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THICK-FILM MATERIALS FOR SILICON PHOTOVOLTAIC CELL MANUFACTURE

by M. B. Field

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16. Abstract

Thick-film technology is applicable to three areas of silicon solar cell fabrication; metallization, junction formation, and coating for protection of screened ohmic contacts, particularly wrap-around contacts, interconnection and environmental protection. Both material and process parameters were investigated. Printed ohmic contacts on n-and p-type silicon are very sensitive to the processing parameters of firing time, temperature, and atmosphere. Wrap-around contacts are easily achieved by first printing and firing a dielectric over the edge and subsequently applying a low-firing temperature conductor. Interconnection of cells into arrays can be achieved by printing and cofiring thick-film metal pastes, soldering, or with heat-curing conductive epoxies on low-cost substrates. Printed (thick) film vitreous protection coatings do not yet offer sufficient optical uniformity and transparency for use on silicon. A sprayed, heat curable SiO_2-based resin shows promise of providing both optical-matching and environmental protection.

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TABLE OF CONTENTS

SUMMARY

The objective of this work was to apply hybrid electronic circuit technology to the manufacture of silicon photovoltaic devices and arrays. Specifically, the technical feasibility and cost-effectiveness of screen-printed conductive contacts, screen-printed insulating films, and interconnection methods was investigated.

The scope of this contract was relatively limited in time and effort. Specific areas of solar cell processing where the use of thick-film techniques were evaluated are (a) ohmic contacts to n-and p-type silicon. Both noble metal (Ag)and non-noble metal (Al, Ni and alloys) were formulated and applied. A Ag paste on n-type layers and Al alloy or Al-Ag mixture on p-type silicon formed ohmic contacts with excellent adhesion, (b) wrap-around contacts, where the n and p pads are coplanar. This configuration was achieved by first printing and firing a dielectric material on the edge of the 2 cm by 2 cm by 0.2 mm cells. The dielectric was well matched in thermal expansion to silicon and exhibited optimal flow characteristics. A low-firing temperature conductive paste was subsequently applied over the edge, (c) interconnection of the cells in modular arrays. These modules can be fabricated and wafers attached by printing and cofiring thick-film pastes at 550°C, soldering, or with heat-curing conductive epoxies on prepatterned anodized aluminum or fiberglass laminate substrates, and (d) passivation (protection) of the cell surface. A sprayed, heat-curable, SiO_2-based resin shows promise of providing both optical-matching and environmental protection. The resin is cured at 200°C or less.

INTRODUCTION

The established procedure for silicon photovoltaic cell manufacture contains expensive vacuum processes and individual, labor-intensive operations performed on a batch or small lot basis. To fully realize the savings inherent in automated production it is necessary to consider other technologies, particularly nonvacuum techniques. Silicon wafers must be metallized, interconnected into grids of series and parallel combinations, provided with optical coatings, and encapsulated or protected from the atmosphere. The method of printing inks through patterned screens can conceivably provide all of these functional coatings without the use of vacuum equipment. This technology is mature, highly automated, and reliable. Materials and sintering schedules must be developed which are specifically directed toward large-area silicon junction diodes, as most pastes available now were invented and optimized for use on ceramic substrates.

Successful printed contacts and silicon solar cel protection were reported in 1975 as part of NASA Contract NAS3-18566. This preliminary study indicated no fundamental barrier exists to screen-printing ohmic contacts on silicon and also pointed up the inadequacies of present materials.

The scope of the work reported here was as follows:

A. Investigate low-cost screen-printable materials for n- and p-type silicon. Evaluate their usefulness.
B. Invent and test materials for edge-insulation of silicon wafers and fabricate ''wrap-around'' contacts.
C. Perform exploratory development applying thick-film materials and processes to the problems of cell interconnection and passivation.

In the time available for this work topics A and B received the most attention. More emphasis was placed on material composition and properties than processes as the largest gap in our knowledge seemed to fall in that area.

MAIN TEXT

I. Printed Thick-Film Solar Cell Contacts

A. Contacts to n-type silicon

Materials

Thick-film metallization is patterned material more than several microns thick. Thick-films are usually applied to substrates ''by silk-screen'' printing a viscous paste. The paste or ink normally contains four constituents: (a) an organic solvent, (b) a polymeric film-former, (c) a bonding agent, and (d) a finely-divided metal powder. The solvent and film-former provide viscosity adjustments and dried (green) strength to the deposited film. The bonding agent both fluxes the metal powder and adheres it to the substrate. The specific metal composition is chosen for its desirable physical properties, i.e., conductivity, solderability, sintering temperature, etc.

