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COMMERCIALIZATION OF A THICK FILM SOLAR CELL

Quarterly Technical Progress Report, January 1—March 31, 1980

By
G. D. McDonald
G. Goodman

Work Performed Under Contract No. EG-77-C-01-4042

Globe-Union Inc.
Milwaukee, Wisconsin

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U.S. Department of Energy

Solar Energy

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SOLAR CELL

QUARTERLY TECHNICAL PROGRESS REPORT
JAN. 01, 1980 TO MARCH 31, 1980

BY

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ABSTRACT

Initial problems encountered in the screen printing of CdS films related to an undesirable surface texture on the film surface have been resolved by modification of ink rheology. Improvements have been made in CdS films through modification in firing conditions, ink composition, and fluxing. The CdS 13 micron thick films are devoid of through pores and have a resistivity of 1.65 ohm cm.

A laser probe technique was developed to determine macro variations in solar cell films.

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1.0. Introduction

This report is the second quarterly report of a program designed to evaluate the use of screen printing as a technique for producing large area solar cells. The attributes of screen printing which make this approach of interest is that screen printing is a well established technique in the electronics industry with well established requirements, a demonstrated capability for producing large areas of electronic quality films with good pattern fidelity, a means for separating conditions required for film deposition from those required for sintering, which allows better control over microstructure, and a high material utilization efficiency. A possible disadvantage of screen printing is that the starting material must be reduced to a powder. The fact that efficient small area solar cells can be produced by screen printing is well documented in the literature⁽¹⁾.

In the first quarterly report was reported the comminution of CdS and CdTe and the preparation of the first trial films of these materials. This report covers the improvements made in the preparation of high quality electronically conductive films on glass in preparation for the subsequent preparation of multilayer solar cells.

2.0. Experimental

2.1. Materials

The sources, purity and comminution of the materials used have been described in the first quarterly report.

2.2. Equipment

The equipment described below augments the equipment described in the previous quarterly report.

A one kilowatt Schoeffel solar simulator with a Xenon lamp, was set up. The current-voltage characteristics of a silicon solar cell were measured using a PAR 175 function generator, PAR 371 potentiostat and a Bascom-Turner 8000 digital recorder. A Carver 9" by 9" heating and chilling plate was used as a support for the solar cell. The temperature was measured using an Analog Devices 6 channel scanning digital thermometer AD2036 equipped with Omega Engineering HYP1-30- $\frac{1}{2}$ -T-G-60-SMP-M thermocouple probes.

A laser probe was constructed to determine macro variations in the light transmission of solar cell layers. A one mm hole was drilled in an aluminum block. A Clairex CL604-397 CdSe photocell was mounted so that the light coming through the hole from the Spectra-Physics model 155 He-Ne laser would strike the photo-active surface (see Figure 1). A slot was cut perpendicular to the laser beam so that a glass slide with a CdS film could be lowered through the beam using a Fisher-Payne dip coater apparatus. A Model DL-40-700 Trygon Electronics power supply was used to maintain a constant potential across the photocell and load resistor. The current flowing in the circuit was monitored by an HP7005AM X-Y recorder across the load resistor (see Figure 2).

Noise level measurements were made with a Quest Electronics Model 215 sound level meter equipped with a Model 215-45 octave band analyzer. This unit was calibrated with a 110dB 1000 Hz Model CA-32 Calibrator.

3. Technical Discussion

3.1. Preparation of Films of Cadmium Sulfide

The initial problems associated with a residual screen pattern being left on the printed film which resulted in pinholes was resolved. Initial films were prepared using an ink consisting of 75 weight percent CdS and 25 weight percent vehicle. The vehicle contained 24 weight percent AB, 38 weight percent BCA, and 38 weight percent AT. By decreasing the CdS loading to 60 weight percent and increasing the AB content to 30 to 35 weight percent an ink was prepared which had suitable rheology for screen printing and produced films with a smooth uniform surface.

