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PROCESS RESEARCH OF POLYCRYSTALLINE SILICON MATERIAL

Quarterly Report No. 1 for November 8—December 31, 1983

By
J. S. Culik

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Solarex Corporation
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QUARTERLY REPORT NO. 1

NOVEMBER 8, 1983 - DECEMBER 31, 1983

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The JPL Flat-Plate Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

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ABSTRACT

Recent reported results of hydrogen-passivated polycrystalline silicon solar cells are summarized. Most of the studies have been performed on very small grain or short minority-carrier diffusion length silicon. Hydrogenated solar cells fabricated from this material appear to have effective minority-carrier diffusion lengths that are still not very long, as shown by the open-circuit voltages of passivated cells that are still significantly less than those of single-crystal solar cells.

The short-circuit current of solar cells fabricated from large-grain cast polycrystalline silicon is nearly equivalent to that of single-crystal cells, which indicates long bulk minority-carrier diffusion length. However, the open-circuit voltage, which is sensitive to grain boundary recombination, is 20 to 40 mV less. The goal of this program is to minimize the variations in open-circuit voltage and fill-factor that are caused by structural defects by passivating these defects using a hydrogenation process.

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I. INTRODUCTION

This report summarizes the work performed during the first quarter of an effort that began on November 8, 1983. The intent of this program is to develop a passivation process (hydrogenation) that will improve the power generation of solar cells fabricated from presently-produced large-grain cast polycrystalline silicon (Semix), a potentially low-cost material.

Section II of this report discusses some of the background of hydrogenation as applied to polycrystalline silicon solar cells, and Section III describes the experimental procedure that will be pursued during the first phase of this research program.

II. PROGRAM BACKGROUND

In the course of work performed by Solarex under JPL Contract No. 955902, it was determined that the fundamental limitation to the light-generated current and open-circuit voltage of solar cells fabricated from presently-produced large-grain polycrystalline sheet silicon (Semix) is recombination in the quasi-neutral (base) region. The quasi-neutral recombination current was found to vary by up to an order of magnitude across a wafer, although it would more typically vary by a factor of two to five. Such changes may make little difference in the light-generated current if the absolute value of the quasi-neutral recombination is low enough. Unlike the light-generated current, however, the open-circuit voltage of a solar cell is extremely sensitive to quasi-neutral current and has the approximate form

$$V_{OC} \sim -(kT/q)\ln(R)$$

where R is the ratio of change in quasi-neutral recombination current. Using this expression, a factor of two increase in quasi-neutral recombination current (R = 2) will result in an 18 mV loss; a factor of five increase will (theoretically) yield a 42 mV loss; and an order of magnitude change will reduce the open-circuit voltage by about 60 mV. If the fill-factor is assumed to be constant (a best-case approximation), then the power generated by the solar cell will vary directly with open-circuit voltage. Thus, a 60 mV open-circuit voltage loss, from a 600 mV best-case cell, translates to at least a 10 percent loss in power.

Measurements of the open-circuit voltage and quasi-neutral recombination of solar cells fabricated from large-grain polycrystalline silicon (Semix) indicated that much of the loss in open-circuit voltage, hence power, was due to localized increases in the quasi-neutral recombination. The open-circuit voltage loss due to excess space-charge (junction depletion region) recombination was less than 10 mV for most of the samples tested.

The cause of this spatial variation in quasi-neutral recombination is not obvious. Assuming the dopant concentration is constant, it could be due either to (1) minority-carrier lifetime-killing impurities that are dispersed non-uniformly within the cast brick, or (2) structural defects that cause local reductions in minority-carrier lifetime. Since certain types of grain-boundaries are known to contain dislocations that can cause minority-carrier recombination, and polycrystalline silicon, by definition, has many grain boundaries, the presence of structural defects is more plausible than spatial impurity variations. This is supported by an earlier study of the spatial homogeneity of polycrystalline wafers [1] and by additional measurements of the light beam induced current (LBIC) of these cells [2]. These LBIC scans show that those cells with excess quasi-neutral recombination also have a large number of electrically-active grain and sub-grain boundaries. Therefore, it is reasonable to infer that structural defects, that is, dislocations, are the major cause of spatial variations in quasi-neutral recombination in large-grain cast polycrystalline silicon solar cells.

