"The surface defects analyzed are dislocation pit density, twin line density and grain boundary length."

Analysis of Defect Structures in Silicon Solar Cell Materials

by

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ABSTRACT

Three (3) solar cells fabricated from EFG ribbons were subjected to quantitative defect analysis on several surface planes. The internal planes were observed by removing surface layers of silicon atoms by chemical dissolution. The results show that the average dislocation pit density varies from one surface plane to another. The procedures for chemical polishing and etching, as well as the process of quantitative defect analysis are also discussed.

INTRODUCTION

The direct conversion of solar energy into electrical energy is one of the alternative energy sources that is still in the developmental stage. The technological feasibility has already been demonstrated but at present it is not yet an economically viable alternative to fossil fuel energy sources.

The most important criteria in the evaluation of various types of terrestial solar cell applications are: (1) cost and (2) conversion efficiencies. At present, the solar cells with highest conversion efficiency are made of high purity single crystals which are free from structural defects such as dislocations, twin boundaries and non-metallic inclusions. But these crystals and their subsequent processing into solar cell arrays are very expensive. On the other hand, silicon grown as Edge-defined Film-fed Growth (EFG) ribbons, Silicon on Ceramics (SOC) ribbons, Heat-Exchange Method (HEM) ingots are not single crystals. They are composed of highly ordered crystals which contain large and differing numbers of dislocations, twin boundaries, grain boundaries and precipitates which result in a lower conversion efficiency as compared to the single crystal, also known as Czochralski crystal. They are, however, much cheaper to produce.

The usual process in the evaluation of silicon solar cell materials is to subject one side of the specimen to surface defect analysis and then fabricate the other side into a solar cell. This is done because surface defect analysis is not really a non-destructive method of testing. Problems, however, are being encountered in correlating the information obtained using this process which eventually questioned the wisdom of using the surface defect analysis data of one surface in the evaluation of conversion efficiency wherein the other surface is actually fabricated into a solar cell.

In this paper, a comparison of the surface defect concentration, particularly dislocation density, is made on several surface levels to determine whether dislocations penetrate the whole thickness of the solar cell material. For this purpose, three (3) EFG solar cells were used. The processes for revealing the dislocations, as well as their quantitative analysis are also presented.

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EXPERIMENTAL PROCEDURE

Solar Cell Material Preparation

Three fabricated solar cells were received from Jet Propulsion Laboratories at Pasadena, California for surface defect characterization. They were made from EFG ribbons. The top surfaces of the cells contained silver solder grids and anti-reflection coatings while the bottom surfaces contained fired aluminum paste. To remove these artifacts from the surface of the solar cells, the samples were alternately dipped in nitric acid and hydrofluoric acid twice for five minutes. This operation removed the silver solder grids and the anti-reflection coating but did not dissolve all the fired aluminum paste, leaving the bottom surface dull and making it unsuitable for surface defect analysis. The solar cells were then given a Sirtl etch for 25 seconds in order to reveal the dislocations. The dislocation density was then measured using an image analyzer. The procedure for the etching and dislocation density measurement is discussed in the following sections.

After the defect analysis on the top surface was completed, the solar cells were subjected to chemical polishing which dissolved layers of silicon atoms from the surfaces of the solar cells. The thickness of the solar cell was measured before and after chemical polishing to determine the amount of material removed. This amount was divided into two, assuming the same rate of material removal for the top and bottom surfaces. The cells were again subjected to a Sirtl etch and quantitative defect analysis. This procedure was repeated until the solar cells were too thin and too fragile to handle.

Chemical Polishing and Etching

Solar cell materials may be classified into two groups: those that are grown as ingots and those grown as ribbons. Silicon grown as ingots are cut into wafers using various types of wafering devices. This step produces rough and uneven surfaces on the silicon wafers which necessitates the mechanical polishing of the wafer prior to chemical polishing and etching. Mechanical polishing involves the removal of material from the surface of the wafer using a succession of abrasives, starting from a 600 grit silicon carbide sand paper to 0.5 micrometer diameter alumina or diamond particles. Silicon grown as ribbons has a relatively flat and shiny surface which does not need any mechanical polishing.