Ohmic contacts to n-type silicon are defined as those metals which (a) are lower in electrical conductivity than the particular n-type Si under consideration, and (b) exhibit a linear behavior on a current/voltage graph. In the special case of ''n on p'' solar cells a further requirement is the formation of ohmic contact to a very thin n-type silicon layer 0.5 microns or less in thickness. For this use the tradeoff is between ohmicity and adhesion. Theoretically many metals, when applied at sintering temperatures and times common to thick-film technology, will not diffuse through the n-type layer of n on p solar cells. Practically it is well known that ''spikes'' or shorted contacts often appear with both noble and non-noble metal contact materials. The work described below was aimed at producing printed thick-film ohmic contacts on thin n-type silicon layers. The major difficulty encountered was diffusion through the thin junctions. Thick-film inks were formulated with a variety of glass frits and both noble and non-noble metal powders. The pastes were fired in air or nitrogen atmospheres in a continuous belt furnace at various times and temperatures on alumina substrates. The conductivity was measured and a qualitative adhesion rating was assigned. The more promising materials were then fired on silicon wafers and finally on n-p junction cells. All cells used in this work, with one exception, were furnished by NASA-Lewis and consisted of n-layers on nominal 10 Ωcm p-type substrates. The sheet resistivity of the n-type layer varied from 25 Ω/sq. to 110 Ω/sq. This first screening is exemplified by Table I. Both noble and non-noble metals, Owens-Illinois manufactured and commercially available pastes, were examined. To meet the contract requirements of low sheet resistivity, the choice of contact materials was narrowed to Ag, Al alloy, or Al-Ag mixtures.

No essential difference in conductivity or adhesion was noted when Ag or Al-Ag pastes were fired on silicon instead of Al_2O_3 substrates. Table II illustrates the differences found for the non-noble metal pastes. As expected, the particle size of the metals was important (see Table III). The addition of small amounts of Ag to the Al alloy pastes had a deleterious effect on conductivity, as shown in Table III.

When pastes containing Al or Al alloy were fired on junction solar cells, one of two distinct results obtained:

1. High contact resistances were measured, or
2. The solar cells were shorted. (A large leakage current would be measured.)

The two conditions were a function of temperature: low firing temperatures, below 600°C, yielded high contact resistance; elevated temperature firing produced shorted cells. These findings forced the abandonment of attempts to utilize non-noble metals for n-layer contacts. It should be noted that (a) this conclusion is only valid for air-fired non-noble contacts containing B or Al, (b) this action was expedient; the contract allowed only five months for investigation of the problem, and (c) the results were obtained on the specific relatively high sheet resistance wafers furnished by NASA-Lewis. The effort was thus focused on Ag pastes. (Silver is not prohibitively expensive for use on large-volume solar cell constructions: roughly $5.00 per two-hundred square inches of metallization, maximum.)

Initially, again, the pastes were optimized for maximum conductivity, best adhesion, and solderability. Table IV is an example of this work illustrating the effect of glass frit type and amount on the fired film properties. Table V is the result of this work. Nominal 10 Ωcm n on p wafers with conventional evaporated Al back contacts were printed with Ag contacts on the front and fired. The control wafer was manufactured at NASA-Lewis. The Ag paste containing five percent of a glass frit (Owens-Illinois G 3196) by weight appears to make excellent ohmic contact when fired between 600°C and 650°C for six to twelve minutes (peak temperature) in air. The sheet resistance of the n-layers in Table V was 35 Ω/sq.

Attempts to use the 5% frit-95% Ag paste on cells with higher sheet resistivity were only marginally successful. When wafers with sheet resistivities above 45 Ω/sq. were processed, very large contact resistances and large reverse leakage currents were obtained. This indicated that (a) the silver or a component of the frit was diffusing through the n-layer, or (b) non-ohmic contact was occurring. Table VI illustrates the problem:

It initially appeared that non-ohmic contact was due solely to the large sheet resistance of the silicon. To obviate this situation, Ag pastes were developed which contained glass frits based on P_2O_5 rather than B_2O_3 or SiO_2. The hope here was to dope the silicon n-layer immediately under the contact. Table VII indicates that this was successful.

Further intensive investigation with this material as a function of temperature and frit content revealed inconsistent results. On many wafers, even some with sheet resistivities near 100 Ω/sq., the material made excellent contact. On other wafers the contact resistance would be high, the reverse current large, or both. Table VIII shows this clearly. (June 24 report)

B. Printed contacts to p-type silicon

The situation for printed contacts to p-type silicon is more favorable. The p-type substrate is quite thick, there is no danger of diffusion to the junction, and the printed pattern is simply a squre. Very little in the way of line definition is required of the paste. Materials investigated included nickel, nickel alloy, aluminum, aluminum alloy, and aluminum-silver mixtures. The major accomplishment in this work was the development of a low-cost Al alloy paste with a wide firing range, excellent adhesion, low resistivity and generally good metallurgical properties. Tables II and III above contain some information about the non-noble metal pastes. Table IX shows the results of firing Al alloy and Al-Ag pastes on 10 Ωcm (35 Ω/sq.) n on p cells whose fronts had conventional evaporated contacts. As would be expected, the non-noble metal pastes were highly sensitive to firing time and temperature. Pastes with Al only yielded generally unsatisfactory physical structures at all times and temperatures. The films tended to be soft, porous, and easily abraded. In addition, upon refiring near the original sintering temperature spheres of aluminum would appear on the film surface.

