CHARACTERIZATION OF SILICON-FILM™ SHEET MATERIAL

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INTRODUCTION

The Silicon-Film™ process produces a continuous sheet of polycrystalline silicon for use in the production of solar cells. This is a relatively new material for the industry considering the growth method, the relatively high level of impurities, and small grain size. This paper reports on the progress in characterizing this relatively new material. The conversion efficiency for Silicon-Film™ solar cells is presently approximately 80% of those achieved with the industry standard CZ or large grain cast materials. The smaller grain size and the lower purity are the logical explanations for performance differences. With advances in the understanding of critical high temperature processes, such as gettering, views on impurity requirements have changed. Similarly, conventional grain size limits are shown to be inaccurate, allowing higher performance than thought possible from smaller grains. To delve into these and other specific material issues, an industry – academic – government team has been established. This paper reports on some of the results found by that team and highlights some of the conclusions that have been drawn as regards impurities and gettering.

Sheet Growth and Solar Cell Processing

AstroPower presently has the fifth and sixth generation of its Silicon-Film™ machines in production. The top surface of the polycrystalline silicon sheet has columnar grains, ranging in size from 100 μm to 5 mm. The total sheet thickness ranges from 600 to 800 μm. Each machine has a production capacity of 15MW per year and a linear sheet speed of 3.1 meters/min [1].

Silicon-Film™ wafers are processed into solar cells using a conventional industrial process sequence. After the sheet is cut square, which is done by laser or a conventional saw, the process sequence is a NaOH-based etch, continuous phosphorus diffusion on a belt furnace, continuous HF etch, SiN anti-reflection coating, and screen-printed metallization [1]. In addition, two novel, high temperature gettering steps are being evaluated as part of the standard processing sequence.

Characterization Requirements

In its pure, single crystal state, silicon is a well understood and predictable semiconductor material, accordingly it is tempting to attribute all the deleterious effects seen in polycrystalline material to grain boundaries and impurities. Historically, it was believed that small grains (100 μm in diameter) limited solar cell performance to efficiencies less than 8% [3]. Similarly, impurity studies in CZ ingots found that certain impurities in concentrations as low as 10^{12} ppma could devastate solar cell performance [4]. Both of these conventional models are inadequate to explain the performance of Silicon-Film™.

To fully understand the impact of defects and impurities on efficiency, a hierarchy of contributing factors is presented in Figure 2. The starting contributing factor remains impurities in the feedstock – with a special delineation for dopants (intentionally added) and high temperature compounds that may react differently than their elemental components. Examples are oxygen, carbon, and nitrogen, and their high temperature silicides.

Extensive studies of the impurity impact on CZ grown wafers were reported in 1980, some details of which are shown in Figure 1. The ranges of some critical impurities found in Silicon-Film™ material are also shown. The levels found are well in excess of the quantity expected to strongly impact efficiency, yet Silicon-Film™ efficiencies remain at roughly 80% of the baseline 14% efficiency reported in that work [4].

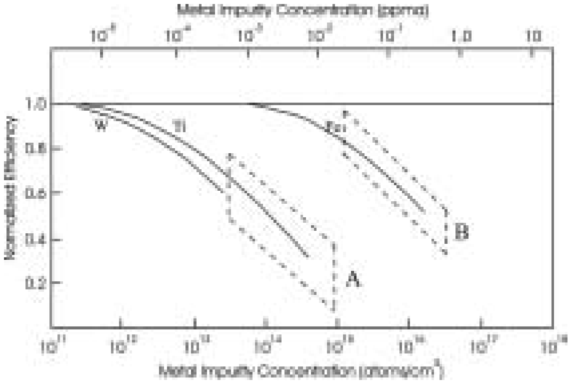

Figure 1. Impact of impurities on CZ ingots as reported in 1980 [4]. The dashed boxes represent the range of impurities found in Silicon-Film™ for Ti and W (box A) and Fe (box B).