Films of CdS produced with the improved ink were free of any macro pores but lacked adhesion to the glass (7059) substrate and were highly resistive. Changing firing temperatures from 630°C to 660 to 700 to 735°C had little effect on adhesion or resistance of the fired films. Replacing 5 to 15 weight percent of the CdS with CdCl₂ did not improve the situation. SEM photographs of these films are shown in Figures 3 and 4. The lack of sharpness of these SEM photographs is due to the low conductivity of the CdS film and to the use of a sputtered carbon coating in place of the usual gold-palladium coating so that probe work could be performed. No appreciable sintering is evident in these photographs. Probe analysis of the films prepared from ink containing 10 weight percent CdCl₂ failed to detect any

Figure 1. Laser Probe

Figure 2. Electrical Circuit for Laser Detector

X 10,000

Figure 3. CdS Film Fired at 735°C

X 10,000

Figure 4. CdS with CdCl₂ Film Fired at 735°C

residual chlorine (limit of detection is 0.01 percent) in the fired samples. No difference in the films could be found when the glass substrate was changed from Corning 7059 to soft glass. Generally films originally containing chlorine were green in color and those without were yellow.

Pressed pellets of CdS and CdS plus CdCl₂ fired at 630°C in nitrogen showed marked densification (63% of theoretical) occurred in the samples containing CdCl₂ while little occurred in its absence. The lack of correspondence between the pellet and film behavior is attributed to the higher surface to volume ratio of the films than the pellets resulting in the former's loss of the CdCl₂ before appreciable sintering could occur.

Attempts were made to increase the CdCl₂ concentration present at the time of sintering. Samples were fired inverted over a boat filled with CdCl₂. Films were fired with boats preceding and following the samples. The samples fired over the CdCl₂ boats lost all the CdS. The glass substrates came out of the furnace completely devoid of any CdS. Samples fired with leading and trailing CdCl₂ boats resulted in samples which had a gradation of properties. The results were not reproducible.

Reduction of the nitrogen flow rate to the kiln from 10 cubic feet per hour to the end zones and 20 cubic feet per hour to the center zone to 5 cubic feet per hour to the end zones and 10 cubic feet per hour in the center resulted in the first films with appreciable adhesion to the substrates.

On the premise that the lack of sintering was due to the premature loss of the CdCl₂ from the very high surface to volume ratio thin film before sintering could occur, a series of different thickness films was prepared by printing two rectangular patterns at right angles to each other. After firing it was found that only the overlap area had appreciable adhesion. Samples were then printed with one, two, and three layers. The fired (630°C), three layer film passed the "adhesive tape" test for adhesion. SEM photographs of that film are shown in Figures 5 and 6. The photographs show the material in the preliminary stages of sintering with the film being very porous.

The CdCl₂ content was increased to 40 volume percent (35 weight percent) to improve sintering. Figures 7 and 8 are the SEM photographs of the three layer, forty volume percent CdCl₂ films fired at 630°C in nitrogen. Sintering has been greatly enhanced. Through porosity is still in evidence. A comparison of the electrical performance of the low and high CdCl₂ containing inks is provided in Table 1. Lower film thickness and higher conductivity are associated with the increased sintering noted in the SEM photographs.

Figure 5. Two Layer Cadmium Sulfide Film Fired at 630°C X 10,000

Figure 6. Two Layer Cadmium Sulfide Film at Higher Magnification X 30,000

X 1000

Figure 7. Cadmium Sulfide Layer with Forty Volume Percent Cadmium Chloride

X 4800

Figure 8. Cadmium Sulfide Layer with Forty Volume Percent Cadmium Chloride at Higher Magnification

TABLE I

Effect of Increased CdCl_2 Content on CdS Films

Volume Percent CdCl_2	Weight Percent CdCl_2	Thickness 10^{-4} cm	Resistivity Ω cm
17	15	35	1225
17	15	28	700
17	15	33	1155
17	15	30	630
40	35	15	15
40	35	15	60
40	35	15	3
40	35	15	3

