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PROCESS RESEARCH ON POLYCRYSTALLINE SILICON MATERIAL
(PROPSM)

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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 sometimes 20 to 40 mV less. The goal of this program was to minimize variations in open-circuit voltage and fill-factor caused by defects by passivating these defects using a hydrogenation process.

Treatments with molecular hydrogen showed no effect on large-grain cast polycrystalline silicon solar cells. The program was terminated prior to the planned plasma hydrogenation (atomic hydrogen) phase due to a reduction in personnel available for the contract effort.

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I. INTRODUCTION

This report summarizes work performed during an effort that began in November, 1983 and ended in June, 1984. The intent of this program was to develop a passivation process (hydrogenation) that would enhance the photovoltaic conversion efficiency of solar cells fabricated from large-grain, cast polycrystalline silicon (such as Solarex Semicrystalline), a potentially low-cost material. The program was to consist of two phases. The first objective was 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 objective was to parameterize and optimize a hydrogenation process for cast polycrystalline silicon, and included a process sensitivity analysis.

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 to be pursued during this research program.

Section IV of this report outlines the sample preparation for the first phase. Section V describes the hydrogenation system; and Section VI summarizes some early results obtained using the hydrogenation system without a plasma. Light-beam induced current (LBIC) measurements of mini-cell samples, and their correlation to dark current-voltage characteristics, are discussed in Section VII. Section VIII contains the Conclusions and Recommendations.

The program was terminated prior to the planned plasma hydrogenation phase due to a reduction in personnel available for the contract effort.

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 then-produced large-grain polycrystalline sheet silicon (such as Solarex Semicrystalline) was recombination in the quasi-neutral (base) region. The quasi-neutral recombination current was found to vary by a factor of two to five across a wafer but could vary by up to an order of magnitude. Such changes may make little difference in the photocurrent if the absolute value of the quasi-neutral recombination is low enough. Unlike the photocurrent, however, the open-circuit voltage of a solar cell is 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 a 10 percent loss in power conversion.

Measurements of the open-circuit voltage and quasi-neutral recombination of solar cells fabricated from large-grain polycrystalline silicon indicated that much of the difference from ideal in open-circuit voltage, hence power, was due to localized increases in the quasi-neutral recombination. The open-circuit voltage restraint 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-life-time-killing impurities that are dispersed non-uniformly within the cast brick, or (2) localized 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 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 silicon wafers [1] and by additional measurements of the light beam induced current (LBIC) of

those cells [2]. These LBIC scans showed that those cells with excess quasi-neutral recombination also have a larger number of electrically-active grain and subgrain 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 sixteen 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 three 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 depletion region) 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 (four 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 Hanoak, et.al. [6]. The samples, 4mc^2 solar cells, were hydrogenated with a Kaufman ion source for four 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 parantheses are the standard deviation about the mean.

TABLE 1

| | <u>V_{OC} (mV)</u> | <u>I_{SC} (mA/cm²)</u> | <u>FF (%)</u> |
|--------|---------------------------------|------------------------------------------------|---------------|
| 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 large compared to the standard deviations,

although there does appear to be a real 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 of that particular solar cell after hydrogenation, 566 mV, was still far below that attainable in 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 such 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 higher-efficiency solar cells. On the other hand, very little work had been done to develop a similar process for 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 which expects that the photocurrent 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 somewhat more affected by grain-boundary recombination.

The intent of this program was development of a hydrogenation passivation process that would 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 silicon can be about 20 to 60 mV less than that of single-crystal cells. When inclusions, which can act as resistive shunts and thereby degrade open-circuit voltage and fill-factor, are excluded, then the effect on open-circuit voltage in polycrystalline silicon is limited to 20 to 40 mV. As noted previously, much of the variation in open-circuit voltage is due to spatial variations of quasi-neutral recombination.

The goal of this program was to minimize the variations in open-circuit voltage and fill-factor which can be caused by structural defects by passivating these defects using a hydrogenation process. Addition of such a process might aid solar cells to be fabricated from particular large-grain cast polycrystalline silicon samples with electrical performance, specifically open-circuit voltage and fill-factor, less sensitive to such particular crystallization structures of the substrate.

III. EXPERIMENTAL PROGRAM

The program was to consist of two phases. The first task was to verify the operation of a DC plasma hydrogenation system and to investigate the effects of hydrogen on the electrical

performance of a variety of polycrystalline silicon solar cells. The second task was to parameterize and optimize a hydrogenation process, and to include a process sensitivity analysis.

The goal of the first phase of this work was to determine the fundamental basis for performance improvements in specific 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 were to establish this by the following experiment.

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

This technique is readily adaptable to developing a hydrogenation process. Wafers with mini-cells were fabricated and analyzed to locate localized areas of lower open-circuit voltage. Sample areas of about 4cm², which are equivalent to a matrix of up to 5-by-5 mini-cells, can be hydrogenated in our system. After characterizing the matrix by dark I-V characteristics and by LBIC to locate electrically-active grain

boundaries, the matrix was to be hydrogenated and re-analyzed. A comparison of before-hydrogenation and after-hydrogenation results would indicate the effect of the process on bulk, junction, and grain boundary recombination. Search for and selection of the matrix mini-cells was made so that the matrix contained 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 would yield qualitative evidence of grain boundary recombination changes; measurement of the quasi-neutral and space-charge recombination by dark I-V characterization would provide a technique to quantitatively investigate the sensitivity of the change to process parameters. This information could be further substantiated by spectral response measurements.

IV. PHASE I SAMPLE PREPARATION

The goal of this program as described above was to determine the fundamental basis for performance improvements in polycrystalline silicon solar cells due to a hydrogenation process. Specifically, the question left unresolved by previous studies is whether hydrogenation, as it affects the electrical performance of large-grain cast polycrystalline silicon solar cells, modifies the bulk or the junction properties of the devices.

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 variation of open-circuit voltage across polycrystalline silicon wafers.

This approach, analyzing small-area photodiodes fabricated on larger area sample substrates, was to be utilized in developing the hydrogenation process. Wafers with mini-cells were to be fabricated and tested to locate areas where the open-circuit voltage is substantially degraded. Sample areas of about 4cm^2 are equivalent to a 5-by-5 matrix of mini-cells. After characterizing the matrix for dark I-V characteristics and by light-beam induced current (LBIC) measurements to locate electrically-active grain boundaries, the matrix would be hydrogenated and re-analyzed. A comparison of before-hydrogenation and after-hydrogenation results was to indicate the effect of the process on bulk, junction, and grain boundary recombination. Selection of the matrix mini-cells was to 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.

