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**HYDROGEN PASSIVATION OF ELECTRICALLY ACTIVE DEFECTS IN
CRYSTALLINE SILICON SOLAR CELLS**

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ABSTRACT

We have observed significant improvements in the efficiencies of dendritic web and edge-supported-pulling (ESP) silicon sheet solar cells after hydrogen ion beam passivation for a period of ten minutes or less. We have studied the effects of the hydrogen ion beam treatment with respect to silicon material damage, silicon sputter rate, introduction of impurities, and changes in reflectance. We have determined that the silicon sputter rate for a constant ion beam flux of 0.60 ± 0.05 mA/cm² exhibits a maximum at approximately 1400 eV ion beam energy. We have observed that hydrogen ion beam treatment can result in a reduced fill factor, which is caused by damage to the front metallization of the cell rather than by damage to the p-n junction.

INTRODUCTION

The effects of hydrogen passivation of grain boundaries and other electrically active defects in silicon materials are well documented (1-3). However, there have been few reports of actual improvement of solar cell efficiencies as a result of such treatment. To date, improvements in efficiency have been reported for Edge-Defined Film-Fed Growth (EFG) (4), Wacker Silso (5), and Dendritic Web (6) solar cells. Although Singh et al. (6) reported a 30- to 40-mV improvement in open-circuit voltage (V_{oc}) for dendritic web cells at the low end of the efficiency distribution, they indicated that further work would be required to elucidate the role of hydrogen in improving web solar cells. They pointed out that low-energy hydrogen ions are not expected to penetrate to depths of several microns in silicon, and they suggested that a passivating effect is provided by the hydrogen ions at the surface, leading to a reduction in surface recombination velocity.

We have systematically studied the hydrogen passivation conditions for web solar cells as a function of beam voltage, treatment time, and sample temperature during passivation. Further results of hydrogen ion treatment of dendritic web research cells having a somewhat higher initial efficiency (7) than those used in this study are reported in another paper given at this meeting (8). We have also studied the effects of hydrogen passivation on edge-supported-pulling (ESP) silicon sheet (9) solar cells for the first time. Furthermore, we have studied the effects of hydrogen passivation using a Kaufman ion source on (100) silicon surfaces and have observed structural damage and introduction of impurities into the surface, as well as silicon sputter rates, and changes in reflectance as functions of beam energy and current.

EXPERIMENTAL PROCEDURE

All hydrogen passivation experiments were carried out in a Commonwealth Scientific Corporation Model IV Kaufman Ion Beam System, equipped with both a Balzers TSH 511 turbo-molecular pump and a mechanical pump. The base vacuum pressure for the system is normally less than 1×10^{-6} torr before the system is back-filled with hydrogen gas to a pressure of about 3×10^{-4} torr. The 4-in.-diameter Kaufman ion gun is equipped with a stainless steel grid assembly and tungsten neutralizer filaments. The 3-in.-diameter, rotating, water-cooled substrate holder is equipped with a heater which is capable of heating samples to 450°C. The sample stage can be tilted with respect to the beam direction. For the experiments described here, the stage was held with its surface perpendicular to the beam direction, so that all samples were bombarded normally. Solar cell samples are mounted with silver paint to a 3-in. silicon wafer clamped to the substrate holder. This silicon wafer reduces the possibility of contamination of the samples by sputtering of the holder, while the silver paint provides good electrical and thermal contact between the wafer and the solar cell sample. In these experiments, all solar cells treated had no antireflection (AR) coatings.

One of the problems commonly encountered in studying the effects of hydrogen passivation on the efficiency of solar cells relates to the reproducibility of efficiency measurements. At the Solar Energy Research Institute (SERI), we have a computer-controlled solar simulator based on a Spectrolab X-25 high-pressure xenon lamp source that meets or exceeds NASA TM 73702 standard testing specifications. Testing conditions include a substrate temperature control of $28^\circ \pm 0.2^\circ$ C and calibration against NASA reference cells at air mass (AM) 1.5. Current, voltage, and fill factor measurements are accurate to at least three significant figures, and efficiencies are reproducible to 0.1%.