In order to reduce the microporosity found in the films the vehicle was modified. It was felt that part of the porosity might be related to the tardy removal of the plastic binder, inhibiting full densification. The content of plastic in the vehicle was reduced from 30 weight percent AB (35 w/o BCA, 35 w/o AT) to 25 weight percent AB (37.5 w/o BCA, 37.5 w/o AT). A two layer film printed with this vehicle loaded to 60 weight percent CdS had a film thickness of 8 microns and a resistivity of 16.7 ohm cm (standard deviation of 6.1) and a three layer film had a film thickness of 13 micron and a resistivity of 1.8 ohm cm (standard deviation of 0.4). Figures 9 and 10 are SEM photographs of the surface of a three layer film. No through porosity is evident anywhere on the film. Figures 11, 12 and 13 are SEM photographs of a cross section of this film. There is evidence of voids of about 2-microns diameter below the film surface. The resistivity of this film was 1.65 ohm cm (standard deviation of 0.52) in room light and 2.34 ohm cm (standard deviation of 1.06) in the dark. Figure 13 shows the interface between the glass (on the bottom) and the CdS layer showing good wetting of the glass.

3.2. Preparation of Films of CdTe

Films of CdTe were prepared using a vehicle containing 30 weight percent AB, 35 weight percent BCA, and 35 weight percent AT. Figures 14 and 15 are SEM photographs of a two layer film sintered at 630°C. Large through pores are in evidence. Following the experience of the CdS work a two layer film was prepared using a vehicle which was lower in plastic content, 25 weight percent AB, 37.5 weight percent BCA, and 37.5 weight percent AT. Figures 16 and 17 are SEM photographs of this film fired at 630°C. Through pores are still in evidence. Three layers of CdTe appear to be required to get a pore free film. The resistivity of this film was 661 ohm cm (standard deviation of 78).

3.3. Film Characterization

In attempting to determine the uniformity of the CdS films a laser probe technique was developed. A one millimeter laser spot was directed onto a CdS film. The light transmitted through the film and glass substrate was detected with a CdSe photoconductive cell. Figure 18 shows a trace of the output of the detector as the substrate with film is lowered through the beam. The line across the bottom of the figure was generated with the laser off. The four downward spikes are the silver metallization. The shoulders on the top of the figure are the uncoated glass substrate and the downward spikes on

Figure 9. Surface of Cadmium Sulfide with Low Plastic Vehicle

Figure 10. Surface of Cadmium Sulfide with Low Plastic Vehicle at Higher Magnification

X 1000

Figure 11. Cross Section of Cadmium Sulfide with Low Plastic Vehicle

X 4800

Figure 12. Cross Section of Cadmium Sulfide with Low Plastic Vehicle
at High Magnification

Figure 13. Glass-Cadmium Sulfide Interface

X 1000

Figure 14. Cadmium Telluride with High Plastic Vehicle

X 10,000

Figure 15. Cadmium Telluride with High Plastic Vehicle at Higher Magnification

Figure 16. Cadmium Telluride with Low Plastic Vehicle

Figure 17. Cadmium Telluride with Low Plastic Vehicle at Higher Magnification

Figure 18. Laser Longitudinal Laser Scan of Cadmium Sulfide Film

either end of the curve are due to light being reflected along the edge of the glass substrate. While this technique could pick up films of unremoved CdCl_2 on the glass substrate, see Figure 19, the films appear to be homogeneous on the one millimeter scale. Detection of the variations found microscopically in CdS films would require a technique which would average over a smaller area, e.g. 0.1 mm diameter.

3.4. Safety

The noise level associated with the operation of the four inch jet mill was measured. The laboratory background sound level was found to be 65dB on the weighted "A" scale. With the jet mill operating the level was 101dB. The frequency distribution, see Figure 20, shows that the venturi feed produces most of its noise at high frequency. Based on the proposed OSHA noise exposure standard of 1975 the maximum exposure time allowed to 102dB noise on the "A" scale is 1.5 hours. With a 10dB attenuation to 92dB permissible exposure is six hours. The Norton 4540 earmuff used during the milling operation provides a 20dB attenuation. The noise level with these earmuffs was found to be uncomfortable and ear plugs were used in conjunction with the muffs.

4. Future Activity

Future activities will entail the improvement of CdTe films by going to three layer films. The problems of forming films of CdTe on top of CdS will be investigated. The possibility of co-firing the CdTe and CdS films will be investigated. Attempts will be made to produce solar cells from the CdS films.

Dr. Guy McDonald, Principal Investigator

Dr. G. Goodman, Project Manager

Figure 19. Laser Transverse Scan of Cadmium Sulfide Film

Figure 20. Sound Level Associated with the Operation of the Jet Mill

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