During the first quarter a set of mini-cell wafers was fabricated from a selection of 10cm x 10cm polycrystalline (Semix) wafers. The wafer set was comprised of sampled wafers from ingots 71-01E, C4-116B, and C4-108 (which were also utilized in the previous work, JPL Contract 955902), and wafers from ingots C4-82E and C4-87E. In addition, several single-crystal wafers were processed as controls.

The mini-cell wafers were fabricated using the mesa etch process developed by the previous program [11]. This process resulted in an array of up to 400 small (approximately 0.20cm² in area) photodiodes ("mini-cells") on 10cm x 10cm wafers. The diodes are isolated from one another by etching away several microns of silicon from between the cells, resulting in a mesa diode structure.

However, electrical tests of this first set of wafers indicated that significant portions of the n⁺ diffused layer were removed from the active area during the mesa etch, thus rendering the wafers unusable. Therefore, fabrication of a second set of mini-cell wafers, from the same ingots, was immediately begun toward the end of the second quarter.

Additional problems delayed the sample fabrication work during the third quarter, due to the fact that the process research laboratory at Solarex was shut down for renovation. As equipment was returned to operation, processing resumed, and a portion of the sample set was finished at the end of the third quarter. Preliminary testing indicated that this wafer set did not suffer from incomplete emitters and that the cell-to-cell isolation is excellent. The remainder of the sample set was then to be completed, and electrical characterization and hydrogenation were commenced. This was, however, the time at which the project was terminated due to reduction in available personnel.

V. HYDROGENATION SYSTEM SAMPLE STAGE

Hydrogenation processes are typically performed with the samples in a hydrogen ambient at a temperature that is usually, but not always, above room temperature. Although some hydrogenation processes utilize molecular hydrogen, most require the atomic form, using either an AC or DC plasma or a Kaufman ion source to obtain the ionized species.

For at least the first phase of this program, hydrogenation was performed using a DC plasma. Some work during the first quarter was dedicated to modifying a vacuum deposition system for hydrogenation, and locating parts for the substrate heater. A schematic diagram of the substrate stage is shown in Figure 1. It consists of a 5cm x 5cm, 0.999 pure, tantalum plate held above the base by ceramic insulators. The plate and sample are heated by a 2.5cm x 2.5cm ceramic heater (Hittman 52800) beneath the plate. The sample temperature is monitored by a type K thermocouple that feeds a temperature controller (Omega 4001KC). A schematic of the temperature control circuit is shown in Figure 2. The heater power is limited by the series resistor to about 20W. This can be adjusted, as needed. Substrate temperatures up to about 400°C are possible with this design; the low thermal mass of this stage allows the temperature to be ramped up or down very quickly, if necessary.

In operation the chamber is evacuated using mechanical and diffusion pumps, then backfilled with ultra-pure hydrogen. For