RESULTS AND DISCUSSION

Our initial experiments on dendritic web pilot production (rather than research) silicon solar cells involved the incremental treatment of individual 4-cm² cells with ion beams of 200 to 1400 eV. The front surface metal contacts of the web cells consist of 400 angstroms of evaporated titanium followed by 400 angstroms of evaporated palladium and 6 to 10 microns of electroplated copper. Exposure to the beams was typically not more than 5 minutes long at a given energy. V_{oc} proved relatively insensitive to beam energy, while short-circuit current density (J_{sc}) improved at energies below 400 eV

and then degraded at higher energies. Fill factor (FF) was also degraded at energies above 600 eV. In all experiments where deliberate substrate heating (to 200°C or above) was applied, the solar cells degraded. We observed no systematic differences between passivation experiments run with and without beam neutralization.

In more recent experiments, 12 additional cells were treated with hydrogen ions at 300 eV beam energy with no deliberate substrate heating. Cell numbers 4, 20, 23, and 27 were treated with beam neutralization and current densities of 0.15 mA/cm² for 5 minutes. This corresponds to a particle flux of 9×10^{14} hydrogen ions per cm², and to a total dose of 2.7×10^{17} hydrogen ions per cm². Cell numbers 3, 10, 14, and 22 were treated with beam neutralization and current densities of 0.38 mA/cm² for 10 minutes. Cell numbers 1, 12, 16, and 25 were treated with nonneutralized beams with a current density of 0.38 mA/cm² for 10 minutes. The values for V_{oc} , J_{sc} , FF, and AM 1.5 efficiency for these cells before and after hydrogen ion treatment are listed in Table I. These results are also presented in Figures 1 and 2. Figure 1 shows the absolute efficiency change vs. the initial efficiency of the cells studied. Figure 2 shows the relative efficiency change vs. initial efficiency. We define the

relative change as the absolute efficiency change divided by the initial efficiency for each cell. The points indicated by the circled dots represent cells whose fill factors increased, while the other points represent cells whose fill factors decreased. Examination of the data shows that the generally held conception that "bad cells improve more than good cells under hydrogen passivation" (10) is not valid, at least up to the limits of the initial efficiencies studied here. The values of the untreated cells are not representative of current pilot production web solar cells but rather were deliberately chosen to give a range of initial values in order to allow passivation effects to be examined over a large range of efficiencies.

Of these 12 cells, all but two exhibited improved efficiencies after hydrogen passivation. For all the cells, V_{oc} and/or J_{sc} improved, as shown in Table I. However, the FF of six cells improved and the FF of the remaining six cells degraded. Note that the three cells that exhibited over 9% efficiency after passivation improved by 12% to 20% relative to their initial values. Examination of these results by sets shows that one relatively poor cell and one relatively good cell in each set improved by nearly the same absolute amount, roughly 1.5%, 1.0%, and

Table I. Air Mass 1.5 Photovoltaic Parameters for Dendritic Web Solar Cells Before and After Hydrogen Passivation

Cell No.	V_{oc} (volts)		J_{sc} (mA/cm ²)		FF (%)		Efficiency (%)	
	before	after	before	after	before	after	before	after
4	0.572	0.574	21.5	22.1	61.3	71.5	7.56	9.09
20	0.434	0.492	19.6	20.2	57.2	64.1	4.87	6.37
23	0.535	0.535	19.9	20.4	58.5	51.7	6.23	5.64
27	0.528	0.528	19.2	19.8	64.2	60.9	6.49	6.36
3	0.570	0.576	21.1	22.9	69.0	70.9	8.32	9.35
10	0.519	0.523	18.5	20.1	77.9	75.5	7.47	7.94
14	0.408	0.452	19.6	21.1	46.2	47.9	3.70	4.57
22	0.520	0.523	18.8	20.2	61.6	58.2	6.03	6.15
1	0.567	0.576	21.6	23.4	66.4	69.5	8.12	9.37
12	0.520	0.524	18.5	20.1	74.9	74.2	7.23	7.82
16	0.467	0.502	20.0	21.5	53.4	57.9	4.99	6.25
25	0.539	0.543	20.3	21.7	67.5	66.2	7.39	7.80