Prior to chemical polishing, the silicon sample is thoroughly cleaned with trichloroethylene to remove any organic substances on the sample surface. Any water spots are removed by an acetone rinse followed by an ethyl alcohol rinse. The surfaces are dried by blowing freon gas over them. The sample is then immersed in concentrated hydrofluoric acid to dissolve any silicon oxide on the sample surface. The sample is again rinsed in distilled deionized water followed by ethyl alcohol.

The polishing solution used is a 1 : 2 : 3 ratio by volume mixture of concentrated nitric, hydrofluoric and acetic acids, respectively. Removal of material is effected by an alternate oxidation of the silicon by the nitric acid and the dissolution of the oxidized layer by hydrofluoric acid. All chemicals used are of Electronic Grade, low sodium MOS quality. The polishing solution is then heated to a temperature of 50°C, 3°C in a Teflon beaker. The silicon sample is immersed in this solution, making sure the solution is not agitated to insure an even dissolution of the silicon. Polishing times differ from sample to sample, depending on the type of sample and the roughness of the starting surfaces. The polishing reaction is stopped by dipping the sample in a beaker of distilled deionized water. Polishing is done in increments of 10 to 20 seconds and the extent of polish determined after each step using a metallograph.

Several etching solutions are available but a variation of the Sirtl Etching Solution has been found to be best suited for solar cell materials. This consists of 10 grams of chromium trioxide in 60 ml. of deionized distilled water and 60 ml of concentrated hydrofluoric acid. This etching solution is able to produce an optical density resolution of 10^7 dislocations per square centimeter. Figure 1 shows the defect structures revealed by chemical polishing and etching on a Silicon on Ceramics sample.

Figure 1. Dislocation Pits, Twin and Grain Boundaries on SOC sample, (100X)

Quantitative Analysis of Defect Structures

A Quantitative Image Analyzer (Quantimet 720: Cambridge-Imanoc, Mansey, N.Y.) linked to a Digital Equipment PDP 11/03 computer was used for quantitative analysis of surface defects on etched silicon surfaces. This system can differentiate and count 64 shades of gray levels between black and white contrast. This allows the operator to set the contrast level such that artifacts are differentiated from true defects on the silicon surface. In addition, it can characterize structural defects by measuring their length, perimeter, area, density, spatial distribution, frequency distribution and is programmable in these measurements.

The Quantitative Image Analyzer, however, is extremely sensitive to the optical contrast of various defects and great care must be exercised during the chemical polishing and etching stages in order to obtain reproducible and meaningful results. The flowchart being used in the analysis is shown in Figure 2 while Figure 3 is a sample of the print out produced by this flowchart.

Data Analysis

The ideal situation would have been to observe particular dislocations and investigate if they persist throughout the whole thickness of the solar cell. Unfortunately, this is not possible such that statistical analysis was applied to the data. Thirty observations are made on each surface level of the 1 cm by 1 cm solar cell. The average dislocation density is then calculated per surface level and compared for the different surface levels using analysis of variance.

RESULTS AND DISCUSSIONS

A summary of the results obtained in the surface defect characterization measurements for the three EFG cells are given in Tables 1 to 3. The surface defects analyzed are dislocation pit density, twin line density and grain boundary length.

As mentioned before, Etch No. 1 did not remove all of the fired alumina paste on the bottom surface of the solar cell such that analysis was only possible on the top surface. Furthermore, Etch No. 1 revealed only the twin lines and grain boundaries but