Table X lists some data obtained for Al-Ag mixtures with two different frits. The major advantage of such pastes is their solderability. In addition, the Al content is controllable for firing temperature adjustment, the films tend to be reasonably dense and well sintered, and sphere formation is minimized. A minor problem with these materials is the appearance of black or dark specks in the fired film. These apprently are due to a reaction with the lead in the frit. The dark areas do not solder.

The outstanding characteristics of the Al alloy pastes are:

1. Can be fired as low as 590°C on silicon to a dense film
2. Can be fired as high as 900°C without undue problems
3. Inexpensive
4. Excellent adhesion to silicon

The fired films are not solderable with lead-tin solders; however, the frit content is quite large, and the lowest cost powders easily available are only obtainable in rather coarse particle sizes.

C. Processing

Nearly all of this work was done in air ambient atmospheres. This constraint was imposed because of the feeling that dielectrics for edge-insulation (see below) would not be compatible with a non-oxidizing atmosphere. There are disadvantages to working in air environments; the silicon must be cleaned after each firing to remove the thermal oxide. It was found that etching was always required before n-contact application. The thermal oxide had little or no discernible effect on the back contact performance. The cells were etched for two minutes in a 2% hydrofluoric acid solution before front contact printing. If printing and firing was not done immediately after etching the wafers were kept in isopropyl alcohol until immediately before printing.

All pastes were optimized for conductivity, adhesion, appearance and solderability, where applicable, by printing and firing test patterns on Al_2O_3 substrates at various times and temperatures. In general, the higher the firing temperature the more dense is the conductor film. Increased density implies lower resistivity and better solderability. This observation must be tempered with the application in mind. Obviously, the higher the firing temperature and the longer the time at peak temperature the more thermal oxide grown on silicon and the better the chance for metal or impurity diffusion through the junction. The following schedules for various materials seemed to yield near optimal properties on silicon:

Material	I.D. No.	Firing Temp.	Time at Peak
n-contacts			
Fritted Ag	6103B	600°C	6 to 12 minutes
Phosphate fritted Ag	N60510	700°C	6 minutes
p-contracts			
Al alloy	N60405	600°C	6 to 12 minutes
87 Ag-12 Al-1 glass	N60330	600°C	12 minutes

These schedules are quite flexible. For example, the Al alloy paste can be fired from 590°C to 850°C without any great degradation in performance. This is a great advantage when dealing with other materials such as the edge-insulation dielectric which has more stringent temperature and time requirements.

Although little work was directed at the question of printing resolution, some comments are in order. In general, most noble metal thick film pastes, when formulated with the correct vehicle and printed intelligently can define lines 0.01 cm in width and height above the substrate of about 0.0012 cm. This is largely due to the fact that (a) the particles are quite fine, less than 10 μm in average particle diameter, and (b) they are relatively soft and malleable metals. Such is not generally true of non-noble metals. The Ni alloy, for example, is available only in coarse powders. The material itself is quite hard and brittle. To reach acceptable line definition with non-noble metal pastes it will be necessary to find or manufacture a source of fine particle size powders.

Cofiring, the practice of printing a pattern, drying the film, then printing and drying a second pattern on the same object and firing both films simultaneously is a desirable process as it eliminates two handling and one firing steps. This is possible if the two materials have a compatible firing range and if the first dried film has sufficient strength. The two proprietary vehicles commonly used by Owens-Illinois do have such green strength. It is assumed that many commercial vehicles are suitable, too. Most of the conductor pastes used here can be cofired, although note that the optimum properties of one or both will probably not be attained at the same time and temperature schedule.

D. Edge insulating layers

Figure 1 illustrates the cross-section of a p-n junction solar cell with edge insulation. Such insulation would be required, for instance, if a cell with the n- and p-contacts on the same side were needed. The problem of edge-insulation <u>per se</u> is twofold: material properties and application.

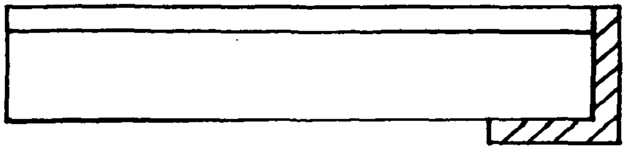


FIGURE 1. CROSS SECTION OF n ON p CELL

An ideal edge-insulating material would:

a. form a good bond to silicon
b. be hermetic
c. be capable of being applied as a thin layer
d. be an excellent dielectric
e. be impact-resistant
f. be low cost
g. be chemically durable
h. not induce strain in the silicon nor
i. contaminate the n-p junction with unwanted impurities.

Vitreous films fulfill most, if not all, the criteria above. There are several difficulties involved with matching a glass composition to this application. The thermal expansion of silicon is near 40 x $10^{-7}(°C)^{-1}$. Glasses with similar expansion coefficients usually have softening points above 800°C and contain certain elements which are known to be fast diffusers in silicon. The approach taken here was to first design a glass with a predicted low softening temperature and thermal expansion coefficient near 40 x $10^{-7}(°C)^{-1}$ which contained no likely poisoner ions, transition metals, etc. The base glass, after melting and grinding, was made into a paste, screened and fired on Al_2O_3 substrates. An upper temperature limit of 750°C was assumed. The films were examined visually for flow, adhesion, and integrity. A large number of melts were designed and evaluated. Most of the compositions were too unstable to form continuous films. Many glasses didnot flow on Al_2O_3 at temperatures below 750°C. The films were examined visually for flow, adhesion, and integrity. The few remaining candidates had large thermal expansion coefficients, as evidenced by cracks in the fired films. This led to the addition of finely-divided ceramic particles to the paste for expansion control. This practice is common in the sealing glass industry. Adding finely divided oxide ceramics to a vitreous material can provide both flow control and expansion/contraction matching; the implicit assumption is that the ceramic filler is not dissolved by the glass.