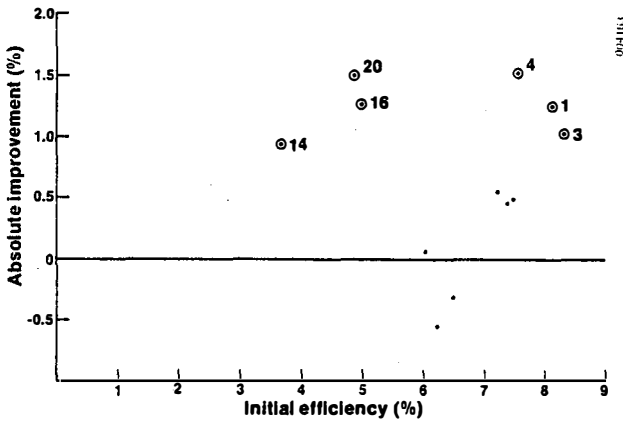


Fig. 1. Absolute Improvement in Efficiency of Dendritic Web Cells vs. Initial Efficiency. Circled data points indicate cells (numbers given) that exhibited an increase in fill factor.

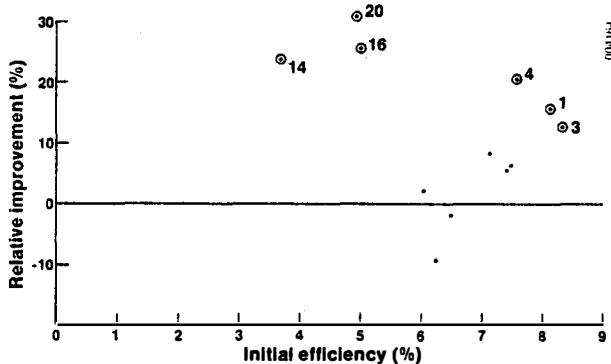


Fig. 2. Relative Improvement (Defined as Absolute Improvement/Initial Efficiency) in Efficiency of Dendritic Web Cells vs. Initial Efficiency

1.25% for the three sets, respectively. Each set of four cells indicated above exhibits interesting results. In all three sets, the two cells that improved only slightly (or degraded) typically exhibited FF degradation, a slightly improved J_{sc} , and minimal improvement in V_{oc} . The cells that improved appreciably all showed improved J_{sc} and FF. Cells 20, 14, and 16, which originally had low V_{oc} , showed significant improvements in V_{oc} (35 to 58 mV), while cells 1, 3, and 4, which had higher initial V_{oc} , showed little improvement in V_{oc} . These results are not too surprising when one realizes that cells 1, 3, and 4 were cut from a single segment of ribbon, while cells labelled with other sets of nearly consecutive numbers were cut from other segments of ribbon. For example, in the first set, cells 4 and 20 both improved by approximately 1.5% in absolute efficiency, although their initial values bracket those of cells 23 and 27. The reader should observe that systematic differences in the samples may exist because of differences in ribbon quality and/or differences in processing particular segments of ribbon from which individual cells were later cut for use in this investigation. In any event, FF changes clearly separate these 12 cells into two groups. Therefore, we turned our attention to discovering why this occurred.