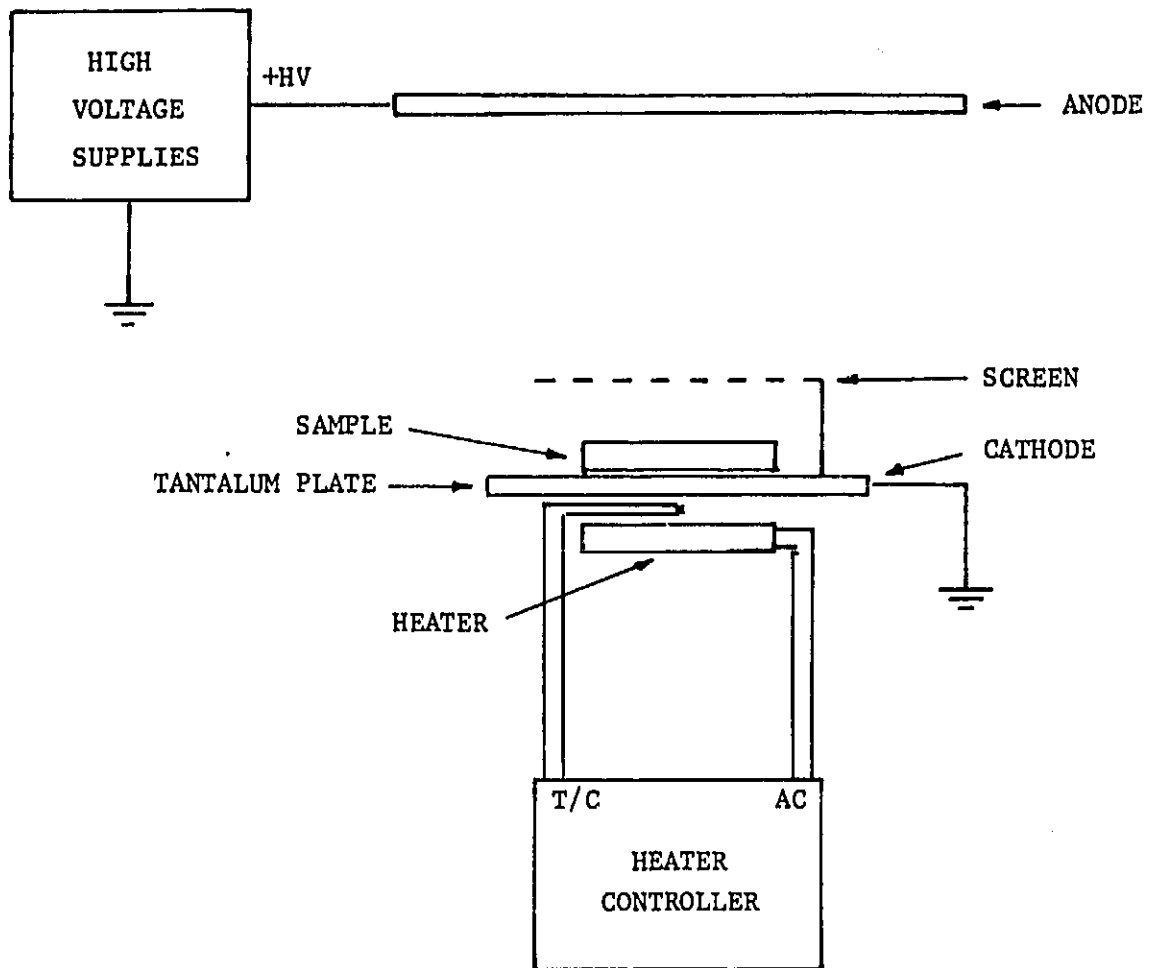


FIGURE 1

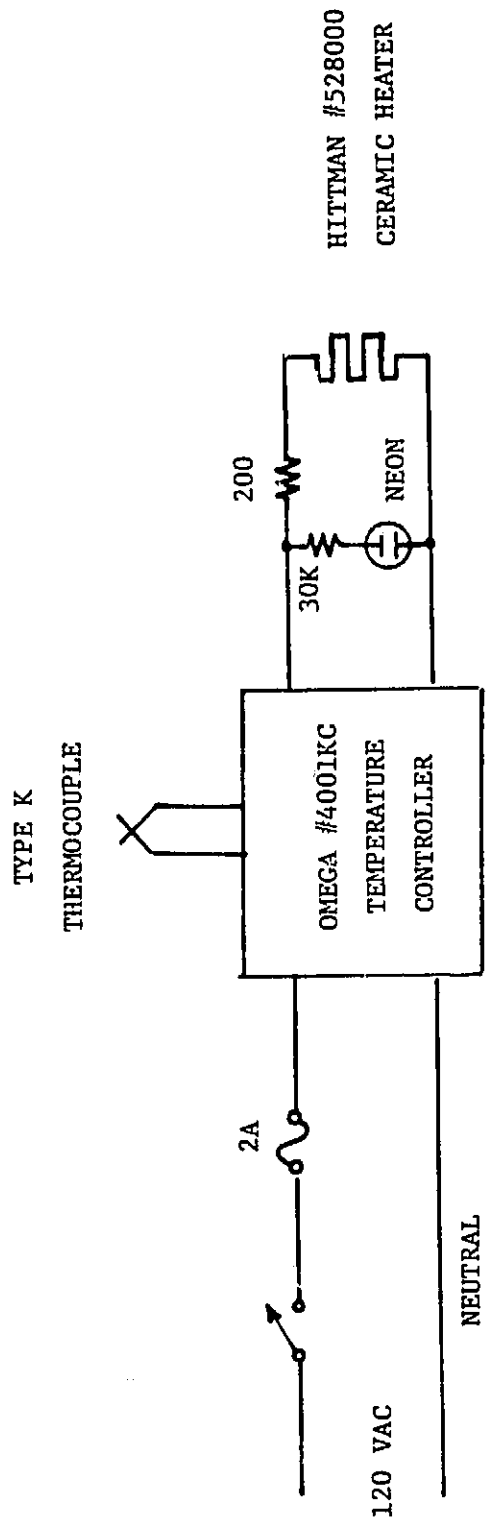


FIGURE 2

molecular hydrogen passivation, no voltage is applied to the top plate. For passivation with ionized hydrogen, a plasma can be obtained by applying a positive voltage in the 300 to 1000 volt range to the top plate (anode). The cathode and screen are both held at ground potential.

Two power supplies are available for obtaining the high voltage. The first (HP Model 712B) is useful for lower voltage, higher current (500V, 200 mA). The other (Kepko Model 1220C) will achieve a higher voltage (1500V) but with a sacrifice of current (50 mA). Assuming a 25cm^2 current cross-section, we may be able to obtain maximum current densities of $2\text{mA}/\text{cm}^2$ (at 1500V) to $8\text{mA}/\text{cm}^2$ (at 500V). We will use both power supplies in order to cover the range of possible accelerating voltages.

VI. MOLECULAR HYDROGENATION

The previous discussion of hydrogenation dealt solely with passivation of polycrystalline silicon by an ionized form of hydrogen, which was obtained by either an AC or DC plasma or by a Kaufman ion source. Some of the research groups that did this work also investigated the use of molecular hydrogen, but found that it apparently does not result in grain boundary passivation. As early as 1979, Seager and Ginley [12] experimented with a number of passivants, including molecular hydrogen, and concluded that molecular hydrogen did not diffuse into the silicon. In 1980, Benton, et.al. [13] passivated defects in laser recrystallized silicon with a 0.38 Torr AC hydrogen plasma at

200°C for four hours. They were, however, unable to effect any measurable defect passivation with a four hour anneal in molecular hydrogen.

In contrast, del Valle, et.al. [14], reported on an increase in the minority-carrier diffusion length of Wacker polycrystalline silicon by annealing in molecular hydrogen at 700°C for one hour. Since there was no improvement after a 700°C anneal in nitrogen, they concluded that the change was due to incorporation of hydrogen. However, Benton's group was able to anneal point defects in their laser-recrystallized silicon by a thermal anneal at 700°C [15], and this thermally-related defect anneal may invalidate del Valle's claim of molecular hydrogen passivation.

To further clarify this difference between atomic and molecular hydrogenation, Johnson, et.al. [16], investigated hydrogen passivation of grain boundaries of silicon deposited by low pressure chemical vapor deposition (LPCVD) using deuterium, in order to be able to detect its presence by using SIMS. They found that monatomic deuterium at 350°C permeated the film, whereas the concentration of molecular deuterium after a 400°C anneal for one hour was negligible. These particular results indicated that little if any, molecular hydrogen was retained by the grain boundaries.

However, several other groups have recently reported that molecular hydrogen is in fact useful for improving polycrystal-

line silicon. In 1982, Lam [17] reported on reducing the sheet resistance (or increasing the conductance) of LPCVD polycrystalline by annealing in molecular hydrogen at 450°C for thirty minutes. After heating to 600°C, the sheet resistance had returned to its pre-anneal value, indicating that the change was due to incorporation of hydrogen in the film.

Amzil, et.al. [18], recently reported that they were able to obtain improvements in the effective minority-carrier diffusion length of Wacker and CGE polycrystalline silicon by both molecular and atomic hydrogen. The increase due to annealing in molecular hydrogen at 300°C for times longer than two hours was similar to, but not as large as, that obtained by AC plasma and Kaufman ion source hydrogenation. Anneals in argon at similar temperature and time had no effect. These results are interesting but not conclusive since there was no solar cell results (such as short-circuit current, open-circuit voltage, and fill-factor) reported.

During the second quarter, we began an experiment to investigate the usefulness of molecular hydrogen annealing on polycrystalline solar cells. Several samples were selected from 4cm² solar cells fabricated from the thickness-resistivity matrix of the previous program (JPL Contract No. 955902). The cells were fabricated from 1.5 ohm-cm polycrystalline silicon wafers supplied by Semix, Inc., chemical-polish etched to a thickness of 250 microns, diffused to 70 ohms/square, and alloyed with Englehard A-3484 aluminum paste to compensate the

back junction. The metallization system was evaporated Ti-Pd with electroplated Ag. The front contacts were a standard Solarex fine-line chevron pattern, which was photolithographically-defined. The wafers were sintered for fifteen seconds at about 475°C before being sawn into 4cm² cells, and were heated an additional fifteen seconds after a tantalum oxide anti-reflection (AR) coating was electron-beam evaporated. For this hydrogen annealing experiment, the AR-coating was removed by an HF-vapor etch.