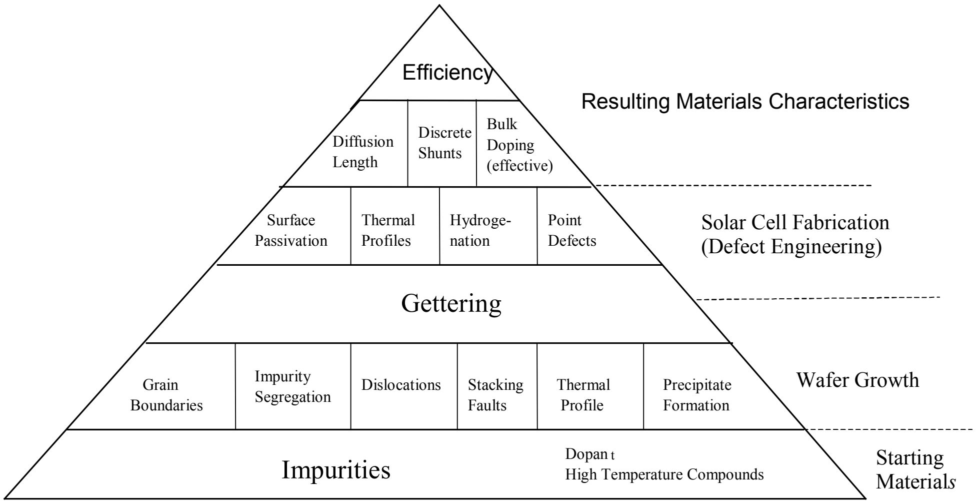

Figure 2. A hierarchical table of the materials factors contributing to solar cell efficiency.

The next tier of contributing factors shown in Figure 2 are those occurring in the wafer formation process. Again, these are very well understood for the CZ and FZ methods, but not yet well known for the Silicon-Film™ sheet process. Critical controlling variables are the impurity segregation effects and the role of inclusions. Critical results are the density of grain boundaries, dislocations, precipitates, stacking faults and the role of point defects in their formation.

Gettering is highlighted in Figure 2, as it spans both wafer formation and solar cell processing. Many exciting advances have occurred in the past decade in gettering for wafers used in the integrated circuits field and photovoltaics [5]. This area holds great promise for the proactive engineering of impurities. The impact in Silicon-Film™ material is actively under study. In addition to gettering, other areas of defect engineering include: surface passivation, hydrogenation, and optimized thermal profiles. The material characteristics resulting from these contributing factors are the minority carrier diffusion length, the effective doping level, and the level of discrete shunts, which when taken as a whole, determine solar cell efficiency.

Impurity Studies by SIMS

Our objective has been to determine the impact of each of the contributing factors shown in Figure 2 to the overall device performance. The first step was to measure the bulk impurity concentration. ICP-MS, NAA, and GDMS have all been evaluated. GDMS was determined to have needed detection limits and also the ability to measure impurities in only the active region of the device. Methods that determine an "average" measurement over the wafer from front to back give misleading results for Silicon-Film™ material. The range of GDMS results for Silicon-Film™ is shown in Figure 1 for Fe, Ti, and W. Analysis of the data shows that there is more than enough Fe, W, Al, Mo and Ti to account for all the lifetime degradation in Silicon-Film™ individually, let alone in total. The level of the impurity did not track lifetime in careful comparisons of material with high and low lifetimes. The question then becomes which impurities are detrimental and which are benign.