The final choice for a wrap-around or edge-insulating dielectric was set after extensive printings and firings on the edge of silicon wafers. The major parameter used to evaluate these dielectrics was no increase in reverse leakage current after dielectric application relative to an uninsulated wafer fired through a similar temperature cycle. This stipulation was necessary as some of the thin junction cells exhibited increased leakage after high temperature firing through the belt furnace with no handling.

Owens-Illinois paste No. N60721, which consists of 63% by weight of O-I glass 76111A1, 7% by weight ceramic filler and 30% by weight organic vehicle, fires to a smooth film with good adhesion to silicon at temperatures between 675°C and 750°C. The peak time at 750°C is at least 12 minutes; the optimal time at 675°C is near 24 minutes. Paste N60721 does not form a transparent film; the film is a translucent off-white. Further, the thickness is important; fired thicknesses above about 25 microns are prone to microcracks. No evidence of the ceramic filler dissolving in this frit was observed. The particle size of the filler is important, however. Pastes with coarse additions did not screen well, were more prone to microcracks, and tended to yield rough surfaces. The ceramic content can be varied between 3.5% and 10% by weight without substantially degrading its performance. Particle size should be substantially below 20 μm (average particle diameter) for best results.

II. Application

Two methods of application were studied during the course of this contract: dipping and screen-printing. Dipping the substrate into a controlled-viscosity slurry was investigated as a function of slurry solid content. Screen-printing was studied as a function of screen mesh, emulsion thickness, and paste characteristics. Two difficulties were noticed immediately:

1) Any material deposited on the very sharp, near ninety-degree angle of the edge would flow away. This left, at best a very thin coating, at worst a discontinuous film.
2) Due to the method of post-diffusion etching the wafers furnished by NASA/Lewis often showed an exposed junction on the top surface; that is, instead of appearing like Figure 2.

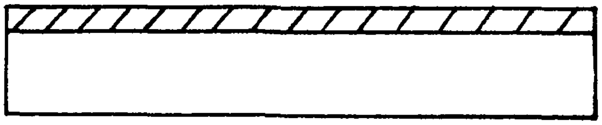


FIGURE 2. IDEAL (RIGHT ANGLE) WAFER EDGE

The edge would be more like Figure 3.

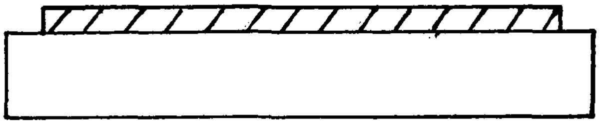
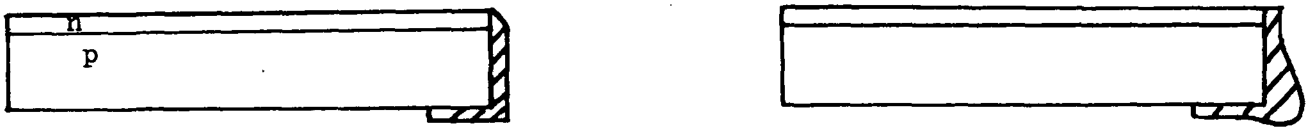


FIGURE 3. OVERETCHED APPEARANCE OF SILICON WAFERS (EXAGGERATED)

Dipping is probably not a feasible method for volume production of edge-insulated wafers. The viscosity and solid content must be controlled too carefully. Screen printing pastes "over the edge" seemed to be almost absurdly simple. Controlled thicknesses with excellent uniformity and coverage were achieved with a variety of screen meshes, emulsion thicknesses, and paste parameters. In every case, however, the material would flow away from the sharp edge during firing. Although continuous films could be produced, it was often accompanied with too thick a layer away from the edge. The two conditions are indicated schematically in Figure 4.



(a) UNIFORM SIDE AND BACK, TOO THIN ON TOP EDGE.

(b) CONTINUOUS EDGE COATING; "BALLING" OR GATHERING ON SIDE AND BACK.

FIGURE 4. THE TWO EXTREMES OF EDGE-COATING ARE ILLUSTRATED

The disadvantage of the first condition is obvious; shorting of the subsequently applied silver. The second condition was as undesirable, however, as cracks would appear in the side and back areas when the coating exceeded 30 µm in thickness. For the purposes of fulfilling this contract the following expedient was chosen: A coating roughly 14 µm (dried thickness) was printed from the back over the edge. After drying a second print was made from the front over the edge. The resultant structure is shown in Figure 5.