The particular cells for molecular hydrogen annealing were searched out using two criteria. They were to have: (1) low open-circuit voltage; and (2) low shunt conductance. Cells that met these conditions had to have an open-circuit voltage loss mechanism that was not related to a simple ohmic shunt, that is, probably not due to process-induced faults. Non-shunted cells with low open-circuit voltages were more likely to have a material-related loss mechanism. As discussed in the following section, a cell which contained a large number of electrically-active grain and subgrain boundaries would have values of open-circuit voltage that were reduced. The first of the poor cells that was annealed (cell 1-8) had an open-circuit voltage of 537 mV (at 135 mW/cm², 25°C) and a shunt conductance of about 0.07 mmho/cm². This rather poor non-AR-coated cell also had a photocurrent density of 22.7 mA/cm² at 135 mW/cm² incident power. For comparison, a good single-crystal cell typically has a photocurrent density of 27 to 28 mA/cm². Illuminated and dark I-V characteristics were measured, and the cell was annealed in

4cm² CELL EXPERIMENTAL FABRICATION SEQUENCE, p-on-n

1. Chemical-polishing etch to 250 micron wafer thickness.
2. Phosphorus diffusion to 70 ohms/square, 890°C.
3. Screen Englehard aluminum-powder ink on backs, dry at 200°C and first thirty seconds at 850°C.
4. Remove aluminum in HCl, rinse and dry.
5. Apply positive photoresist to front, expose grid pattern, develop, rinse and dry.
6. Evaporate Ti and Pd to 800-1000 Angstroms, both sides.
7. Solvent lift-off of photoresist and front field metal film.
8. Plate Ag to 10 micron thickness.
9. Sinter contacts fifteen seconds at 475°C.
10. Saw 4cm² cells out of wafers.
11. Evaporate Ta₂O₅ AR coating.
12. Heat to 475°C for fifteen seconds in air.

high purity hydrogen at 1 Torr and 300°C for one hour. The illuminated and dark I-V characteristics were again measured, and the cell was then returned to the hydrogenation system. Measurements were made after 1, 2, 5, 10 and 20 (total) hours. Figure 3 shows the dark I-V curve before annealing and after ten hours. There is no improvement in the dark characteristics. In fact, the space-charge component appears to have increased slightly. The open-circuit voltage change was within the measurement uncertainty. Therefore, we concluded that basically no change occurred as a result of molecular hydrogen passivation.

It may be, however, that this particular poor cell has a low value of open-circuit voltage due to a short minority-carrier diffusion length that is not related to electrically-active grain or subgrain boundaries. This problem was suggested by the value of photocurrent that is considerably lower (by about 15%) than that of single-crystal cells. Therefore, we continued this experiment by seeking out additional cells for molecular hydrogenation under the following new criteria: (1) low open-circuit voltage; (2) low shunt conductance; and (3) high photocurrent. This criteria should insure that the open-circuit voltage is degraded solely by grain-boundary-related defects.

Two additional 4cm² polycrystalline cells (1-10 and 1-14) were chosen for molecular hydrogenation. Their electrical characteristics before hydrogenation are shown in Table 2.