We were concerned that the possibility of sputtering away an appreciable fraction of the junction depth, especially in shallow junction devices (on the order of 0.3 microns or less), might explain our results regarding FF degradation. Accordingly, we began a detailed investigation of the sputtering rate of silicon under a variety of beam energy and current conditions. For this portion of the work, we employed commercial, 3-in.-diameter (100) Czochralski zone silicon wafers that were boron-doped to approximately 16 or 17 ohm-cm resistivity. These wafers were approximately 20 mils thick, with polished fronts and bright etched backs, and were flat to within $7 \mu\text{m}$.

Surface regions of these wafers were covered with single-crystal silicon masks and bombarded with hydrogen ions, without deliberate substrate heating, for a period sufficient to remove roughly 4000 angstroms of material. These bombardments took from about 2 to 20 hours. The heights of the steps so produced, in the central region of the wafers (i.e., in the region of the substrate holder where we had placed our test cells), were then measured using a TENCOR Alpha-Step stylus profiler, which can detect a step as small as 200 angstroms, and the average etch rate was calculated. As shown in Figure 3, we have determined the sputter rate of silicon from a (100) surface using a constant beam current of $0.60 \pm 0.05 \text{ mA/cm}^2$. The sputter rate peaks at approximately 1400 eV beam energy, with a sputter rate of approximately $8 \times 10^{-12} \text{ m}^3/\text{coul}$. In the case of a passivation experiment carried out under these beam conditions (for example, as we used in ESP cells for 2 minutes), one would expect to lose 60 angstroms of silicon by sputtering, or perhaps as much as 2% of the diffused layer in a shallow junction. Under the conditions we used for web (i.e., 300 eV), we conclude that the sputter rate will be very nearly zero. To be completely certain of this result, one should repeat these etch rate studies using (111), (110), and polycrystalline wafers to observe the dependence, if any, on substrate orientation. This is clearly a time-consuming task which we have not yet carried out. Examination of the sputter rate under constant, relatively high, beam energy and

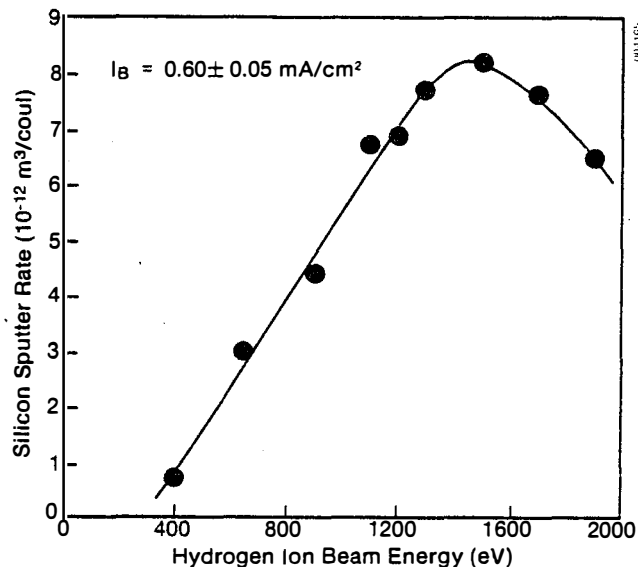


Fig. 3. Sputter Rate of (100) Single-Crystal Silicon Under Constant Beam Current ($I_b = 0.60 \pm 0.05 \text{ mA/cm}^2$) as a Function of Beam Energy

varying beam current, as shown in Figure 4, shows the rate decreasing as current density increases.

Four samples prepared for these etch rate studies were then subjected to Rutherford back scattering (RBS) experiments. We determined the extent of structural damage and the impurities that hydrogen passivation introduced into the samples. The reader should keep in mind that three of these samples were subjected to this hydrogen ion treatment for periods far in excess of those likely to be applied to solar cell devices.