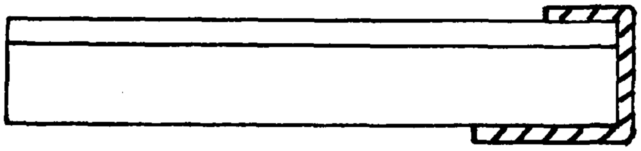


FIGURE 5. TWO PRINT STRUCTURE AFTER FIRING

Such a procedure has the advantage of ensuring that the n-p junction is covered. It has the twin disadvantages of an extra processing step and obscuring part of the active front collection area.

III. Wrap-around Cells

The desired wrap-around contact configuration is illustrated in Figure 6.

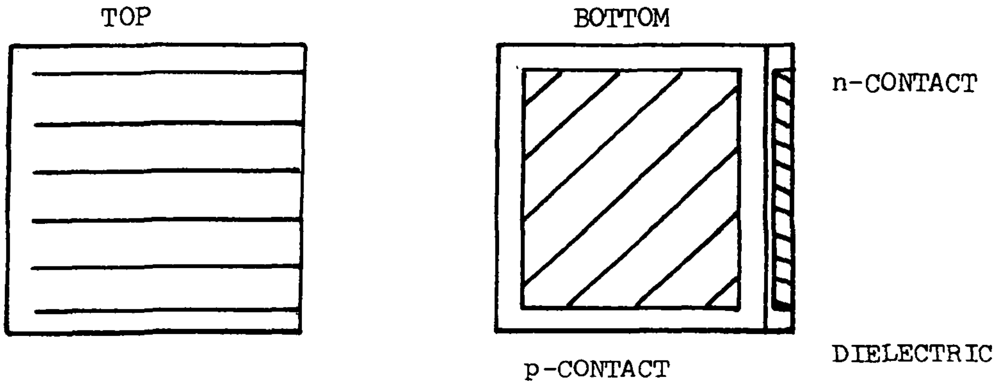


FIGURE 6. WRAP-AROUND CONTACT CONFIGURATION

The optimal, least-step, application procedure is:

a. Print dielectric on back and edge. Dry.
b. Print front (n) contact and edge. Dry.
c. Print back (p) contact. Dry.
d. Print back and edge wrap-around contact. Dry.
e. Cofire dielectric and conductors.

It was not possible to cofire the dielectric and wrap-around conductors in this study. Every time this was attempted the silver shorted through the dielectric on the edge. This was due largely to the need for twelve minutes at 750°C for dielectric maturation. The frits in the silver pastes and the silver itself, were very active at those temperatures and either interfered with the dielectric sintering or simply allowed the silver to diffuse to the silicon. The following compromise procedure was found to be workable:

a. Print dielectric on back pad and edge. Dry.
b. Print dielectric on front and edge. Dry. Cofire.
c. Print back (p) contact. Dry.
d. Etch front to remove thermal oxide.
e. Print conductor on back pad and edge. Dry.
f. Print conductor on front and over edge. Dry.
g. Fire conductors.

IV. Interconnection

The major benefit expected from the production of wrap-around cells is ease of interconnection into an array. It's argued that with both contracts on one side approaches such as the cumbersome Z-tab or wire-bonding can be eliminated. The question then becomes one of what substrate and which bonding agent. Three methods of bonding cells to three different substrates were investigated. The substrates were anodized aluminum, copper-clad, resin-impregnated printed circuit board, and soda-lime glass. The bonding media were silver-filled epoxy, lead-tin-solders, and thick-film silver pastes.

Anodized Al substrates are relatively low cost, readily available, and offer large thermal conductivity with low mass. It was found that thick-film silver contacts could be fired on anodized aluminum at temperatures below 550°C which did not short through the anodized layer. The silver films had excellent conductivity and appeared to be well adhered at thickness of 13 μ or less. The silver paste composition was 95% Ag powder, 5% glass frit at a 78% loading into a standard vehicle. When fired at 550°C the films soldered very well with lead-tin solders containing 2% silver. Subsequent investigation consisting of pulling soldered copper wires perpendicular to the substrate revealed that the Ag-anodized layer bond was not particularly strong, however. The average force required to separate the two was five pounds. This is in contrast to the same silver on Al_2O_3 ceramic substrates which registers ≥ 15 pounds in the same test. Similar measurements with Ag-filled epoxy and wet-fired silver pastes confirmed that the bond was quite susceptible to thermal shock. That is, wet-fired silver paste to silver paste at 500°C was much weaker than soldered contacts applied at about 230°C. Both were much inferior to epoxy contacts processed at 110°C.

Copper laminated to resin-impregnated fiberglass (printed circuit boards) substrates and subsequently tinned with Pb-Sn solder provided excellent bonds to soldered Ag paste contacts. Silver filled epoxy was also an acceptable bonding medium. The wet paste procedure was not attempted as the printed circuit board would not withstand the 500°C temperature unharmed.

V. Passivation and Protection

Silicon cell front surfaces need protection from the atmosphère, space or terrestrial, and an antireflection optical coating. Attempts were made to print and fire vitreous films on silicon at temperatures less than 750°C. These experiments suffered from the same difficulties enumerated in the edge-insulating dielectric section: glass compositions which flowed well were not well matched thermally and <u>vice versa</u>. A further problem was reactivity; several glasses when fired on silicon generated gas bubbles at the film-silicon interface.