FIGURE 3

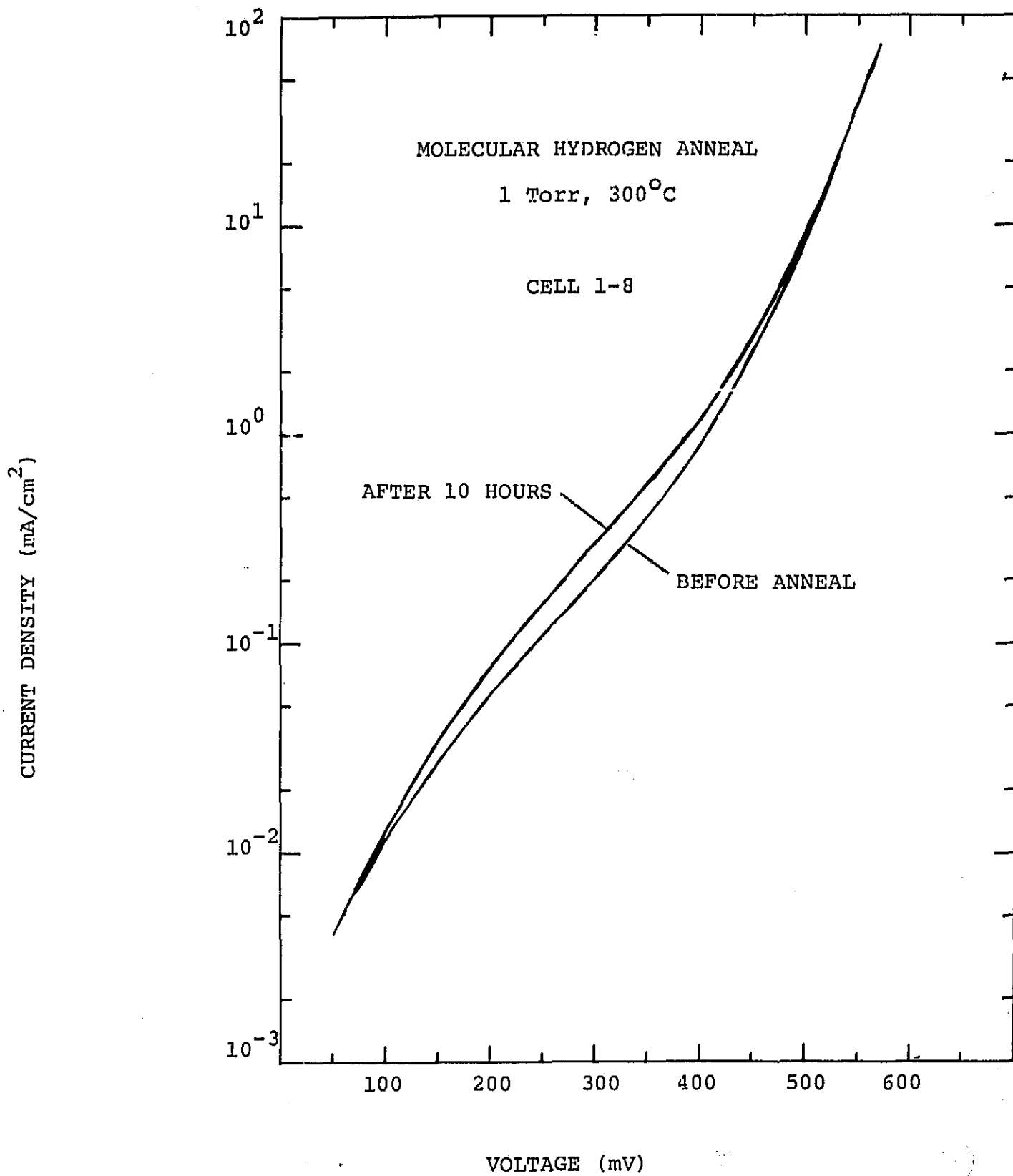


TABLE 2
ELECTRICAL CHARACTERISTICS OF TWO 4cm² POLYCRYSTALLINE
SILICON SOLAR CELLS BEFORE HYDROGENATION

| CELL NO. | V_{oc} (mV) | J_{sc} (mA/cm ²) | G (mmho/cm ²) |
|----------|------------------|-----------------------------------|------------------------------|
| 1-10 | 551 | 23.5 | 0.11 |
| 1-14 | 562 | 25.5 | 0.10 |

These cells were hydrogenated in molecular hydrogen (H₂) at a temperature of 300°C for a total time of 1, 2, 5, 10, and 20 hours. Dark I-V characteristics were measured before hydrogenation and after each cycle. The results are shown in Table 3.

TABLE 3
DARK I-V CHARACTERISTICS OF CELLS 1-10 and 1-14
DURING MOLECULAR HYDROGENATION

| CELL NO. | CUMULATIVE HYDRO- GENERATION TIME (hours) | J_{QNO}^* $\times 10^{-9}$ (mA/cm ²) | J_{SCO}^{**} $\times 10^{-3}$ (mA/cm ²) | n-factor |
|----------|-------------------------------------------------|----------------------------------------------------------|-------------------------------------------------------------|----------|
| 1-10 | 0 | 8.4 | 1.2 | 2.4 |
| | 1 | 7.9 | 0.7 | 2.3 |
| | 2 | 8.4 | 1.6 | 2.6 |
| | 5 | 8.4 | 1.5 | 2.5 |
| | 10 | 8.1 | 2.2 | 2.6 |
| | 20 | 8.8 | 2.1 | 2.6 |
| 1-14 | 0 | 6.3 | 0.4 | 2.2 |
| | 1 | 6.8 | 0.5 | 2.4 |
| | 2 | 6.8 | 1.1 | 2.6 |
| | 5 | 6.5 | 1.2 | 2.6 |
| | 10 | 8.5 | 1.4 | 2.6 |
| | 20 | 6.6 | 1.0 | 2.5 |

* J_{QNO} = quasi-neutral recombination current density at V=0

** J_{SCO} = space-charge recombination current density at V=0

TABLE 4

ELECTRICAL CHARACTERISTICS OF TWO 4cm² POLYCRYSTALLINE SILICON
SOLAR CELLS AFTER 20 HOURS IN MOLECULAR HYDROGEN AT 300°C

| CELL NO. | V_{oc} (mV) | J_{sc} (mA/cm ²) | G (mmho/cm ²) | V_{oc} (mV) | I_{sc} (mA/cm ²) |
|----------|------------------|-----------------------------------|--------------------------------|------------------|-----------------------------------|
| 1-10 | 553 | 24.1 | 0.09 | +2 | +0.6 |
| 1-14 | 565 | 26.0 | 0.08 | +3 | +0.5 |

The differences between the before and after hydrogenation values are so slight as to be negligible. These cells, unlike the previous cells, have photocurrent densities that are indicative of fairly long minority-carrier diffusion lengths. The open-circuit voltage appears to be degraded, and the quasi-neutral recombination current enhanced, by electrically-active grain boundary defects. Therefore, since there is essentially no change in the bulk (quasi-neutral) recombination, we conclude that molecular hydrogen is not useful for passivating electrically-active defects. There was no significant improvement in open-circuit voltage, short-circuit current density, or shunt conductance.

VII. LIGHT-BEAM INDUCED CURRENT (LBIC)

Electron-beam induced current (EBIC) and light-beam induced current (LBIC) measurements are techniques that are commonly used to locate and image electrically-active defects in devices. The two techniques are complementary in that EBIC has much finer resolution (less than ten microns), but very shallow penetra-

tion, while LBIC, though not as fine in resolution (much greater than ten microns), allows one to choose the penetration depth by varying the wavelength of the light. Thus, both surface and bulk defects, if large, can be imaged with LBIC by choosing the correct wavelength.

