Identification and Characterization of Performance Limiting Regions in Poly-Si Wafers Used for PV Cells

Preprint

Harvey Guthrey
Colorado School of Mines and National Renewable Energy Laboratory

Brian Gorman
Colorado School of Mines

Mowafak Al-Jassim
National Renewable Energy Laboratory

Presented at the 37th IEEE Photovoltaic Specialists Conference (PVSC 37)
Seattle, Washington
June 19-24, 2011

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Conference Paper
NREL/CP-5200-50645
July 2011

Contract No. DE-AC36-08GO28308

Available electronically at http://www.osti.gov/bridge

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information

P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: mailto:reports@adonis.osti.gov

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/help/ordermethods.aspx

Cover Photos: (left to right) PIX 16416, PIX 17423, PIX 16560, PIX 17613, PIX 17436, PIX 17721

Printed on paper containing at least 50% wastepaper, including 10% post consumer waste.

IDENTIFICATION AND CHARACTERIZATION OF PERFORMANCE LIMITING REGIONS IN POLY-SI WAFERS USED FOR PV CELLS

Harvey Guthrey[1,2], Brian Gorman[1], Mowafak Al-Jassim[2]
[1]Colorado School of Mines, Golden, Colorado, United States
[2]National Renewable Energy Laboratory, Golden, Colorado, United States

ABSTRACT

As demand for silicon photovoltaic (PV) material increases, so does the need for cost-effective feedstock and production methods that will allow enhanced penetration of silicon PV into the total energy market. The focus on cost minimization for production of polycrystalline silicon (poly-Si) PV has led to relaxed feedstock purity requirements, which has also introduced undesirable characteristics into cast poly-Si PV wafers. To produce cells with the highest possible conversion efficiencies, it is crucial to understand how reduced purity requirements and defects that are introduced through the casting process can impair minority carrier properties in poly-Si PV cells. This is only possible by using multiple characterization techniques that give macro-scale information (such as the spatial distribution of performance-limiting regions), as well as micro and nano-scale information about the structural and chemical nature of such performance-limiting regions. This study demonstrates the usefulness of combining multiple techniques to analyze performance-limiting regions in the poly-Si wafers that are used for PV cells. This is done by first identifying performance-limiting regions using macro-scale techniques including photoluminescence (PL) imaging, microwave photoconductive decay (µPCD), and reflectometry), then using smaller-scale techniques such as scanning electron microscopy (SEM), electron backscattered diffraction (EBSD), laser ablation inductively coupled mass spectrometry (LA-ICP-MS), cathodoluminescence (CL), and transmission electron microscopy (TEM) to understand the nature of such regions. This analysis shows that structural defects as well as metallic impurities are present in performance-limiting regions, which together act to decrease conversion efficiencies in poly-Si PV cells.

BACKGROUND

Crystalline silicon has been studied extensively over several decades. Despite a large body of knowledge on crystalline silicon photovoltaics, the research has not shown a clear correlation between processing conditions and the spatial distribution and character of defects in directionally solidified silicon. In addition, researchers do not completely understand the exact mechanisms by which conversion efficiencies are limited. Because the conversion efficiencies are directly related to the properties of minority charge carriers, this is an important characteristic of poly-Si PV cells to study. Studies on minority carrier properties in poly-Si are typically based on the analysis of a transient associated with carrier excitation or some form of luminescence [2]. Information about the structure of different regions within poly-Si materials is gained through research techniques such as transmission electron microscopy(TEM) [3, 4] and electron backscatter diffraction (EBSD) [5]. Methods such as electron beam induced current (EBIC), cathodoluminescence (CL) and photoluminescence are used for the identification and study of defects [6, 7]. However, the most useful studies employ multiple techniques where each technique complements another and, thus, presents a more complete understanding of factors related to conversion efficiencies. The studies that use multiple techniques typically focus on one aspect of the poly-Si such as distribution of carrier lifetimes, distribution of impurities, defect structure, or grain morphology. Because of this approach, no definitive study has been done to relate the macro-scale phenomena associated with processing to atomic-scale phenomena that are responsible for the limitations of poly-Si PV cell-conversion efficiencies.