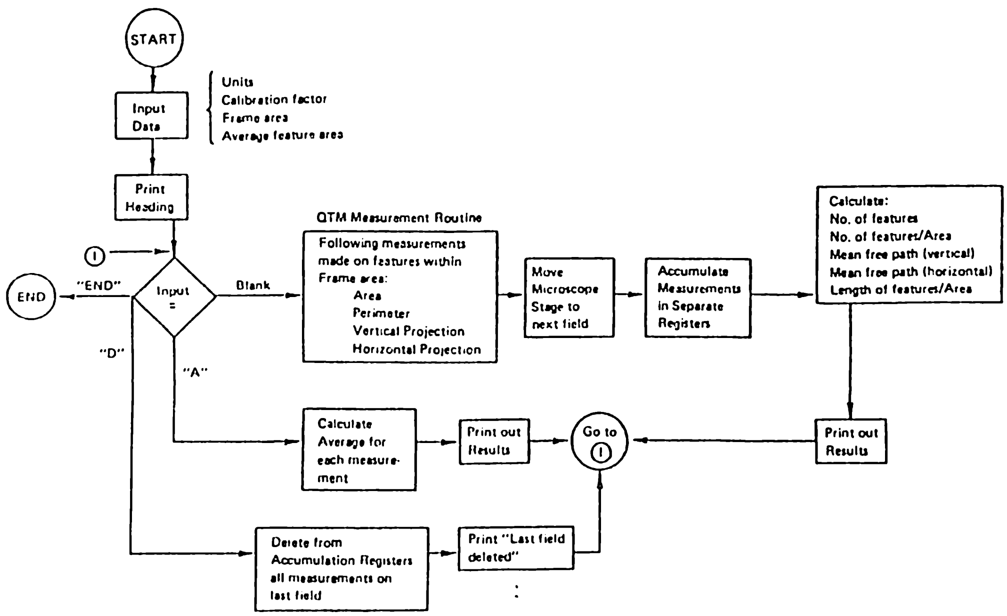

Figure 2. Basic Flowchart and Data Reduction Used in Defect Analysis

not the dislocation pits. Etch No. 2 removed enough material from the bottom surface which allowed measurement on this surface. It also revealed dislocation pits on both the top and bottom surfaces. Etch No. 3 allowed observation of defects on internal planes 1.55 to 2.50 mils from the original surfaces. The original solar cell is about 0.5 mm (20 mils) thick.

From Tables 1 to 3, the range in defect structure values in the EFG cells are 1.315×10^{-2} to 9.114×10^{-2} pits per square micrometer for dislocation density, 40.027 to 1172.860 lines per square millimeter for twin density, and 0.060 to 0.240 millimeter per square millimeter for grain boundary length.

An analysis of variance was performed on the dislocation pit density as a function of the different sample planes for each of the three solar cells to determine whether the differences observed in the average dislocation pit densities are a result of changing the surface level or due to differences in the observation within planes. The results of these tests are summarized in Tables 3 to 6.

The results show that the dislocation pit density varies from level to level. This means that the practice of using the defect analysis of one surface to correlate the performance of the solar cell obtained from another surface is unreliable and incorrect.

SOLAR CELL EFG-3 BOTTOM PITS SECOND ETCH

OPERATOR IS JMS MAGNIFICATION = X800
UNITS = MICRONS CALIBRATION FACTOR (UNITS/PP) = .3407
FRAME AREA = 160000 QTM OUTPUT WAS DIVIDED BY 1 AND CORRECTED
AVERAGE FEATURE AREA (PP) = 9.5

FLD	NO.	NO./AREA	MFPV	MFPH	L/A
1	138.211	7.44178E-03	97.8671	107.096	.0156571
2	144.421	7.77618E-03	94.8035	96.9964	.0173173
3	500.947	.0269729	31.8411	33.9639	.0497413
4	4.63158	2.49382E-04	3893.71	2180.48	4.03581E-04
5	885.789	.0476943	21.0066	21.3271	.0758457
6'	1538.42	.0828345	19.9313	20.9018	.07336
7	1632.11	.0878788	16.2868	15.8834	.0946948
8	3212.21	.172958	7.97659	7.59537	.199837
9	2497.37	.134468	8.36587	8.30976	.19093
10	998.105	.0537418	19.7579	22.4329	.0727546
11	3375.05	.181726	7.20772	7.42468	.221025
12	1510.95	.0813552	13.215	12.8173	.12168
13	1500.53	.0807941	16.8455	16.0708	.0941077
14	2271.68	.122316	8.18253	8.47381	.181758
15	2828.63	.152304	8.78376	7.79077	.193224
16	2646.42	.142493	13.3281	13.3772	.121093
17	1301.16	.0700593	19.9824	17.7448	.0844585
18	914.842	.0492586	23.8565	23.2858	.0676457
19	1197.79	.0644936	18.2193	18.1525	.0869809
20	2462.32	.13258	13.4266	12.2802	.120175
21	359.789	.0193724	46.0405	45.4267	.0347722
22	897.474	.0483234	21.9718	21.5037	.0741488
23	1568.84	.0844725	16.1469	15.5971	.0958413
24	2806.74	.151125	11.9361	11.2558	.13409
25	1774.74	.0955586	12.3919	11.0192	.135741
26	2586.42	.139263	12.8748	11.198	.133998
27	814.421	.0438515	23.9193	23.1179	.0671687
28	3689.16	.198638	8.92615	8.74571	.179098
29	2404	.129441	19.9167	13.8778	.0997028
30	2317.47	.124782	11.9022	10.8073	.141088