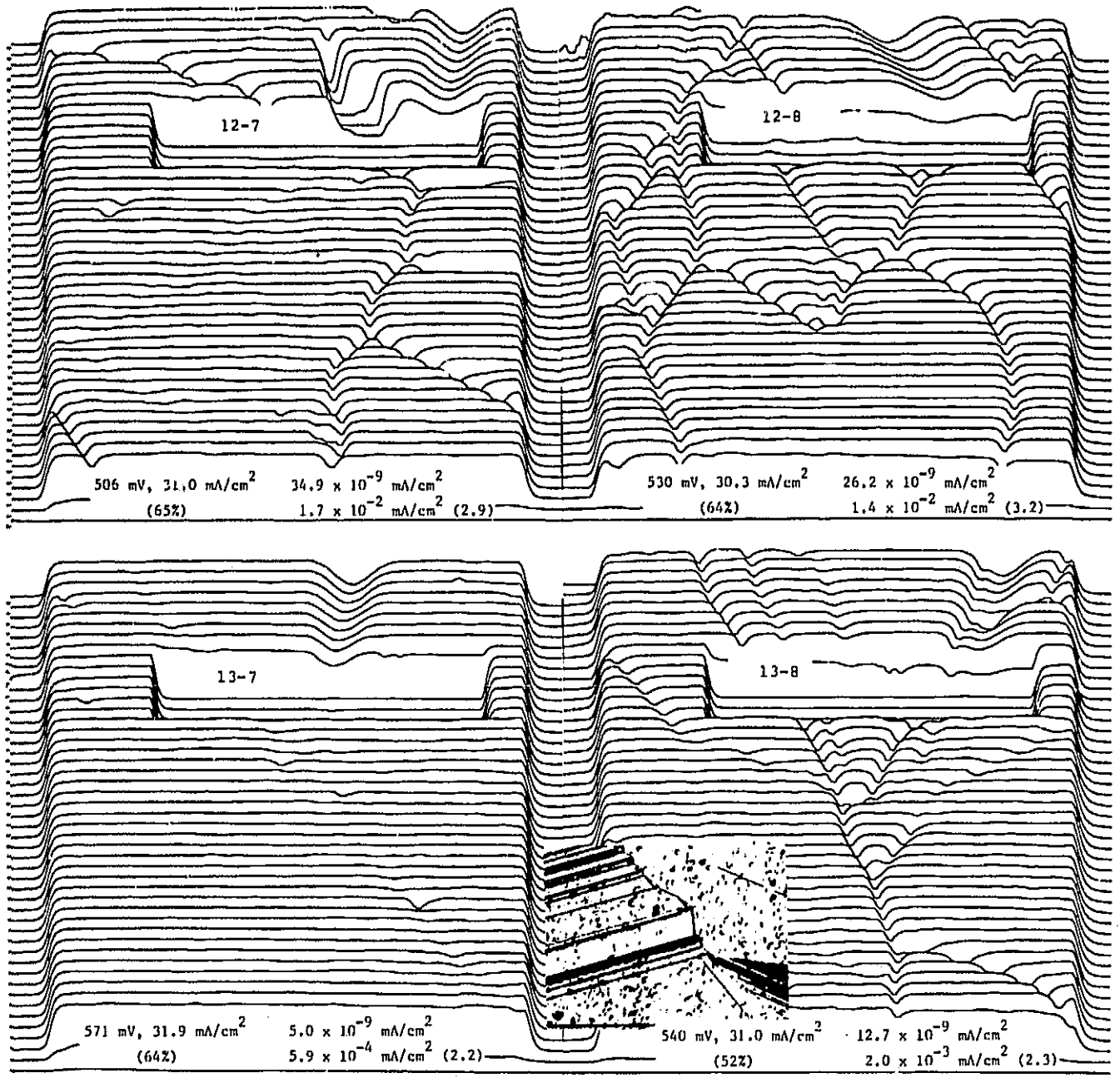
Results from the previous contract (JPL Contract No. 955902) indicated that much of open-circuit voltage differences in large-grain polycrystalline solar cells was due to excess quasi-neutral (bulk) recombination. Thus, significant improvements to the performance of these cells will occur only if bulk recombination processes are reduced. Techniques to evaluate bulk recombination processes, specifically dark I-V characteristics and long-wavelength LBIC, were to be used in this program to study the effect of hydrogen passivation on polycrystalline silicon solar cell performance.

Solarex has had LBIC capabilities for several years. However, the system was originally designed for 4cm² solar cells. During the second quarter, the LBIC system was modified to accomodate mini-cell wafers. This was accomplished by adding a magnetic probe and a steel baseplate to the existing sample stage. No changes to the system software were required. However, a considerable amount of effort was needed to eliminate noise sources in the system and to determine the system parameters for use with mini-cells.

LBIC system capability was demonstrated by scanning selected areas of two mini-cell wafers used in the previous program (JPL Contract No. 955902). Measurements were made at an LBIC wavelength of 800 nm; the light penetration depth into the silicon is about ten microns at this wavelength. Figures 4 and 5 show two LBIC scans from regions of mini-cell wafer C4-116B. In Figure 4 (mini-cells 12-7, 12-8, 13-7, 13-8), there is a strong correlation between electrically-active grain-boundary content, open-circuit voltage, and quasi-neutral recombination. Cell 13-7 has very little grain-boundary activity and the lowest value of J_{QNO} . The inset shows a photograph of an area to the left; there are many twin boundaries in cell 13-7. But they are not electrically-active and do not cause the quasi-neutral recombination current to increase. In contrast, cells 13-8 and 12-8 have progressively more LBIC-imaged grain-boundary activity, greater quasi-neutral and space-charge recombination, lower open-circuit voltage, and lower light-generated current density. Cell 12-7 has the lowest open-circuit voltage and the greatest amount of quasi-neutral recombination, but less LBIC-imaged grain-boundary activity.

Similar correlation between grain-boundary activity and quasi-neutral recombination is shown in Figure 5 (mini-cell wafer C4-116B; cells 13-2, 13-3, 14-2, 14-3). Cell 13-2, which has the least amount of LBIC-imaged grain-boundary recombination, also has the lowest bulk recombination and the highest open-circuit voltage. Next to it, cells 13-3 and 14-2 have considerably more grain-boundary activity, lower open-circuit

FIGURE 4



KEY

V_{oc}, J_{sc}
(FF)

J_{QNO}

J_{SCO} (n-factor)