EXPERIMENT

In this study, a series of poly-Si wafers were removed from a brick toward the center of a directionally solidified ingot. This allows multiple techniques to be performed on essentially the same region, even if they are of a destructive nature. The wafer was as-cut and received no preparation for the PL imaging or µ-PCD mapping. PL imaging was performed with a Princeton Instruments/Acton PIXIS 1024BR camera cooled to -70˚C. The optical excitation source is four 30W laser diodes with 808nm wavelength. µ-PCD mapping was performed on a SEMILAB tool with 904nm excitation wavelength. To create the reflectometry map, the sample was polished and then etched to reveal the defects and allow them to scatter incident light. The other techniques including CL, EBSD, TEM and LA-ICP-MS required polishing; and, in the case of CL, passivation for the measurements. The passivation was achieved by an HF dip and subsequent storage in an iodine/methanol solution. CL was done on a JEOL 5800 SEM equipped with a Ge detector for imaging. EBSD was performed on a JEOL 4300 SEM with Oxford Instruments EBSD software. A FEI T30 TEM was used to image individual defects. The dimensions of the wafers used are 156mm x 156mm and 0.18mm thick.

RESULTS

The photoluminescence image (Figure 1) reveals the presence of non-radiative recombination centers, which are represented by the dark regions in the image. The light regions are where radiative recombination is dominant and photon emission is more likely. These dark regions include grain boundaries as well as defect clusters. Certain grains also appear darker than neighboring grains, which indicates a difference in luminescence from grain to grain.

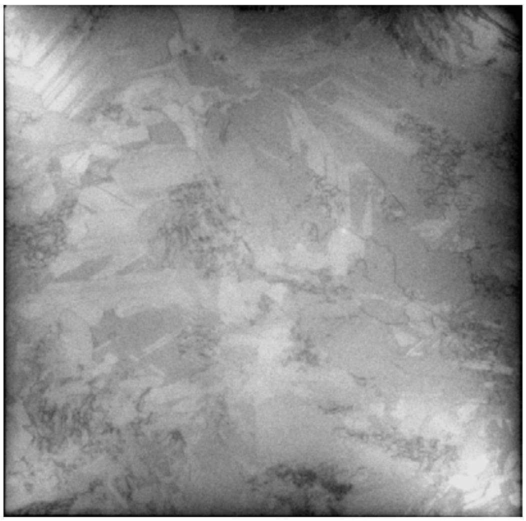

Figure 1 Photoluminescense image of the entire wafer.

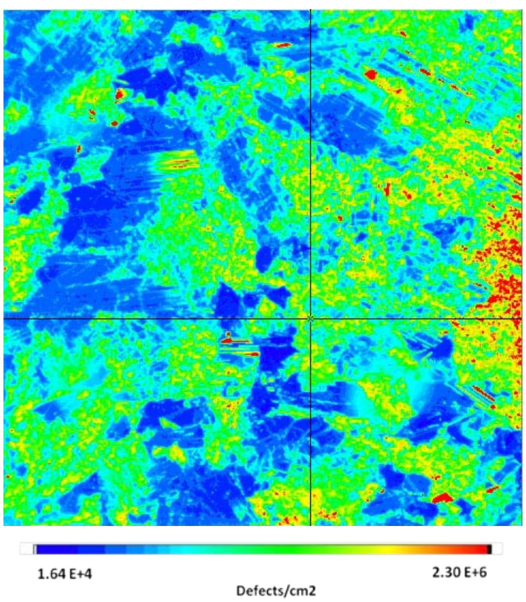

Figure 2 Reflectometry map of the entire wafer.

The results of the reflectometry mapping (Figure 2) allow for identification of regions of the wafer with dislocation densities that are higher than the average for the wafer. The blue regions indicate a low dislocation density, and the red and yellow regions represent a high dislocation density. The right side of Figure 2 has the highest dislocation density where the red regions indicate a defect density of approximately 10^6 cm^{-2}.

The microwave photoconductive decay technique was used to create a map (Figure 3) of the minority carrier lifetimes across the wafer. Because the wafer was not passivated prior to the measurement, surface recombination was dominant as indicated by the measured lifetimes of less than 2 μs. The right side of the wafer, as well as a region toward the bottom of the wafer, exhibit very poor minority carrier lifetimes.

A region identified as having poor minority carrier properties was isolated, and an EBSD orientation map was constructed for the region (Figure 4a) using the inverse pole figure color scheme (Figure 4b). This technique identified the presence of twin boundaries as well as other randomly oriented boundaries.