The first wafer we examined was bombarded with 400 eV hydrogen ions at a current density of 0.35 mA/cm^2 for 970 minutes. Approximately 1330 angstroms of silicon were found to have been removed. No amorphous silicon layer could be detected on the sample surface, structural damage to a depth of up to 1600 angstroms was found, and approximately 500 angstroms of oxide-containing impurities of mass range 55-64 and 168-207 had been deposited on the wafer surface. We believe that the mass 55-64 impurity is principally iron-derived from the stainless steel grid assembly and that the mass 168-207 impurity is tungsten from the neutralizer filaments. Furthermore, at low beam energies (i.e., low acceleration voltages), the ion beam tends to be somewhat diffuse and may "scrub" adsorbed oxygen off the walls of the system, which could account for the build-up of oxide in this case.

The second sample was treated at 900-eV beam energy with 0.50-mA/cm^2 current density for 344 minutes. Approximately 3300 angstroms of silicon were removed from this sample. The third sample was treated at 1500-eV beam energy with 0.80-mA/cm^2 current density for 300 minutes. Approximately 8400 angstroms of silicon were found to have been removed from this sample. At 900 eV, an amorphous silicon layer can be detected to a depth of 300 angstroms, and at 1500 eV, to a depth of about 1000 angstroms. Structural damage in both cases appears to extend to a depth of about 3500 angstroms. Oxygen and heavy impurities are found to a much smaller extent at 900-eV beam energy than at 400 eV, while at 1500 eV they are virtually undetectable.

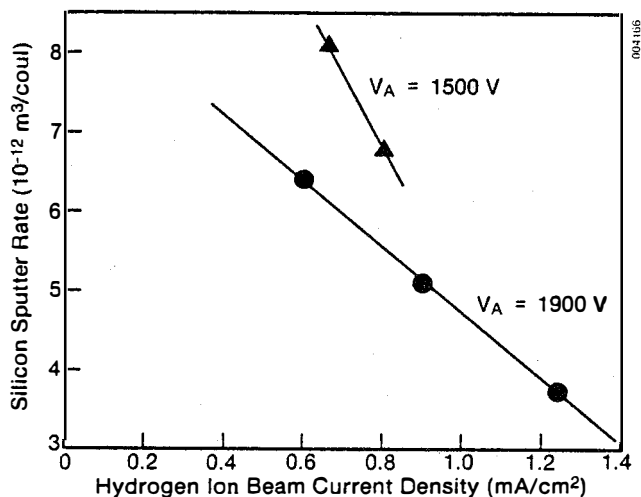


Fig. 4. Sputter Rate of (100) Single-Crystal Silicon under Constant, Relatively High, Beam Energies as a Function of Beam Current

The fourth sample was treated in a sequence of hydrogen ion experiments in an attempt to replicate the earlier experiments on web cells. We wished to determine whether those cells degraded because of loss of material from the emitter side of the junction. This wafer was exposed to a beam of 200 eV energy at 0.20 mA/cm^2 for 5 minutes, followed by a 400-eV beam at 0.38 mA/cm^2 for 2 minutes, a 600-eV beam at 0.48 mA/cm^2 for 2 minutes, and an 800-eV beam at 0.46 mA/cm^2 for 3 minutes. Only 40 angstroms or less of silicon were removed by this treatment. An oxide layer of perhaps 500 angstroms' thickness was observed, as well as damage to a depth of approximately 2500 angstroms. In this case, virtually no heavy impurities were found on the surface, and no indication of an amorphous silicon layer was observed. We conclude that at the low beam energies used to passivate the dendritic web, neither the removal of silicon nor the introduction of structural damage are severe enough to explain the FF reduction, even if we ignore the improvement in the FF of other cells processed at the same time.

We have also observed optical changes in the surfaces of the above samples. For bombardment with beam energies of 400 eV or less, there is essentially no change in the reflectance spectrum of the wafers. However, for bombardment with beam energies of 900 eV or greater, very large decreases in the reflectance (i.e., increases in the absorptance) are observed. This is consistent with the strong absorption exhibited by amorphous silicon, compared with crystalline silicon, which we observed after high beam energy bombardment.

