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OVERVIEW OF THICK-FILM TECHNOLOGY
AS APPLIED TO SOLAR CELLS

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OVERVIEW OF THICK-FILM TECHNOLOGY AS APPLIED TO SOLAR CELLS

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Summary

Thick-film technology was developed by the electronics industry as a means of fabricating components and miniature circuitry. Today, the solar cell industry is looking at screen printing as an alternate to more expensive, high-vacuum techniques in several of the production steps during the manufacture of silicon solar cells. Screen printing is already fairly well established as a means of providing electrical contact to a cell and for the formation of a back surface field. Now under investigation are the possibilities of non-noble metal contacts and protective and anti-reflective coatings applied to solar cells by the use of screen printing. Most exciting is the work being done in the non-silicon area on the fabrication of the active layers of a solar cell, using thick-film inks made up of II-VI semiconductors.

Introduction

Thick-film technology has been used in the electronics industry for the last 30 years in the manufacture of components and, more recently, miniature circuitry. A screen-printing technique for depositing a thin layer (15-50 μ) of material, the thick-film process involves a comparatively inexpensive, non-vacuum technology¹ and lends itself to mass production. The actual process has three steps: 1) squeegee ink or viscous paste through a screen onto a substrate (Figure 1 is a picture of a laboratory model automatic screen-printer), 2) dry the layer of ink, usually under an infrared heat source, and 3) fire in an infrared or conventional belt furnace. The inks used for screen printing are usually composed of a fine powder of metal, an organic solvent, a glass frit or binder, and a fluxing agent. The solvent controls the viscosity of the ink, the binder holds the film together, allows a certain amount of flow at high temperatures, and bonds the film to the substrate. The flux lowers the melting point of the metal and catalyzes the metal particles into forming a continuous film. Drying the ink allows most of the organic solvent to escape from the printed film. During the firing, which usually takes place at a temper-

ature in the range of 400-900°C, the metal powder is sintered and the remaining solvent is driven off.

The properties of the resulting film depend upon such parameters as: the constituents of the ink and its viscosity during printing, the size of the screen's strands and mesh, the thickness of the emulsion on the mesh, the angle, downward pressure, and travel speed of the squeegee, the elapsed time between printing and drying, the times and temperatures of drying and firing, and the rate of heating to and cooling from the firing temperature.

Silicon Solar Cells

Today's commercial solar cells are typically made of single crystal silicon. Boron-doped silicon is grown into a large p-type ingot that is then sliced into wafers. A phosphorus dopant is diffused in, forming a thin n-type layer and thus a pn junction. Figure 2 shows the resultant valence and conduction bands in a single-crystal silicon cell plotted versus distance. Incident light is absorbed within the cell, providing the energy necessary for the formation of electron and hole carriers. The junction field then separates the carriers, creating a current. Conductive contacts to the cell permit this current to flow through an attached external circuit.

Figure 2. Energy Band Diagram for Single Crystal Silicon Solar Cell

Electrical contact to the cell is made by applying a metal film to the back surface (the p-side) and a metal grid pattern to the front (the n-side) of the cell. Figure 3 shows the different layers in a simple silicon cell.

Screen Printing and Silicon Cells

The solar cell industry has begun to take an interest in thick-film technology as it has become apparent that screen printing can, to advantage, replace more complex and expensive technologies in several of the production steps in silicon solar cell fabrication. The metallization necessary to provide electrical contact to the cell has traditionally been deposited by vacuum evaporation through a metal mask, a labor-intensive and time-consuming process. Several manufacturers have begun using screen printing instead

Figure 1. A Laboratory Model Automatic Screen Printer

Figure 3. Cross-Sectional Diagram for Single Crystal Silicon Solar Cell

of vacuum evaporation for this metallization process, the advantages being: automated equipment with throughput rates of about 3000 parts per hour is commercially available; no high-vacuum is involved; and the metal is deposited only on the cell where it is wanted - very little is wasted.

Top Grid Contact

Figure 4. Top View of Single Crystal Silicon Solar Cell with Screen Printed Grid Contact

Because most of the sunlight hitting a silicon cell is absorbed near the top surface, carriers freed by the light have a better chance of reaching the pn junction and of producing external current if that junction is also near the top surface of the cell. Thus, the n-layer is made to be very thin and has a nonnegligible sheet resistivity. The effect of this sheet resistance on the collection efficiency of the metal contact would be minimized by making the contact a solid sheet covering the entire surface of the cell, but then no sunlight would reach that surface. Optimizing the cell power output results in a pattern of very thin grid lines connected to a wider bus bar. The practical lower limit on line width obtainable by screen printing is between 6 and 10 mils, whereas 1-2 mil lines are preferable and are obtainable using vacuum evaporation. This limitation on a screen-printed grid pattern can cause a 5% decrease in the cell's maximum power output, but the

accompanying reduction in cell production cost provides an economically attractive compromise².