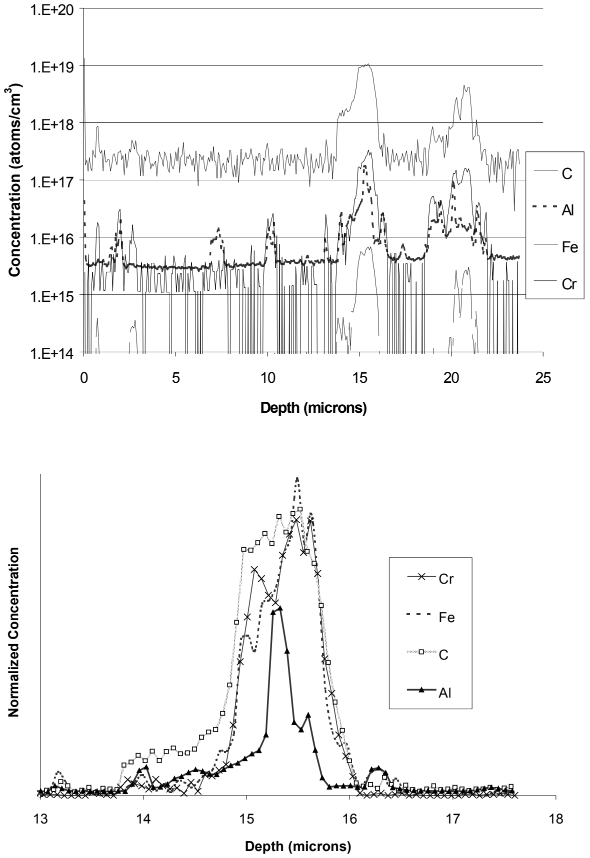

Figure 3. SIMS depth profiles showing a large carbon precipitate, with high levels of chromium, aluminum, and iron at the same site. The lower scan shows an expanded view of a single precipitate containing C, Cr, Fe, and Al with the peak concentrations normalized. The striking similarity in the C, Cr, and Fe scans led to the conclusion that the particulate was an inclusion, as opposed to being precipitated in the process. (SIMS done at NREL).

In an attempt to quantify the role of the impurities, SIMS (Secondary Ion Mass Spectroscopy) depth profiles were taken at the National Renewable Energy Laboratories. An example of a SIMS depth profile is shown in Figure 3 where a number of precipitates can be found.

One plausible conclusion from the SIMS data is that the transition metals are gettering to the larger carbon precipitate. The similarity of shape of the profiles in Figure 4 implies that the impurities are uniform through the precipitate, which is not what would be expected from a gettered impurity. A detailed analysis was carried out on 13 different carbon precipitates by calculating the total concentration of Al, Fe, and Cr, and comparing it to the concentration of carbon. Figure 4 shows the relative impurity concentrations are surprisingly uniform in both raw sheet samples (virgin) and processed materials. This has led to the conclusion that the particulates are not precipitated from the melt at all, but are inclusions. The characteristic impurity profile has been traced to certain insulation materials in the Silicon-Film™ furnace.

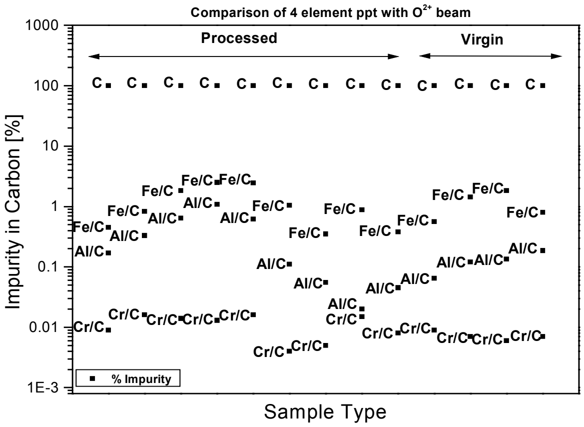

Figure 4. Analysis of 13 different carbon precipitates as identified by SIMS. The impurity concentration for Fe, Al, and Cr was calculated and compared with C. The data shows that the ratio of Fe to C, and ratio of Cr to C, varies over a relatively narrow range, where the ratio of Al to C varies greatly. Combined with the inconsistent shape of the Al peak, this has lead to the conclusions that the Al is gettered to the site, and the Cr and Fe are present in the carbon inclusion.

TEM Results

TEM studies have been carried out at both at NREL and at NCSU. A review of the NCSU findings is presented in a separate paper at this workshop [6]. Carbon particulates were identified in Silicon-Film™ material through TEM analysis done by NREL. One example is shown in Figure 5. The image shows a particulate surrounded by a network of dislocations. Clusters such as these have also been identified in EBIC images and have a significant impact on device performance.

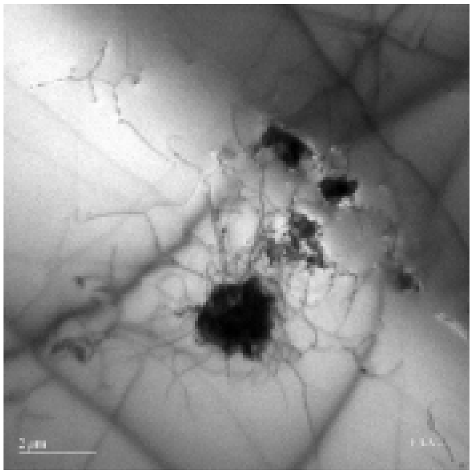

Figure 5. A TEM image of a particulate with a corresponding network of dislocations (work done by NREL).