*****AVERAGE*****

	NO.	NO./AREA	MFPV	MFPH	L/A
	1692.69	.0911408	15.2077	14.5674	.105945
SD	1005.92	.0541627			.0565773
SE	183.655	9.88871E-03			.0103295

Figure 3. Sample Teletype Print-out.

Table 1. Summary of Analysis of EFG-3.

Etch Number	Surface Analyzed	Distance from Orig. Surface mils	Dislocation Pit Density pits per m^2	Twin Density lines per mm^2	Grain Boundary mm per mm^2
1	Top	0	-----	71.982	0.240
2	Top	0.75	1.315 E-02	317.080	0.240
	Bottom	0.75	9.114 E-02	168.144	0.240
3	Top	1.55	3.224 E-02	72.632	0.240
	Bottom	1.55	3.930 E-02	40.027	0.240

Table 2. Summary of Analysis of EFG-13.

Etch Number	Surface Analyzed	Distance from Orig. Surface mils	Dislocation Pit Density pits per m^2	Twin Density lines per mm^2	Grain Boundary mm per mm^2
1	Top	0	----	322.892	0.060
2	Top	0.75	1.99 E-02	636.844	0.060
	Bottom	0.75	4.450 E-02	542.678	0.060
3	Top	2.45	3.414 E-02	1172.860	0.060
	Bottom	2.45	2.746 E-02	475.622	0.060

Table 3. Summary of Analysis of EFG-33.

Etch Number	Surface Analyzed	Distance from Orig. Surface mils	Dislocation Pit Density pits per m^2	Twin Density lines per mm^2	Grain Boundary mm per mm^2
1	Top	0	----	207.833	0.180
2	Top	1.25	2.227 E-02	386.874	0.180
	Bottom	1.25	4.324 E-02	190.946	0.180
3	Top	2.50	2.012 E-02	382.469	0.180
	Bottom	2.50	1.425 E-02	339.582	0.180

CONCLUSION

The analysis of variance shows that for the EFG samples, the average dislocation pit density changes with the surface plane taken and is not the same throughout the thickness of the sample. This could be the reason why correlation between conversion efficiency measurements and surface defect analysis are incongruent. This, of course, assumes that only the defects on the surface of the solar cells actively reduce the conversion efficiency. More work has to be done along this line, however, using more samples and taking more observations per sample to validate and verify this finding.

Table 4. Analysis of Variance for Solar Cell EFG-3. (Dislocation Pits)

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	$F_{computed}$	F_{test} $\alpha = .05$
Different Surface Planes	9.996 E-02	3	3.332 E-02	23.20	2.68
Difference Within a Plane	1.665 E-01	116	1.436 E-03		
Total	2.665 E-01	119			

Conclusion: The average dislocation pit density for solar cell EFG-3 varies from plane to plane.

Table 5. Analysis of Variance for Solar Cell EFG-13. (Dislocation Pits)

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	$F_{computed}$	F_{test} $\alpha = .05$
Different Surface Planes	1.055 E-02	3	3.517 E-03	2.86	2.68
Difference Within a Plane	1.429 E-01	116	1.232 E-03		
Total	1.535 E-01	119			

Conclusion: The average dislocation pit density for solar cell EFG-13 varies from plane to plane.

Table 6. Analysis of Variance for Solar Cell EFG-33. (Dislocation Pits)

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	$F_{computed}$	F_{test} $\alpha = .05$
Different Surface Planes	1.437 E-02	3	4.790 E-03	5.58	2.68
Difference Within a Plane	9.963 E-02	116	8.589 E-04		
Total	1.140 E-01	119			

Conclusion: The average dislocation pit density for solar cell EFG-33 varies from plane to plane.

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