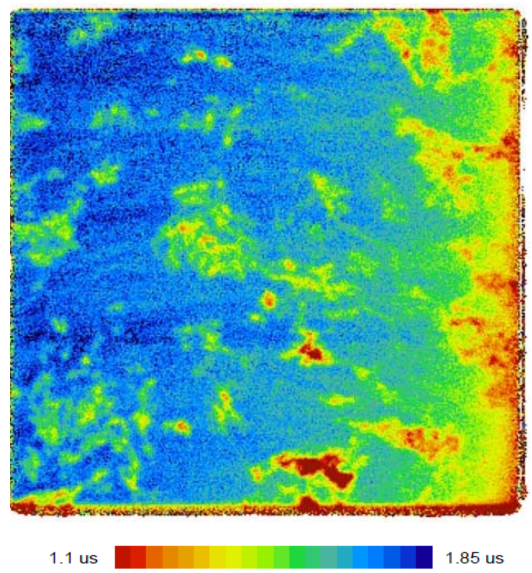

Figure 3 μ-PCD map of the entire wafer.

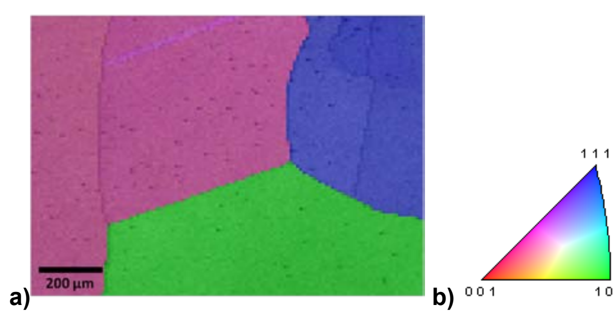

Figure 4 a) EBSD orientation maps of the region of interest. b) Inverse pole figure color scheme.

The cathodoluminescence image in Figure 5 shows multiple non-radiative recombination centers (dark areas) contained in the same region isolated to create the EBSD map (Figure 4). The dark line extending from the top to the bottom of the image indicates a grain boundary, while the smaller scattered features represent individual dislocations or clusters of dislocations. The contrast associated with the non-radiative recombination centers varies and indicates the degree to which minority carriers are hindered in a particular region.

LA-ICP-MS identified 19 impurity elements within this performance-limiting region. Of the 19 detected, the elements Al, Cu, Cr, Fe, and Ti are known to introduce energy levels deep in the band gap of silicon. Because the type of impurities was not known prior to analysis, no standard was used and the data is purely qualitative.
The TEM image (Figure 6) confirms the presence of dislocations within this region. The contrast associated with dislocations originates from distortions of the lattice surrounding the dislocation.

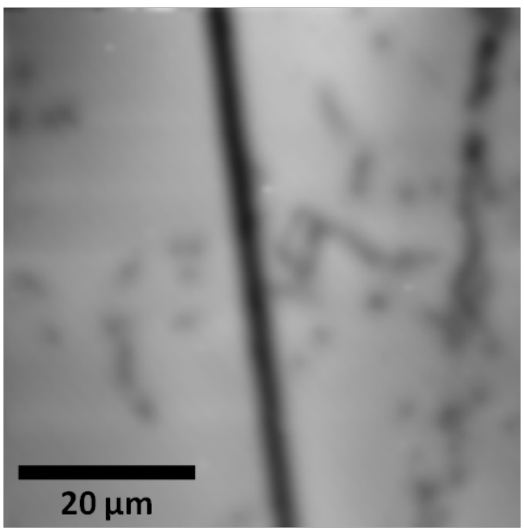

Figure 5 CL image from performance-limiting region.

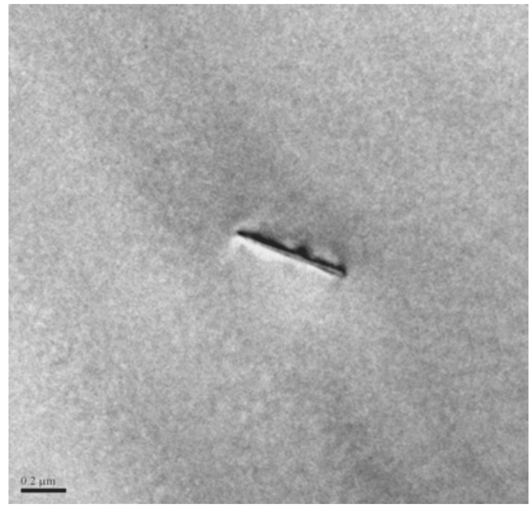

Figure 6 Bright-field TEM image of dislocations in a performance-limiting region.

DISCUSSION

The results of mapping the entire wafer identify the performance-limiting regions. The PL image is representative of the intensity of luminescence associated with band-to-band recombination. Luminescence is decreased in regions that harbor non-radiative recombination centers associated with energy levels deep in the band gap. Thus, the dark regions in the PL image indicate where minority carriers will most likely encounter non-radiative recombination centers, which will limit conversion efficiencies. The µ-PCD technique extracts the minority carrier lifetimes at various positions on the wafer through analysis of the excitation transient.