This was not the first time that we have observed a reduction in FF after hydrogen ion beam passivation. Silicon solar cells fabricated without an AR coating on ESR ribbon (Edge-Stabilized Ribbon, ESR, is the terminology used by A. D. Little for ESP ribbon) grown at A. D. Little, Inc., under SERI subcontract, have been passivated using a variety of conditions. With treatments using low beam energy, (from 200 to 600 eV, which was effective for web cells) no change in efficiency was observed for ESR cells. Treatment using a hydrogen ion beam with 1400-eV beam energy and 40-mA/cm^2 beam current density, no deliberate substrate heating, no beam neutralization, and 2 minutes of exposure were effective. On a 4.3-cm^2 sample prepared in 1982, the following cell parameter changes were observed: V_{oc} changed from 0.502 to 0.529 V, J_{sc} from 12.2 to 14.3 mA/cm^2 , and FF degraded from an initial value of 0.76 to 0.64. However, after the cell was returned to A. D. Little, it was noted that the silver front contact metallization was reduced in thickness from $0.6 \mu\text{m}$ to $0.2 \mu\text{m}$. When the front contact was replated to its original thickness, the FF was restored to 0.76, while V_{oc} and J_{sc} remained at their posthydrogenation values. This represents a 23.6% relative improvement in efficiency, from 4.66% to 5.76%. The obvious conclusion in this instance was that the FF reduction was directly attributable to damage to the front grid metallization. We point out that more recent ESR cells have been larger and higher in efficiency (11).

This observation caused us to wonder whether the metallization on the six web cells that suffered FF degradation might also have been damaged. We had returned cells number 4 and 20 to Westinghouse for corroboration of our measurements of improvements in efficiency. However, the remaining ten passivated cells, as well as other untreated cells, were still available to us. We measured the heights of the front grid lines, using the

stylus profiler. Three untreated cells were also measured. As few as four and as many as 11 readings per cell were taken on randomly chosen grid line segments. These results are presented in Table II (with the number of readings taken per cell in parentheses) and in graphical form in Figures 5 and 6. These figures show the absolute and relative changes in FF vs. the front grid thicknesses we measured on the passivated cells, respectively. The graphs clearly show an approximately linear relationship between change in FF and front grid thickness. At thicknesses above about $10\ \mu\text{m}$, there may be an indication of saturation of this improvement. We find, using least square fits to our data, that the FF improves for cells having more than approximately $6.7\ \mu\text{m}$ -thick grids after passivation.

Cells 9, 10, and 12 were cut from the same piece of web. Comparing the grid thickness for cell 9 ($5.1\ \mu\text{m}$) with these measured on cells 10 and 11, and observing that the former was untreated while the latter were treated for 10 minutes, we deduce that approximately $0.5\ \mu\text{m}$ of copper was removed by the treatment. This is qualitatively in agreement with the observation that approximately $0.4\ \mu\text{m}$ of silver was removed from the A. D. Little cell after treatment for 2 minutes under somewhat different conditions. The implication of this observation is that in order to optimize the improvement in efficiency due to hydrogen passivation it will be necessary to apply metallization that does not degrade under the influence of hydrogen ion beam bombardment. We conclude, therefore, that copper grids at least $7.2\ \mu\text{m}$

Table II. Front Grid Thicknesses for Dendritic Web Solar Cells

Cell	Thickness (μm)	
Untreated Cells		
5	10.3	(11)
8	12.4	(4)
9	5.1	(10)
28	2.45	(4)
Passivated Cells		
23	0.71	(9)
27	1.39	(6)
3	8.69	(9)
10	4.67	(6)
14	8.78	(7)
22	4.25	(7)
1	12.1	(4)
12	4.39	(5)
16	9.37	(8)
25	4.69	(9)