The film making up the grid contact, once printed and fired, must be stable; the metal must not migrate through the thin n-layer, as this would reduce the current collection efficiency and possibly even short out the pn junction. In order to be a useable contact, the film must be a good electrical conductor and must have good adhesion to the silicon, good solderability, and low contact resistance. These properties have been found to be consistently obtainable^{3,4} by using a silver-based ink and by carefully controlling the firing stage. The firing temperature must be high enough to melt the glass frit and to cause sintering of the metal, thereby insuring adhesion and conductivity, respectively, but high temperatures can cause degradation of the junction and diffusion of the grid contact metal into the silicon. Although a variety of silver-based conductor inks is commercially available, manufacturers using the screen-printing process are usually modifying to some extent whatever commercial ink they use.

Power output is very sensitive to the series resistance of the cell. The sheet resistivity of the n-layer, the resistance at the interface between cell and metallization, and the resistance of the grid lines are major contributors to a solar cell's series resistance. Figure 5 shows a plot of current versus voltage (IV curve) for a good solar cell and a plot showing what a small increase in series resistance does to the cell output.

Figure 5. I-V Curve of Single Crystal Silicon Solar Cell before and after HF Etch

Immediately after firing, a silicon cell with screen-printed grid contact has an unacceptably high series resistance. The output can be drastically improved by dipping the cell in a 2-5% solution of hydrofluoric acid (HF) for 5-10 seconds. The plots in Figure 5 are IV curves taken from the same cell before and after an HF etch. Precisely what happens during the HF etch is not yet understood, but the result of etching for too long (see Figure 6) makes it clear that, among other things perhaps, the HF etch attacks the glass binder in the film.

Figure 6. Loss of Grid Contact Adhesion

One means of avoiding the necessity of an HF etch has been found. Firing the silver contact for a fraction of a minute in an infrared furnace rather than for many minutes in a conventional belt furnace seems to keep the series resistance of the cell from becoming a problem.

In addition to an HF etch, cells are often dipped in solder to lower the series resistance of the silver grid lines themselves. Figure 7 shows cells with good and bad solderability after solder-dipping.

Figure 7. Solder Dipped Cells, with and without Good Solderability

Back Surface Field

One recent contribution to increased silicon cell efficiency was the development of the back surface field. By diffusing in a p dopant, forming a highly doped region at the back surface of the cell, the carrier collection efficiency of the pn junction is increased. From the energy band diagram in Figure 8, it can be seen that the p+ region forms a potential barrier that reflects electrons approaching the back surface back toward the junction.

Figure 8. Energy Band Diagram for Single Crystal Silicon Solar Cell with Incorporated Back Surface Field (BSF)

In forming a back surface field, screen printing can be used to deposit the dopant (often aluminum) on the back surface of the cell.

Contact to the Back of the Cell

Making electrical contact to the p-side of the solar cell is less demanding because of the comparative thickness of the p-type layer and by the fact that there is no need for sunlight to reach the p-surface of the silicon. A solid sheet of conductive material can be used instead of the grid pattern needed on the front of the cell. Metal migration causing reduced current collection or shorting of the pn junction is not a serious problem because of the distance between the p-surface and the junction.

Screen-printed aluminum has been found to work well as a back contact. It is far less expensive than silver and the sintered layer of aluminum forms a highly conductive contact with excellent adhesion to the silicon. During sintering, the aluminum tends to diffuse into the silicon cell, forming a back surface field as well as a metal contact. The only major problem with using aluminum for the back contact is its lack of solderability. The interconnection of cells in a photovoltaic module requires soldering of connectors to each cell. The most common solution to this problem is not to use aluminum but a silver ink with a small proportion of aluminum in it. The cost is thus somewhat less than it would be if no aluminum were in the silver ink, and the solderability remains good as long as the percentage of aluminum does not exceed about 12%.

Another solution is to print and fire a film of aluminum, then print a patch of silver-based ink over it. The subsequent firing cycle allows the aluminum to diffuse into the cell while the silver is sintered to form a solderable contact.

Silicon Cells

Deposition of front grid and back contacts onto a silicon cell, as well as the formation of a back surface field, are production steps that can currently be accomplished quite satisfactorily by screen printing. In fact, there are solar cell manufacturers who use screen printing for these production steps. Research is being done on using screen printing for other production steps also. Formation of the pn junction and application of protective and antireflective coatings are being investigated, but to date results have not been adequately reproducible.

Another area of research being looked into is the possibility of using a non-noble metal for silicon cell contacts. Because of the high price of silver, the use of a non-noble metal would cause a noticeable decrease in metallization costs. With this cost decrease in mind, several organizations are attempting to formulate new inks that can be used for cell contacts. The major problems encountered^{4,5,7} include instability of the printed films (the metals tend to migrate into the cell), unacceptably high contact resistance and, in many instances, lack of solderability.