Because the wafer was not passivated prior to the measurement, the measured lifetimes are not representative of the bulk lifetime for the wafer. Even with this consideration, the analysis still shows the variation of minority carrier lifetimes across the wafer. This is useful in correlating poor minority carrier lifetimes with non-radiative recombination centers. The dislocation density maps produced by the reflectometry technique generally reinforce the assumption that high dislocation densities result in poor minority carrier properties. The combination of these three mapping techniques used on the same region of a poly-Si wafer reveal the relationship among defects, non-radiative recombination centers, and poor minority carrier lifetimes. In general, regions with high concentrations of defects and non-radiative recombination centers also exhibit poor minority carrier properties.

Based on the results of the mapping techniques, the researchers selected a region that exhibited non-radiative recombination, high dislocation density, and poor minority carrier lifetimes. The electron backscatter diffraction (EBSD) technique provided an orientation map (Figure 4a) of this region showing the presence of grain boundaries of various characters. The cathodoluminescence (CL) image (Figure 5) shows that grain boundaries as well as individual dislocations are present within this region and act as non-radiative recombination centers. The different features in the CL image have varying degrees of contrast, and it is not clear from the data what the origin of this variation is. The bright-field TEM image (Figure 6) confirmed dislocations in which one is visible due to the contrast produced by lattice distortions around the dislocation.

Because of the lack of prior information about the impurity content within the wafer, it was not possible to use a standard for the LA-ICP-MS analysis. This makes the data purely qualitative. However, LA-ICP-MS did identify

19 impurity elements. Of these, Al, Cr, Cu, Fe, and Ti are known to introduce energy levels that lie deep in the band gap of silicon. The presence of these elements even at the ppb level is known to have detrimental effects on PV device performance.

SUMMARY

This study investigates how researchers can combine multiple characterization techniques to produce a greater understanding of the performance limitations associated with directionally solidified poly-Si for PV cells. Large-scale mapping techniques (PL imaging, μ-PCD, reflectometry) are shown to be effective in identifying spatial variations in performance-limiting regions. The results of the mapping techniques are then used to select appropriate areas where more information about the performance-limiting factors can be extracted. The performance-limiting regions were found to contain both structural features (EBSD, CL, TEM), as well as impurities (LA-ICP-MS) that contribute to the overall performance limitations of poly-Si PV cells.

ACKNOWLEDGMENTS

Thanks to Steve Johnston for providing the PL images and Bhushan Sopori for providing the reflectometry maps. This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08-GO28308 with the National Renewable Energy Laboratory.

REFERENCES

[1] J. Hofstetter, J. F. Lelièvre, C. del Cañizo *et al.*, “Acceptable contamination levels in solar grade silicon: From feedstock to solar cell,” *Materials Science and Engineering: B,* vol. 159-160, pp. 299-304, 2009

[2] R. K. Ahrenkiel, and S. W. Johnston, “An advanced technique for measuring minority-carrier parameters and defect properties of semiconductors,” *Materials Science and Engineering B,* vol. 102, no. 1-3, pp. 161-172, 2003.

[3] M. Itsumi, “Analysis of grown-in defects in Czochralski Si,” *Journal of Crystal Growth,* vol. 210, no. 1-3, pp. 1-6, 2000.

[4] A. Lotnyk, J. Bauer, O. Breitenstein *et al.*, “A TEM study of SiC particles and filaments precipitated in multicrystalline Si for solar cells,” precipitated in multicrystalline Si for solar cells,” *Solar Energy Materials and Solar Cells,* vol. 92, no. 10, pp. 1236-1240, 2008.

[5] T. Buonassisi, A. A. Istratov, M. D. Pickett *et al.*, “Metal precipitation at grain boundaries in silicon: Dependence on grain boundary character and dislocation decoration,” *Applied Physics Letters,* vol. 89, no. 4, pp. 042102-042102-3, 2006.

[6] R. K. Ahrenkiel, N. Call, S. W. Johnston *et al.*, “Comparison of techniques for measuring carrier lifetime in thin-film and multicrystalline photovoltaic materials,” *Solar Energy Materials and Solar Cells,* vol. 94, no. 12, pp. 2197-2204.

[7] M. Kittler, W. Seifert, T. Arguirov *et al.*, “Room-temperature luminescence and electron-beam-induced current (EBIC) recombination behaviour of crystal defects in multicrystalline silicon,” *Solar Energy Materials and Solar Cells,* vol. 72, no. 1-4, pp. 465-472, 2002.