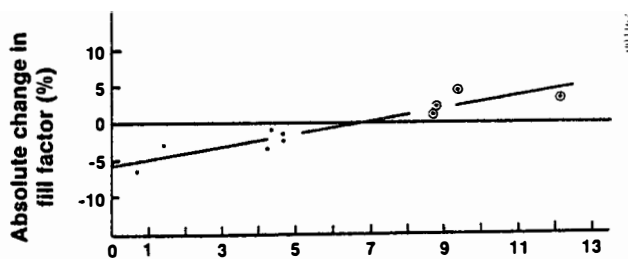


Fig. 5. Absolute Change in Fill Factor as a Function of Front Metal Grid Thickness, Measured after Passivation

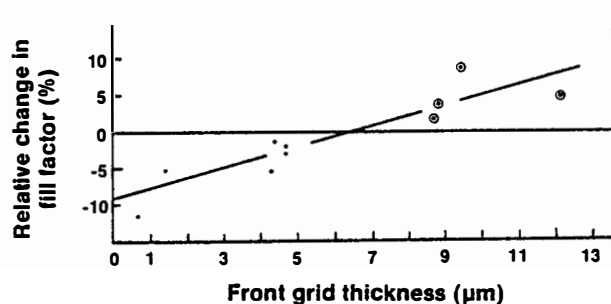


Fig. 6. Relative Change (Defined as Absolute Change/Initial Fill Factor) in Fill Factor as a Function of Front Metal Grid Thickness, Measured after Passivation

thick, and preferably 9 to $10\ \mu\text{m}$, need to be plated onto cells that will be passivated in hydrogen ion beams. Plans have been made to return some of these cells to Westinghouse to replat the grids in an attempt to duplicate our observations on the ESP cells.

Comparing the results on the web and ESP cells, we note the far lower energy required for effective passivation of the former. Crystallographic requirements for web ribbon growth implies that the web surface will be (111), which has as its immediate consequence the presence of "channels" (12) lying along the [111] direction, i.e., normal to the web surface. From our studies of the structure of ESP ribbon (13), we can assert that for thick ESP (i.e., thickness greater than $500\ \mu\text{m}$), the grains in the sheet are randomly oriented with respect to the surface normal of the sheet. Parenthetically, we note the report (4) that for an EFG sheet, where the surface normal is predominantly [011], high beam energy is also required for effective passivation. While we cannot yet conclusively prove this conjecture, we suspect that the presence of the "channels" in web may permit atomic or ionic hydrogen to enter the lattice more readily than in the case of a more random structure. It is known that for channels lying along [100], [110], and [111] directions, there are relatively narrow "critical angles" for ion implantation of common dopants into silicon, within which the dopant ions enter the lattice more readily.

EBIC studies on passivated ESP cells fabricated on material prepared at SERI have also been carried out and are reported in another paper presented at this conference (14), as well as elsewhere (15), as have EBIC studies of hydrogen in polycrystalline silicon reported by others (16).

CONCLUSIONS

We have observed significant improvements in web and ESP silicon sheet solar cell efficiencies using the optimum hydrogen passivation conditions determined to date. We have observed a degradation in fill factor in certain instances, which we can conclusively ascribe to damage to the front grid metallization in ESP cells, and which we strongly believe is caused by a similar mechanism in the case of web cells that we have treated. We suggest that copper grids of at least 8 μm , and preferably 10, are required to avoid this problem. We conclude that occasional reductions in the fill factor as a consequence of hydrogen ion bombardment is not caused by removal of silicon from the emitter (i.e., damage to the p-n junction) in the cases we have studied. We have determined sputter rates, introduction of structural damage and impurities, and changes in reflectance produced by hydrogen ion beam treatment of single-crystal silicon. We think we see the beginnings of a consistent picture which relates the hydrogen ion beam energy and current density, sputter rates, reflectance data, structural damage, and impurity incorporation to observable changes in solar cell I-V characteristics.

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