The best candidate to be discovered furing the above rather extensive work could be printed and fired on silicon and front grid lines to a thickness of 15 μm to 20 μm without crazing or reacting at a temperature of 750°C. The film appeared quite homogeneous and transparent under low power magnification. Examination at NASA-Lewis revealed that the illuminated current-voltage plots indicated low photovoltaic efficiency relative to an identical, uncoated cell. Further testing showed that the glassy films were not optically homogeneous; incident light was rather badly scattered in the plane of the coating. The cause of this condition is not definitely established. It could be microbubbles, trapped dust or residue from the vehicle, insufficient sintering, phase separation, or incipient crystallization. Whatever, the films were not of high enough optical quality for use.

Owens-Illinois, Inc., markets a family of resins whose structure is based on random Si-O bonding. These Glass Resins™ contain up to 86% SiO_2 by weight, are heat-curable, and can be applied by spraying, dipping, or painting. These materials are excellent dielectrics and are unusually transparent in the ultraviolet region.

Type 650 Glass Resin films were sprayed on silicon solar cells and cured at 200°C for 10 minutes. The films adhere very well. Limited testing has shown that they resist liquid water penetration very well. Their behavior in moist atmospheres or in actual use conditions is not known. Formulations of these resins with fillers are space-qualified, however, and have been under test at the Desert Sunshine Research Center for some time. The coatings have shown little or no degradation in adhesion or appearance after several years of exposure in Florida. Table XI displays some of the properties of the resin.

Work at Owens-Illinois and elsewhere has shown that organometallic titanate and silicate solutions can be used to generate films with refractive indices between 1.4 and 2.2. This appraoch offers an excellent opportunity to produce high-quality efficient antireflection films without the use of vacuum equipment. Combined with Glass Resin outer layers the result could also offer adequate atmospheric protection.

DISCUSSION OF RESULTS

The results reported above show, again, that there is no inherent reason thick-film technology cannot contribute to the automated production of silicon solar cells. They also point up, again, the lack of really suitable materials for such production. The failure of the phosphate glass and Ag pastes to make low resistance contacts to high resistance n-type silicon consistently is very disappointing. The problem must be one of thin junctions or simply lack of ohmicity. The silicon wafers and their processing simply might not be suitable for use with thick-film contacts. Ideally, a non-noble metal such as Cu or Ni should be used for the n-layer metallization. This will require either a non-ambient firing atmosphere, an eutectic-type metallurgical bond, or both.

The edge-insulating material works reasonably well. Further work on it would only be to (a) reduce the firing temperature, and (b) develop a smoother, more uniform fired film. A major concern for utilization of this technique in volume will lie in methods and machinery for wafer handling. The question of automatically presenting and conveying the wafer to a screen and furnace for up to seven printings and dryings is a challenge for equipment manufacturers.

Connecting cells in an array will require automated handling and positioning machinery. A choice of substrate and adhesive type will apparently be based on factors other than technical. The most cost-effective and reliable system for the particular application will be specified.

It is not promising to pursue the use of screened vitreous films for use on silicon solar cells front surfaces. Any such film would still leave the edges and back unprotected. No single glass composition will be found that provides a fraction of the index-accommodation required for efficient optical matching of the atmosphere to silicon. Such films could not be applied a quarter wavelength thick.

The ideal coating would provide antireflection and atmosphere exclusion in thin layers. It would be applied by spraying and mature at low temperatures. Films of Glass Resin^{TM} modified with the addition of metallo-organic derived Ti-O (TiO_2) might well accomplish this task. This development should proceed.

CONCLUSIONS

This investigation concentrated on four areas: ohmic contacts, dielectric for edge insulation and wrap-around contacts, interconnection of solar cells into arrays, and passivation or protection.

Ohmic Contacts

Under the limitations of air-firing on n-type silicon layers less than 0.5 μm thick, only Ag pastes formed non-shorting, reliable ohmic contacts.

N-type silicon above 70 Ω/sq. needed a phosphate frit addition to the Ag for low-resistance contacts.

An Al alloy plus frit mixture made excellent contacts to p-type silicon substrates. The material is not solderable directly.

Mixtures of Al, Ag, and frit with the Al content less than or equal to 12% by weight formed acceptable contacts to p-type silicon. Fired at 600°C or below the films are solderable.

More work on materials for shallow junction cells is necessary before silk-screen printing is reliable in production.

Dielectric for Edge Insulation and Wrap-around Contacts

An Owens-Illinois glass frit with ceramic powder added, paste No. 60721 can be fired on silicon at 725°C to a relatively smooth film. Such films under 25 μ thick appear to be well matched in thermal expansion to the silicon. Ag films overprinted and fired at temperatures up to 700°C do not short through.

Wrap-around contacts can be produced with two firing steps and five printing and drying operations.

Interconnection

Two types of substrates, anodized aluminum and glass-fiber laminates were investigated. Both types have advantages; neither has an overwhelming attraction.