Hydrogenation has been used to improve the performance of polycrystalline silicon solar cells for several years. In 1980, Seager, et.al. [3] reported that hydrogenation of silicon-on-ceramic (SOC) material in a 2 Torr RF plasma at 350°C for 16 hours resulted in a reduction of both the diode reverse leakage current and the dark forward current. There were indications from an electron-beam induced current (EBIC) scan that grain boundaries were electrically inactivated by the process.

In 1981, Robinson and D'Aiello [4] used a 200 mTorr RF plasma at 400°C for 3 hours to hydrogenate solar cells fabricated from epitaxial silicon on upgraded metallurgical grade (UMG) silicon substrates. They reported that the improvements obtained in their solar cells, in open-circuit voltage and fill-factor but not in short-circuit current, were consistent with the previous work, and implied that the improvement was due to reduction of space-charge (junction) recombination.

In 1982, Seager, et.al. [5] reported on hydrogenation of SOC and SOG (silicon-on-graphite) by a Kaufman ion source. By analyzing the EBIC contrast at grain boundaries, they determined that very short (4 minute) exposures were sufficient to reduce the contrast to an equilibrium value. They found that the quantum efficiency of the fine grain (grain size less than 100 microns) material at long wavelengths was improved by the process.

Hydrogenation of ribbon (EFG) silicon was recently reported by Hanoka, et.al. [6]. The samples, $4cm^2$ solar cells, were hydrogenated with a Kaufman ion source for 4 minutes at 275°C. Solar cells with lower values of open-circuit voltage and short-circuit current tended to improve more after hydrogenation than cells with higher starting values. In effect, the open-circuit voltage and short-circuit current distribution narrowed, as shown in Table 1, which gives the average before-hydrogenation and after-hydrogenation values for eleven cells. The numbers in parentheses are the standard deviation about the mean.

TABLE 1

	V_{OC} (mV)	I_{SC} (mA/cm^2)	FF(%)
BEFORE	530 (9)	22.0 (1.1)	72.6 (1.5)
AFTER	550 (7)	23.3 (0.5)	74.3 (1.5)

The improvements in the short-circuit current and the fill-factor are not very large, although there does appear to be a significant improvement in the open-circuit voltage. The open-circuit voltage of one particular cell was reported to have increased by 58 mV after hydrogenation. However. the open-circuit voltage after hydrogenation, 566 mV, was still far below that of single-crystal silicon.

In summary, while there have been a number of interesting reports of hydrogenation used to passivate polycrystalline silicon, most of the studies have been performed on very small grain or low-quality (short minority-carrier diffusion length) silicon. The hydrogenated solar cells fabricated from this material appear to have effective minority-carrier diffusion lengths that are still not very long, as evidenced by open-circuit voltages of passivated cells that are still substantially less than those of single-crystal solar cells. Very little work has been done to develop a process that will improve large-grain polycrystalline silicon solar cells.

It has been shown that the short-circuit current of solar cells fabricated from large-grain polycrystalline silicon is fairly tolerant of the grain boundary content [7,8]. This is consistent with theory that states that the light-generated current is not substantially affected by recombination at grain boundaries when the grain diameter is several times larger than the minority-carrier diffusion length [9,10]. However, even though the short-circuit current may be tolerant, the open-circuit voltage and fill-factor are sensitive to grain-boundary recombination.

The intent of this program is development of a hydrogenation passivation process that will improve the performance of large-grain polycrystalline silicon solar cells. Although there has been no extensive survey of this material, it has been shown [8] that the open-circuit voltage of solar cells fabricated from non-hydrogenated large-grain cast (Semix) silicon is about 20 to 60 mV less than that of single-crystal cells. When the effect of inclusions, which act as resistive shunts and therefore degrade open-circuit voltage and fill-factor, are excluded, then the open-circuit voltage loss in polycrystalline silicon is closer to 20 to 40 mV. As noted previously, much of the variation in open-circuit voltage loss is due to spatial variations of quasi-neutral recombination.

The goal of this program is to minimize the variations in open-circuit voltage and fill-factor that are caused by structural defects by passivating these defects using a hydrogenation process. Addition of such a process will allow solar cells to be fabricated from large-grain cast polycrystalline silicon whose electrical performance, specifically open-circuit voltage and fill-factor, is less sensitive to the particular crystallization structure of the substrate.