Screen-Printed Active Layers

An exciting work, and one that holds great promise for both thick-film and solar cell technologies, is the research into screen printing the actual semiconductor layers of a CdS-based solar cell. Low efficiency solar cells were made from vacuum evaporated films of CdS in 1954. Since that time, much research has gone into developing large-area, relatively high efficiency thin-film cells, an example of which can be seen in Figure 9. This cell was fabricated by a vacuum deposition of CdS onto a copper film, followed by a chemical dip to form the Cu₂S layer.

Figure 9. CdS/Cu₂S Thin-Film Solar Cell (Courtesy of IEC)

Films of sintered CdS were used in developing an effective CdS/Cu₂-xS solar cell⁹ and work is still being done on these cells. The research being done today on actually screen printing CdS for solar cell fabrication is focused on CdS/CdTe cells. The pioneering work on entirely screen-printed solar cells has been done by a group of scientists at Matsushita Electric Industrial Company in Osaka, Japan^{9,10}. A cutaway side view of their 8% efficient, CdS/CdTe, backwall cell is shown in Figure 10.

Figure 10. Cross-Sectional Diagram of a Screen Printed Solar Cell Developed by Matsushita

Several groups in the U.S. are now working on screen printing CdS/CdTe cells^{11,12} in an effort to verify and perhaps improve upon the Japanese cell. One of the major problems encountered is an incomplete understanding of the cell structure and operation. Another problem and a drawback of screen printing that has not yet been addressed, is the thickness of a printed layer. Screen-printed CdS is usually 15μ thick. In a CdS/CdTe cell, a CdS layer 1μ thick would be preferable and would require less cadmium. Especially as photovoltaic power becomes more prevalent, the value of cadmium as a resource may become a serious consideration.

Because screen printing is a non-vacuum, non-labor-intensive technology, and because there is almost no waste of material in the printing process, these thick-film cells could be manufactured at a very low cost. Mass production of solar cells made of inks printed and fired on glass substrates would be economically very practical and research is now going into developing the necessary stability, performance, and repeatability to make mass production of these cells feasible.

Conclusion

Thick-film technology is worthy of notice and consideration by people involved in research or manufacture of solar cells. Screen printing can be used to provide metal contacts and a back surface field on a silicon solar cell. New non-noble metal inks are being formulated in an attempt to further reduce the cost of putting metal contacts on a cell. The possibilities of using screen printing to deposit dopants, antireflective layers, and protective coatings are being investigated. The fabrication of solar cells made by screen printing CdS and CdTe layers onto glass substrates has been demonstrated in a laboratory situation. In manufacturing solar cells, thick-film technology can be used to accomplish steps that otherwise would involve high vacuum, high labor requirements, and high cost. Automation of screen printing has long been accomplished; automatic screen printers with high throughput rates are available, making mass production possible and practical.

References

- 1) D.W. Hamer and J.V. Biggers, Thick Film Hybrid Microcircuit Technology, Wiley-Interscience, 1972.

- 2) W.E. Taylor, N. Mardesich, and C.F. Gay, "The Impact of Screen Printing on the Cost of Solar Cell Metallization", ASME publication, Paper No. 79-SOL-6.
- 3) L. Frisson et al, "Screen Printed Contacts on Silicon Solar Cells with Low Series Resistance", Proceedings of 13th PV Specialists Conference, 1978, P.590.
- 4) M.B. Field, "Thick-Film Materials for Silicon Photovoltaic Cell Manufacture", Final Report, Contract No. NAS3-19441, Report No. NASA CR-135134.
- 5) E.L. Ralph, "Recent Advancements in Low Cost Solar Cell Processing", Proceedings of 11th PV Specialists Conference, 1975, P.315.
- 6) M.B. Field and L.R. Scudder, "Application of Thick-Film Technology to Solar Cell Fabrication", Proceedings of 12th PV Specialists Conference, 1976, P. 303.
- 7) Bernd Ross Associates, "Development of Economical Improved Thick Film Solar Cell Contact", DOE/JPL LSA Contract No. 955164, 13th Project Integration Meeting handout, Aug. 1979, P.57.
- 8) S. Kanev, V. Stojanov, and R. Stefanov, Bulgarian Patent No. 11127, 1965; Compt. Rend. Acad. Bulg., Sci. 20, No. 5, 1967.
- 9) N. Nakayama et al, "Ceramic Thin Film CdTe Solar Cell" Japan. J. Appl. Phys., 15, 2281, 1976.
- 10) S. Ikegami and T. Yamashita, Matsushita Electric Industrial Co., Ltd., Proceedings of 21st Annual Electronic Materials Conference, 1979.
- 11) J.B. Mooney, "Sprayed CdS/CuInSe₂ and Sintered CdTe Low Cost Solar Cells", Abstracts of Presentation CdS/Cu₂S and CdS/Cu-Ternary Compound Program Contractors Review Meeting, Dec. 1979, P. 44.
- 12) G. McDonald and G. Goodman, "Commercialization of Thick-Film Solar Cells", Abstracts of Presentation CdS/Cu₂S and CdS/Cu-Ternary Compound Program Contractors Review Meeting, Dec. 1979, P. 185.