega \text{cm}^2$$

10 Amp.

CONTROLS

600°C - 10 Hz

100 mA/cm

TEXTURED
FRONT SO63

650°C - 10 min

H₂

100 mA/cm

100 mV/cm

T₁ P₁ D₁ 2C

FRONT

SOL4- 650° - 10 Hz

100 mA/in

100 mV/in

T. P. A. B. C.
FRONT S064 - 600°C/10 Hz ✓

100 mA/11

100 mA/12

Fig. 36. Equilibrium Phase Diagram of Nickel-Antimony System.

Fig. 37. Equilibrium Phase Diagram of Nickel-Zinc

Fig. 38. Equilibrium Phase Diagram of Nickel-Bismuth.

Fig. 39. Equilibrium Phase Diagram of Copper-Zinc.

Fig. 40. Equilibrium Phase Diagram of Copper-Aluminum System.

Fig. 41. Equilibrium Phase Diagram of Copper-Germanium System.

Fig. 43. Equilibrium Phase Diagram of Copper-Tin System.

APPENDIX A.4 Milling Procedure For All Metal Pastes

Materials

An Anthony four-by-eight three roller mill is used in this procedure. Auxiliary tools are a single edge razor blade, a stainless steel spatula, an elastomer squeegee 2 1/2" x 2 1/2", 4" diameter bowl, 6" Petri dish with cover, grind gage.

Procedure

- ① A four inch bowl is used for the metal powder, low melting metal frit and vehicle.
- ② The silver fluoride is taken from the hermetically sealed bottle just prior to milling and placed into a 6" Petri dish with cover.
- ③ is applied to the first roller with the stainless steel spatula, approximately 25 grams prior to starting the mill. The mill is started. The remainder of ① is added after the mill is running. The third roller remains out of contact with the second until after the mill is started. The third roller is engaged after 2 minutes of running time.

The endplate separation determines the grinding speed and fineness of grind (other parameters remaining constant). Closest plate distance - coarsest grind.

The end apron picks up the slurry from the third roller. The metal is bladed back from the third to the first roller. Material thrown or squeezed beyond the endplates is scraped off the turning rollers with the razor blade (after about three minutes of running time).

After about 10 minutes of milling time the fineness of grind is checked by blading on the grind gage. A typical grind number at this point for nickel paste is $\sim 12\mu\text{m}$ (depending upon a number of parameters including particle size of starting material, roller speed ⁽¹⁾ and spacing, ⁽²⁾ endplate setting, powder-vehicle ratio, etc.)

At 15 minutes milling time the silver^② fluoride is added to the paste accumulation. This is done by adding 25% of the total amount of silver fluoride at a time (for instance x times 0.5 grams in a typical composition). The number of silver fluoride additions will depend upon the amount of total ink to be prepared, and the amount of silver fluoride to be added.

- (1) Roller #1 ~ 46 RPM
Roller #2 ~ 180 RPM
Roller #3 ~ 800 RPM
- (2) Roller adjustment: Generally when the rollers are too close (tight adjustment), the paste tends to run beyond the endplates. When the roller spacing is too large (loose adjustment) the paste tends to run between rollers as a visibly unequal bead. Also the paste transport between rollers is too rapid - bead loss between rollers.

A typical mill run takes about 30-35 minutes including mill stopping times. At the end of the milling run the material on the rollers is scraped off, in addition to the paste on the apron and on the endplates. This material is added to the milled end product. A final grind size check should be made on the grind gage with possible remilling if the grind is too coarse or the distribution too wide.

Mill cleanup is done by washing all paste exposed parts of the mill with toluene or a suitable substitute solvent (for instance 3 to 5% toluene in kerosene).

It has been noticed that milling of silver fluoride may result in dark stains on the surface of the steel roller. This can be minimized by use of dry raw material, extreme low humidity conditions during milling, the use of stainless steel rollers or alumina faced rollers.

REFERENCES

1. A. Uhler Jr., Bell Syst. Techn. Journ. 34, 105 (Jan 1955)
2. H.J. Hovel, Semiconductors and Semimetals, R.K. Willardson & A.L. Beer, Editors, Vol. II, p. 64, Academic Press (1975)
3. L.D. Swanson and L.W. Schmidt, Hoffman Semiconductor Division Publication (1960)
4. Hower, Hooper, Cairns, Fairman and Tremore in Semiconductors and Semimetals, Volume 7 Part A, p. 178-183, Academic Press (1971)
5. B. Ross Final Report Automated Array Assembly Task DOE/JPL 955164-79/7 p. 38 (Apr 1979)
6. B. Ross Final Report Automated Array Assembly Task DOE/JPL 955164-79/7 p. 36 (Apr 1979)
7. M. Hansen and K. Anderko "Constitution of Binary Alloys", 2nd Edition McGraw-Hill, New York, N.Y. (1958)
8. C. B. Collins and R.O. Carlson, Phys. Rev. 108, 1409 (1957)
9. B. Ross and J.R. Madigan, Phys. Rev. 108, 1428 (1957)
10. R.H. Hopkins, J.R. Davis, P.D. Blais, A. Rohatgi, R.B. Campbell, P. Rai-Choudhury, R.E. Stapleton, H.C. Mollenkopf and J.R. McCormick, Fifteenth Quarterly Report, Silicon Materials Task DOE/JPL-954331-79/7, p. 43 (Jul 1979)
11. W.C. Dash, J. Appl Phys. 37, 1193 (1956)