III. EXPERIMENTAL PROGRAM

The program will consist of two phases. The first task will be to verify the operation of a DC plasma hydrogenation system and to investigate the effect of hydrogen on the electrical performance of a variety of polycrystalline silicon solar cells. The second task will be to parameterize and optimize a hydrogenation process, and will include a process sensitivity analysis.

The goal of the first phase of this work is to determine the fundamental basis for performance improvements in polycrystalline silicon solar cells due to the hydrogenation process. Specifically, the question left unresolved by previous studies is whether hydrogenation, as it affects the electrical performance of large-grain polycrystalline silicon solar cells, modifies the bulk or the junction properties of the devices. We will establish this by the following experiment.

As a result of the previous contract, JPL No. 955902, we have developed the capability for fabricating and testing small-area photodiodes (so-called "mini-cells") on large-area (10cm x 10cm) polycrystalline silicon wafers. We have used this capability, together with dark current-voltage ("dark I-V") junction characterization, to analyze the spatial variations of open-circuit voltage in cast polycrystalline silicon wafers.

This technique is readily adaptable to developing the hydrogenation process. Wafers with mini-cells will be fabricated and tested to locate areas where the open-circuit voltage is substantially degraded. Sample areas of about $4cm^2$, which are equivalent to a matrix of up to 5 by 5 mini-cells, can be hydrogenated in our system. After characterizing the matrix for dark I-V characteristics and by LBIC to locate the electrically-active grain boundaries, the matrix will be hydrogenated and re-analyzed. A comparison of before-hydrogenation and after-hydrogenation results will indicate the effect of the process on bulk, junction, and grain boundary recombination. Selection of the matrix mini-cells will be made so that the matrix contains both good performance cells (that is, with low quasi-neutral and space-charge recombination), as well as poor in order to provide a self-controlled test. LBIC will yield qualitative evidence of grain boundary recombination changes; measurement of the quasi-neutral and space-charge recombination by dark I-V characterization will provide a technique to quantitatively investigate the sensitivity of the change to process parameters. This information may be further substantiated by spectral response measurements.

The hydrogenation process will be performed using a DC plasma technique. This particular technique is "faster" than an RF plasma process and equivalent in speed to hydrogenation performed by Kaufman ion source [11]. It is inherently simpler than either RF or Kaufman hydrogenation. Its speed and simplicity makes it the ideal technique for use during the first phase of this program.

A schematic of the system that will be used to hydrogenate the sample solar cells is shown in Figure 1, which details the sample stage. The chamber is evacuated by a mechanical pump and, if desired, a diffusion pump. Ultimate chamber pressure is in the 10^{-6} Torr range. After being pumped, the chamber is back-filled with ultra-pure hydrogen. The 5cm x 5cm sample base plate is 3-9's pure tantalum and is heated with a 2.5cm x 2.5cm ceramic heater (Hittman 528000) on the bottom side. The substrate temperature can be controlled to within $\pm 2^{\circ}$C (up to about