Ag paste printed and fired on anodized aluminum at 525°C does not short through to the substrate. Such films solder well.

Cells were attached to the aluminum with solder, silver-filled epoxy, or cofired Ag paste films. The mechanical bond of paste to paste is weak; the electrical continuity appears adequate.

Passivating and Protecting Layers

The attempts to find a screen-printable, low-firing temperature, vitreous composition for application over the Ag contacts were not successful. The films were not optically homogeneous.

A commercially-available, heat-curable resin whose structure consists of alternating Si-O atoms appears to offer some protection to the silicon. The material, Glass Resin^{TM}, available from Owens-Illinois, Inc., can be sprayed, dipped or spun onto surfaces. The material cures to a highly transparent film at 200°C. The possibility exists of tailoring similar materials to provide optical matching (antireflection).

TABLE I. INITIAL SCREENING OF METALLIZATIONS

			PEAK TEMPERATURE					
			600°C		650°C		700°C	
			ATMOSPHERE					
LOT NO.	DESCRIPTION	% FRIT	AIR R_s(milliΩ/sq) ADHESION	N_2	AIR	N_2	AIR	N_2
N50818-4	Al	25	46 k poor	82.1 k poor	620	1410	320 poor	1200 poor
N50819		15	896 poor	716 poor	88	114	74 poor	113 poor
N50819-2		10	410 poor	253 poor	54	60	50 poor	63 poor
N50819-4		5	285 poor	203 poor	33	47	27 poor	40 poor
N50825-4		3	-	-	-	-	16	12.5
N50818-5	Al alloy	25	40 poor	53 poor	61	37	42 poor	37 poor
N50919-1		15	109 poor	136 poor	193	156	77 poor	91 poor
N50819-3		10	390 poor	853 poor	320	340	221 poor	426 poor
41317	Al alloy		37 poor	34 poor	23	21	15 poor	21 poor
41826	Al		43 poor	46 poor	32	35	31 poor	35 poor
N50515	Ni alloy	10	46 poor	46 poor	38	36	35 very good	29 good
N50430	Ni alloy	0	137 poor	131 poor	89	80	77 fair to good	61 good
T40812-2	Ag		2 good	4 fair	2	3	2 good	3 good

200-mesh screen; Air Firing: 7 to 9 minutes (2"/minute)
N_2 Firing: 14 to 18 minutes (1"/minute)

96% Al_2O_3 substrates

TABLE II. COMPARISON OF SHEET RESISTANCE ON CERAMIC AND SILICON

LOT NO.	METAL	% FRIT	TEMP./TIME	ATMOS.	CERAMIC (milliΩ/sq)	SILICON (milliΩ/sq)
N50818-5	Al alloy	25	700°C/ 2"/min.	N_2	43	39
''	''	25	''	Air	42	41
N50819-4	Al	5	''	Air	27	15
41317	Al alloy	-	''	Air	15	13.5
N50515	Ni alloy	10	''	Air	35	35

TABLE III. THE EFFECT OF PARTICLE SIZE ON CONDUCTIVITY

LOT NO.	METAL	% FRIT	DESCRIPTION	TEMP./TIME	ATMOS.	R_s (milliΩ/sq)
N50818-5	Al alloy		-37 µm powder	700°C/ 2"/min.	Air	42
N50825-3	''		-20 µm diameter powder	''	Air	9
N50825-6	''		N50825-3 plus 1% Ag	''	Air	17

TABLE IV. Ag PASTES

Lot No.	wt.% Glass	Glass Type	Other	R_s (milliΩ/sq.) 600°C 2"/min.	600°C 1"/min.	650°C 2"/min.	Solder?
T60116	0	-	-		3.5		Leaches rapidly
N60204	1	G3196	-				
N60120	1.5	XS1007	-		3.0		
N60120-1	1.5	''	0.5% mol.bond.		3.2		
N60120-2	1.5	G3196	-		2.8		
N60120-3	1.5	''	0.5% mol.bond.		3.5		
T50909-4	5	''	-		4.3	5.0	Good
T60217	5	''	-		5.0	5.3	Good
N60316-1	5	XS2371	-	3.0	2.6	2.3	Poor to Fair
N60316	7.5	G3196	-	3.0	2.7	2.3	Poor
A3233				6.2	5.5		Leaches rapidly

TABLE V. WAFERS WITH EVAPORATED BACK CONTACTS (Al) AND PRINTED FRONT ELECTRODES

Wafer No.	f(n)(V)	R_c(Ω)	I at 0.6V (μa)	Front Contact	Firing Temp.(°C)
Control No. 9	0.125	0.20	1240	Evaporated Al/Ag	-
539-1	0.127	0.75	96	Fritless Ag	700
-4	0.250	0.70	1330	1 Frit-99 Ag	600
-12	0.150	0.60	420	1.5 Frit-0.5 other-98 Ag	600
-14	0.115	0.55	760	1.5 Frit-98.5 Ag	600
-15	0.082	0.35	205	5 Frit-95 Ag	600
-7	DEAD SHORT			Al Alloy	600

TABLE VI. CONTACT RESISTANCE AS A FUNCTION OF n-LAYER SHEET RESISTIVITY

n-layer sheet Resistivity (Ω/sq)	Contact Resistance R_c(Ω)
45	2.4
24	0.8
13	0.75
12	0.9
8	0.9

TABLE VII. DARK DIODE CHARACTERISTICS. PHOSPHATE FRIT IN Ag n-CONTACT.