Similar large dislocation networks have been identified by NCSU with precipitates, inclusions, and voids at their core. Utilizing EELS analysis, C and O have been found to be present in these particles. There is also evidence of transition metal gettering to these sites. As sample sizes and areas are small with TEM studies, further studies are required before conclusions with regard to overall material performance can be drawn.

Oxygen Precipitates

Work done at North Carolina State University (NCSU) has focused on direct observation of defects through polishing and defect etching. An example of that work is shown in Figure 6. This sample shows a clearly delineated denuded zone (DZ) and a uniform distribution of stacking faults inside the grain.

A detailed study of this effect has focused on oxygen levels and is presented at this workshop in a separate paper [7]. In that study stacking fault formation in samples with high and low oxygen levels were analyzed after gettering and phosphorus diffusion steps. Stacking fault formation was evident in the high oxygen samples and missing in the low oxygen sample. Minority carrier properties correlated with stacking fault presence. A conclusion is draw that for Silicon-FilmTM material with the annealing schedule presently in use, initial interstitial oxygen concentrations need to be below about 12 x 1017 cm-3 to avoid the formation of stacking faults.

The size of the denuded zone in Figure 6 indicates that the mechanism causing the nucleation of the oxygen precipitates has the ability to diffuse on the order of 50 microns during the thermal schedule of the growth and processing sequences. This distance rules out slowly diffusing interstitial oxygen, but includes carbon,

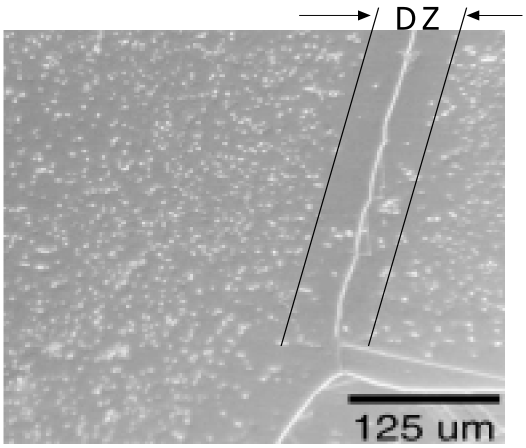

Figure 6. Optical micrograph of an annealed sample SECCO etched for 1 minute. A clearly defined denuded zone (DZ) can be seen around the grain boundary. High initial interstitual oxygen levels have been associated with the high density of stacking faults formed in the intergrain regions. This work was done at NCSU.

nitrogen, and iron – all known to enhance oxygen precipitation, and all present at high levels in Silicon-FilmTM material. Following this theory, the nucleation causing agent is gettered to the grain boundary, leaving an oxygen precipitation free zone. The gettering of self-interstitials is another plausible cause for the formation of the denuded zone put forth in [7].

The impact of the denuded zone can be seen qualitatively in the EBIC image of Figure 7. If the stacking fault defects dominate device performance, a conclusion could be drawn that smaller grain material would make better solar cells. The impact of the grain boundaries on shunt conduction needs to be taken into consideration.

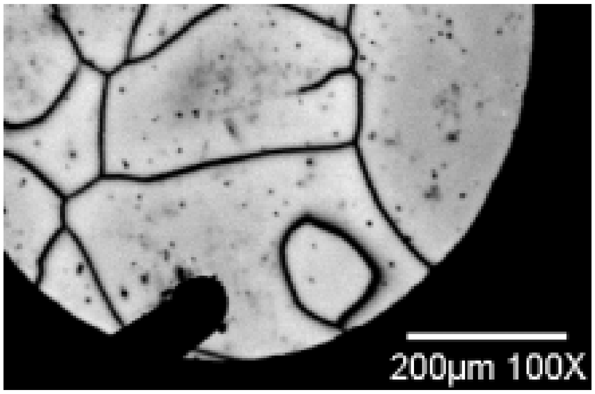

Figure 7. EBIC of a sample showing enhanced performance near grain boundaries.

Conclusion

The application of new processing steps and better understanding of defect and impurity interactions is allowing small grain polycrystalline silicon sheet material to produce solar cell efficiencies approaching that of cast material and CZ. To realize the full benefit of working with this highly defected, impure material, a thorough understanding of which impurities and defects are benign and which are limiting performance is needed. Several characterization techniques are being evaluated and their effectiveness in addressing these issues reviewed.

Acknowledgements

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