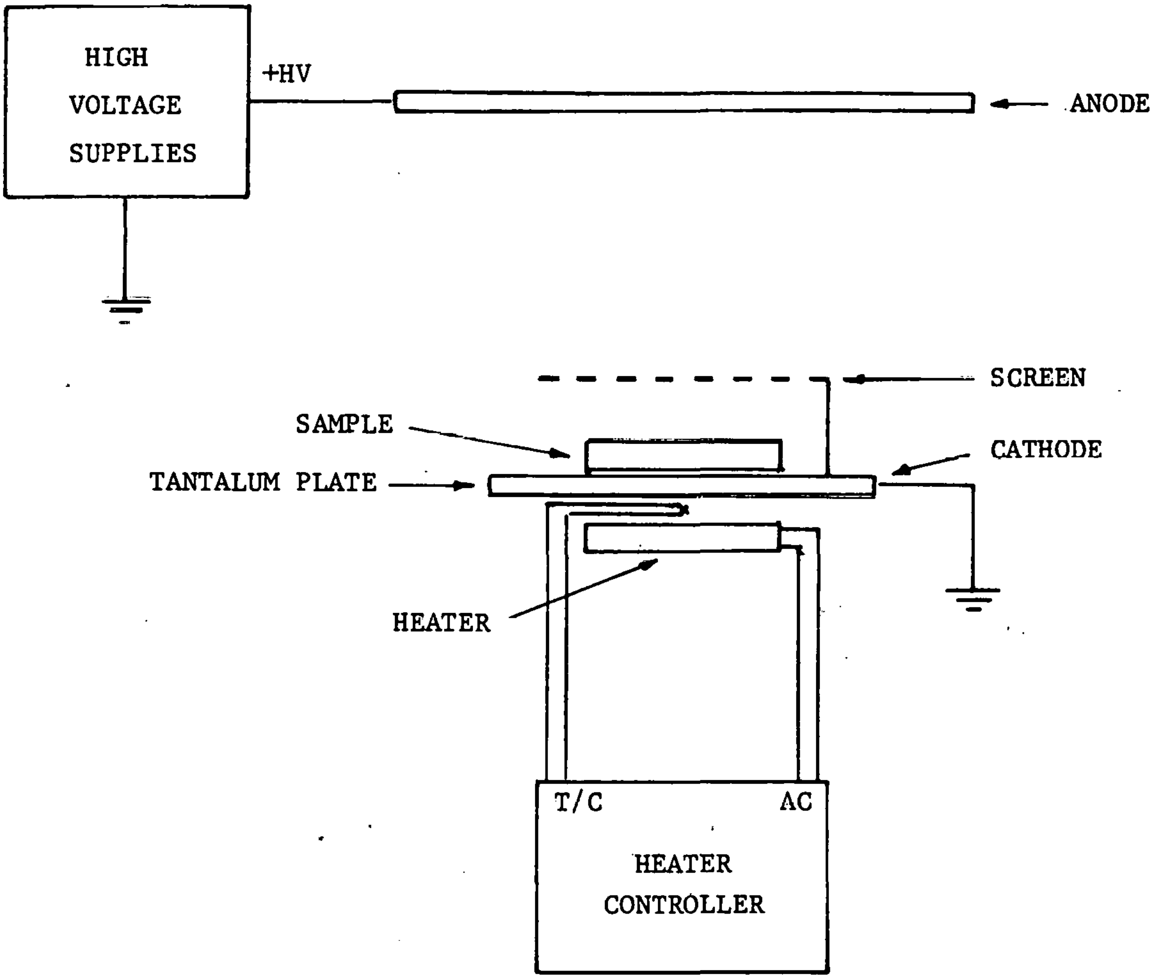
HIGH
VOLTAGE
SUPPLIES
+HV
ANODE
SCREEN
SAMPLE
CATHODE
TANTALUM PLATE
HEATER
T/C
AC
HEATER
CONTROLLER

FIGURE 1

700°C, if needed). By using several power supplies, we will be capable of obtaining plasmas of up to 500 V (at 10 mA/cm^2) or 1500 V (at 2 mA/cm^2).

The process parameters of DC plasma hydrogenation include:

1. acceleration voltage,
2. current density,
3. hydrogen pressure,
4. cell temperature, and
5. time.

In addition, there may be electrode-sample geometry effects. The impact of these variables on the effect of hydrogenation for a selection of samples, to account for variations in the polycrystalline material, will be investigated, and will result in a fairly general understanding of the effect of hydrogenation on the bulk, junction and grain boundary recombination of cast large-grain polycrystalline silicon solar cells.

IV. PLANS

Work during the next quarter (January to March, 1984) will be primarily directed toward fabricating and characterizing the mini-cell wafer set that will be used in the first phase of this contract. The sample stage and associated electronics will be built and the hydrogenation system will be tested. Some baseline experiments on the effect of a low temperature hydrogen anneal will be performed, and an existing LBIC system will be modified to accept mini-cell-sized samples.

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	PROGRAM SCHEDULE												
	MONTH												
WORK ELEMENT	1	2	3	4	5	6	7	8	9	10	11	12	
HYDROGENATION													
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3. QUARTERLY TECHNICAL REPORT			▽			▽			▽				
4. DRAFT FINAL TECHNICAL REPORT												▽	
5. FINAL TECHNICAL REPORT													▽
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