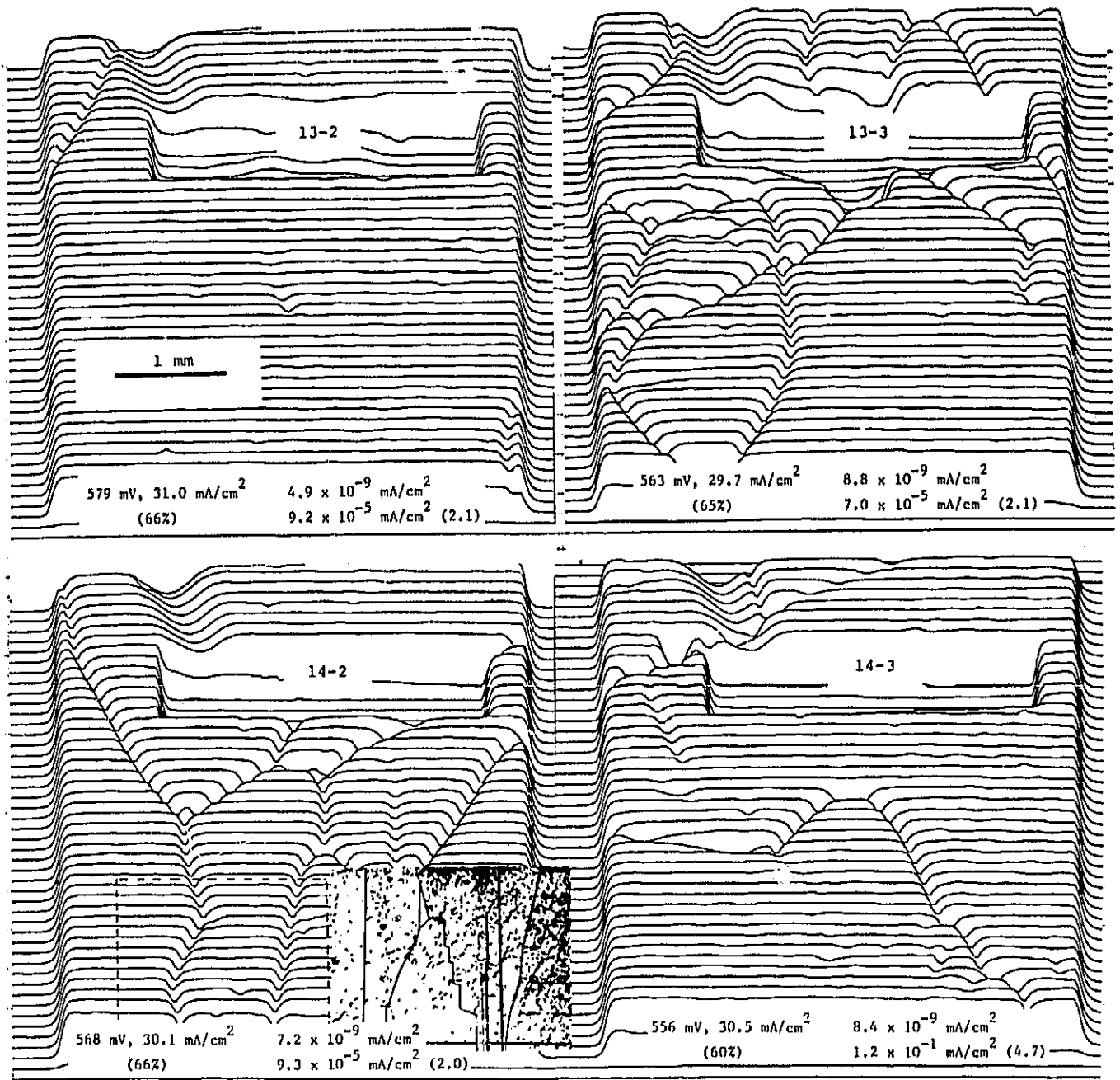


FIGURE 5

voltage, significantly greater quasi-neutral recombination, but space-charge recombination that is only slightly greater than cell 13-2. Cell 14-3 has an extremely large value of space-charge recombination but much less grain-boundary activity than cells 13-3 or 14-2. These results would seem to indicate that space-charge recombination is not correlated with grain-boundary recombination. Also, the fill-factor does not appear to suffer due to grain-boundary recombination (compare cells 13-2 and 14-2).

Figure 6 and 7 show LBIC scans from two regions of mini-cell wafer 71-01E/TOP that have a large number of subgrain (small-angle) boundaries. These scans were also made at an LBIC wavelength of 800 nm. Figure 6 (cells 3-4, 4-4, 3-3, and 4-3) once again shows a very strong correlation between LBIC-imaged grain-boundary activity and quasi-neutral recombination. The insets are of an area to the right which has a considerable amount of LBIC-activity. The right inset shows that there are not many grain boundaries in this area. However, the left inset, of a defect-etched serial wafer, shows that there are many dislocations in this region which form subgrain boundaries that act to reduce the electrical grain size. Quasi-neutral recombination increases progressively from cell 3-3, to 3-4, 4-4, and 4-3 by a factor of two. The open-circuit voltage decreases by 21 mV. The fill-factor of all of these cells is not significantly different. However, the space-charge recombination of cell 4-3, with the greatest number of electrically-active grain boundaries, is significantly less than that of cell