Wafer No.	Resistance	f(n)(V)	R_c(Ω)	I_R@0.6V	Fired @
29	62 Ω/sq.	0.120	0.45	850 µa	675°C
30	59	0.120	0.50	730 µa	725°C
31	55	0.165	0.65	1400 µa	750°C

TABLE VIII. EXAMPLES OF INCONSISTENCY WITH PHOSPHATE FRIT AND Ag

Cell	Ag Paste	P_2O_5	Cofire	f(n)(V)	R_c(Ω)	I_R@0.6V	Fill	Eff.
E15	N60510	5% Hard	675°C 2"/min	.225	.60	2.5 ma		
E16				.275	1.95	1.1 ma		
D38				.215	.65	1.2 ma		
D39				.215	.75	290 µa		
E17			700°C 2"/min	.265	.85	2.5 ma		
E18				.235	1.95	750 µa		
D40				.425	1.30	4.0 ma		
D41				.120	.45	280 µa		
E19			725°C 2"/min	.230	.40	1.7 ma	59.6	5.20
E20				.150	.50	1.5 ma	66.2	5.75
D42				.350	.55	10.6 ma	55.8	4.35
D43				.110	.60	550 µa	69.6	6.02
E21	N60510	5% Hard	725°C 2"/min	.210	.65	1.7 ma	64.6	5.14
22*				.265	2.20	550 µa	27.0	2.02
23*				.110	1.35	175 µa	27.5	2.19
24				.130	.50	575 µa	59.0	4.55
26				.135	.50	500 µa	63.8	5.06
26				.120	.35	550 µa	63.7	5.11
27				.385	.70	5.4 ma	56.2	4.42
28*				.290	1.90	1.3 ma	23.5	1.76
29				.455	3.80	5.4 ma	24.8	1.24
30				.500	2.00	5.2 ma	29.9	1.81
31*				.225	2.20	1.0 ma	24.9	1.94
32*				.210	2.10	190 µa	24.0	1.98
33				.155	.45	865 µa	63.0	5.21
34				.375	2.40	20 ma	26.5	1.73
35				.135	.55	180 µa	59.8	5.17
36*				.415	2.40	5.0 ma	26.4	0.34

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*Refired 650°C to a lower R_c not shown

TABLE IX. WAFERS WITH EVAPORATED FRONT CONTACTS (Al/Ag) AND PRINTED BACK CONTACTS

Wafer No.	f(n) (V)	R_c (Ω)	I_R at 0.6V (μa)	Rear Contact	Firing Temp. (°C)
Control No. 9	0.125	0.20	1240	Evaporated Al	-
538-1	0.178	0.30	550	Al Alloy	650
-6	0.217	0.47	1460	''	625
-4	0.250	0.30	2100	''	600
-7	0.139	0.55	300	''	575
-14	0.355	0.35	6500	24Al·75Ag	600
-13	0.190	0.45	890	12Al·87Ag	600
-9	0.352	0.45	8000	9Al·86Ag	600

TABLE X. Ag·Al PASTES

					R_s(milliΩ/sq)			
Lot No.	wt.% Al	wt.% Ag	wt.% Glass	Glass Type	600°C 2"/min.	650°C 2"/min.	700°C 2"/min.	Solder?
N60210-2	12	87	1	G3196	9.2			Yes
N60330	12	87	1	''	5.5			Yes
N60210-1	24	75	1	''	31			At 600°C firing
N60210	49	50	1	''	-			No
N60127-4	85	12	3	G3196			3810	
N60127-3	91	6	3	''			1786	
N60127-2	95	2	3	''			820	
N60127	97	0	3	''			255	
N60127-1	98.5	0	1.5	''			175	
N60217-1	9	86	5	G3196		8.0	9.7	
N60217-2	9	86	5	XS2371		8.3	9.3	
N60319-1	9	86	5	''		5.5		Hand.
N60319	9	86	5	''		7.2		''
N60319-2	9	86	5	''		8.0		Fair
N60322	9	86	5	''		7.0		Fair
N60316-2	12	86	5	XS2371	5.5	3.9		Poor
N60316-3	15	80	5	''	6.5	4.4		Poor
N60316-5	9AlSi	86	5	XS2371	5.0	3.8		No
N60316-4	15AlSi	80	5	''	8.0	7.8		No

TABLE XI. PROPERTIES OF CURED GLASS RESIN FILMS. TYPE 650

Index of Refraction	$\eta_o = 1.42$
Density	$\rho = 1.3$ gm/cm^3
Hardness	120 to 140 Rockwell R
Tensile Strength	3500 psi
Optical Transmission	85% or more between 3600 and 7000Å
Dielectric Constant	3.2 at 10^6 Hz
Dissipation Factor	0.007
Volume Resistivity	1×10^{14} $\Omega \cdot$cm at 25°C