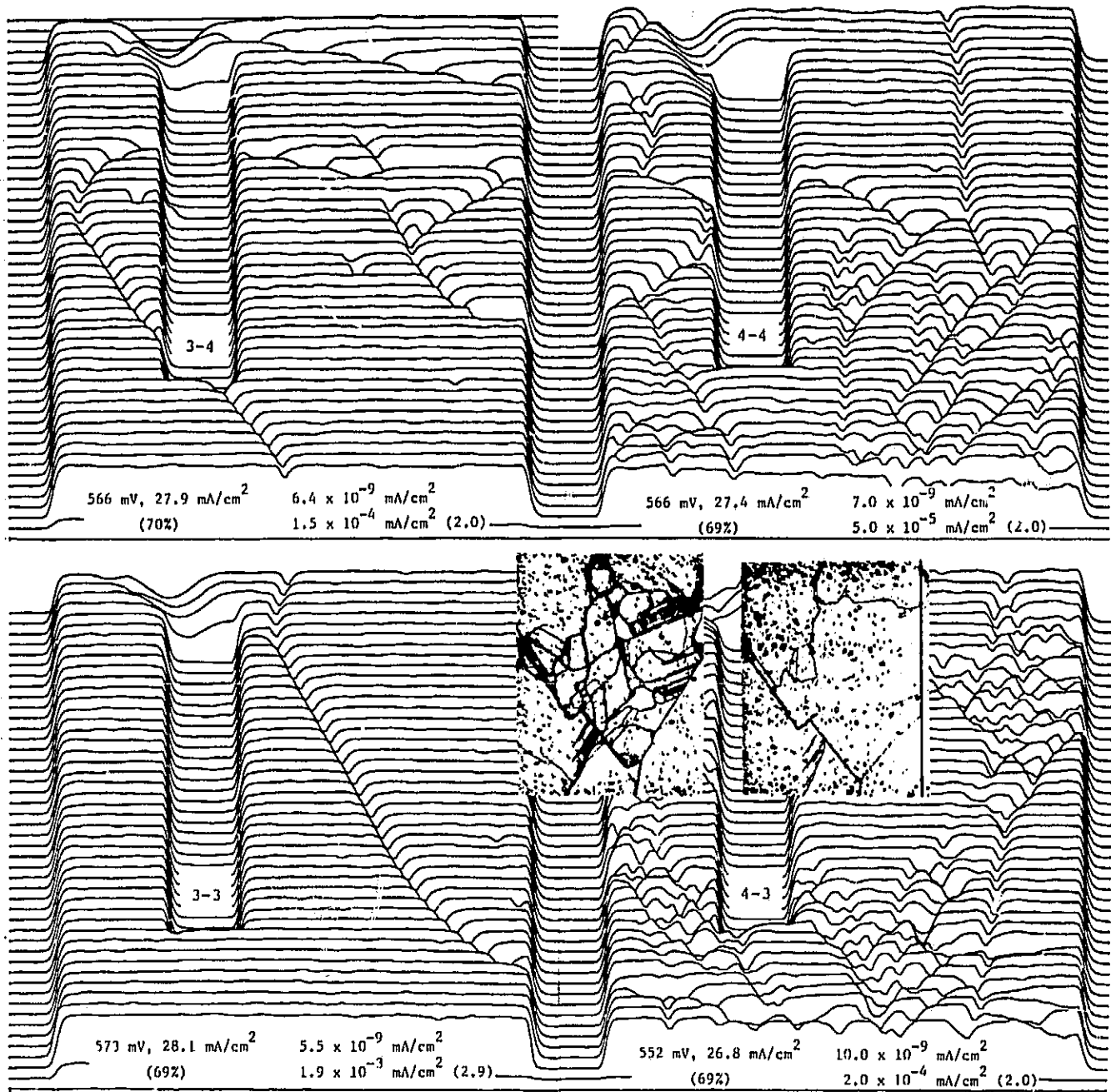


FIGURE 6

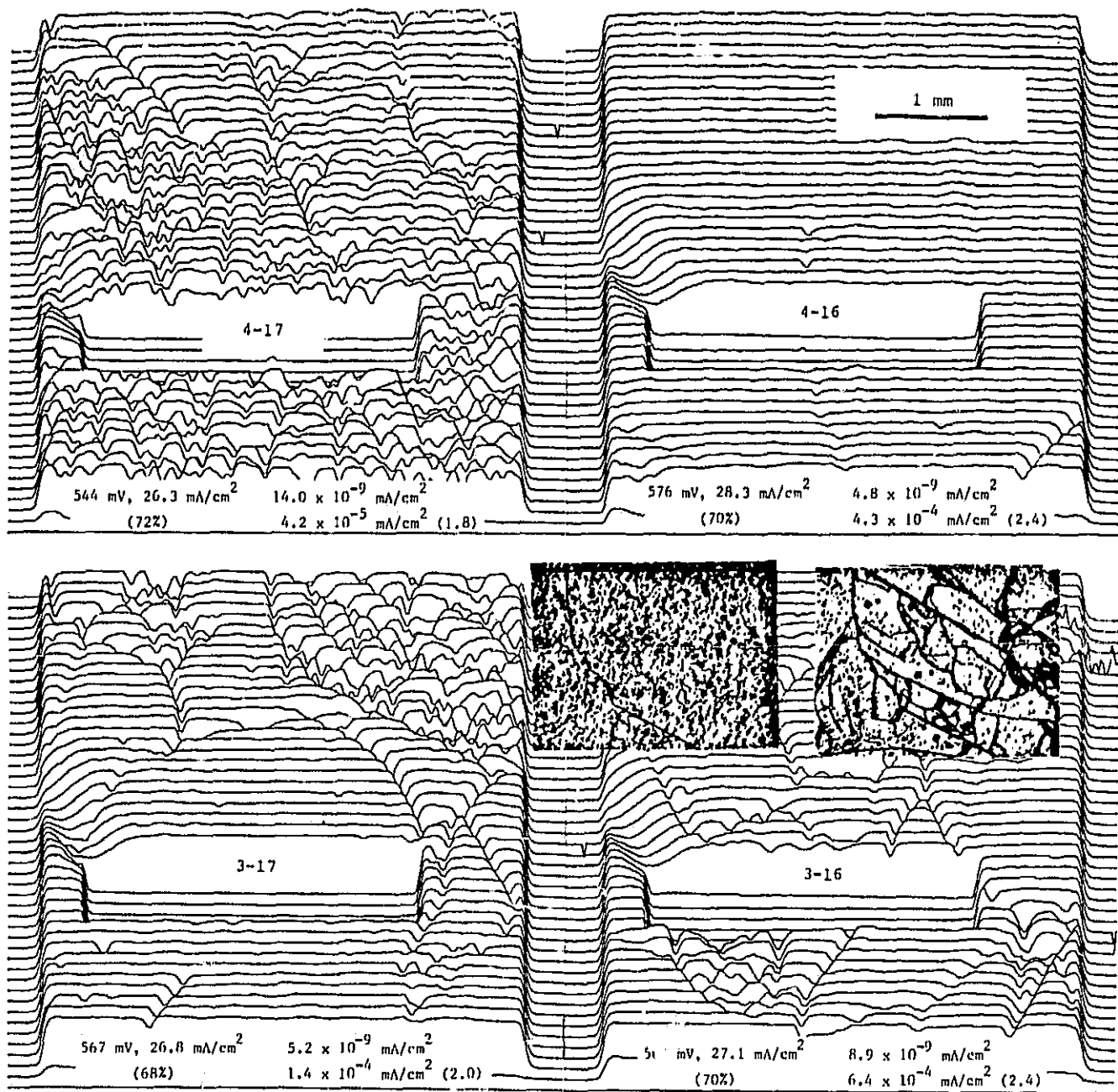


FIGURE 7

3-3, which has the least amount of LBIC-imaged grain boundary activity.

Figure 7 (mini-cell wafer 71-01E/TOP; cells 4-17, 4-16, 3-17, and 3-16) shows another area that has a large number of subgrain boundaries. The effect of these boundaries is to significantly increase the bulk recombination (by a factor of three in this case; compare cell 4-17 to 4-16). Several small areas of localized subgrain boundaries apparently degrade the cell more than one larger area, as shown by comparing cells 3-16 and 3-17. Space-charge recombination is not significantly affected by subgrain-boundary recombination. The fill-factors of these cells are not significantly different.

In summary, electrically-active grain and subgrain boundaries can impact the bulk recombination of large-grain, cast polycrystalline silicon solar cells. In most cases, no change is observed in space-charge recombination; however, there does appear to be an additional "defect" that can (rarely) cause the local space-charge recombination to increase by several orders of magnitude. This defect appears to be localized to areas smaller than one mini-cell (about 0.2cm^2) and is not resolved by LBIC.

VIII. CONCLUSIONS AND RECOMMENDATIONS

Mini-cell samples made on large-grain polycrystalline cast silicon wafers used to map spatial variations in electronic

activity mainly showed a variation in quasi-neutral recombination, with little effect on space-charge recombination.

Treatment with molecular hydrogen had no significant effect on quasi-neutral recombination or resulting open-circuit voltages.

LBIC analysis of electrically active recombination regions on selected mini-cells did not correlate with the cells' space-charge recombination currents, but rather confirmed localized fluctuations in quasi-neutral recombination current.

Future investigations of hydrogenation effects on large-grain polycrystalline silicon should concentrate on evaluating variations in quasi-neutral recombination resulting from atomic hydrogenation. This phase of activity was not reached in this study prior to its termination.

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