NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Defect Band Luminescence Intensity Reversal as Related to Application of Anti-Reflection Coating on mc-Si PV Cells

Preprint

Harvey Guthrey
Colorado School of Mines and National Renewable Energy Laboratory

Brian Gorman
Colorado School of Mines

Steve Johnston, Fei Yan,
and Mowafak Al-Jassim
National Renewable Energy Laboratory

Presented at the 2012 IEEE Photovoltaic Specialists Conference
Austin, Texas
June 3–8, 2012

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-5200-54176
June 2012

Contract No. DE-AC36-08GO28308

NOTICE

The submitted manuscript has been offered by an employee of the Alliance for Sustainable Energy, LLC (Alliance), a contractor of the US Government under Contract No. DE-AC36-08GO28308. Accordingly, the US Government and Alliance retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

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.

Defect Band Luminescence Intensity Reversal as Related to Application of Anti-Reflection Coating on mc-Si PV Cells

Harvey Guthrey[1,2], Steve Johnston[2], Fei Yan[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
*Current Affiliation – Applied Materials

***Abstract* — Photoluminescence (PL) imaging is widely used to identify defective regions within mc-Si PV cells. Recent PL imaging investigations of defect band luminescence (DBL) in mc-Si have revealed a perplexing phenomenon. Namely, the reversal of the DBL intensity in various regions of mc-Si PV material upon the application of a SiN_x:H anti-reflective coating (ARC). Regions with low DBL intensity before ARC application often exhibit high DBL intensity afterwards, and the converse is also true. PL imaging alone cannot explain this effect. We have used high resolution cathodoluminescence (CL) spectroscopy and electron beam induced current (EBIC) techniques to elucidate the origin of the DBL intensity reversal. Multiple sub-bandgap energy levels were identified that change in peak position and intensity upon the application of the ARC. Using this data, in addition to EBIC contrast information, we provide an explanation for the DBL intensity reversal based on the interaction of the detected energy levels with the SiN_x:H ARC application. Multiple investigations have suggested that this is a global problem for mc-Si PV cells. Our results have the potential to provide mc-Si PV producers a pathway to increased efficiencies through defect mitigation strategies.**

***Index Terms* — defect luminescence, photoluminescence, silicon processing, silicon, silicon nitride.**

I. Introduction

Photoluminescence imaging of silicon has proven to be a valuable tool in studying the spatial distribution of minority carrier properties over entire wafers[1]. In addition to the study of unprocessed wafers and finished cells, PL imaging can also be successfully performed on the wafer after other processing steps[2]. This is particularly useful for studying defects in mc-Si PV cells as the change in activity after various processing steps can yield information regarding the nature of the defects. Changes in luminescence intensity after a phosphorus diffusion step can reveal whether the defects are in too great a density or if enough oxygen is present to limit the effectiveness of the external gettering step[3]. An increase in luminescence intensity after SiN_x:H ARC is applied could suggest that the defects were passivated by the hydrogen contained in the coating[4].

The temperature at which the SiN_x:H ARC is applied also needs to be considered. Typical temperatures for PECVD deposition of SiN_x:H ARC range from 250̊C to 450˚C [5]. Thermal treatments in this range of temperatures has been shown to reduce the concentration of interstitial iron through internal gettering associated with extended defects and grain boundaries[6]. This gettering of impurities by various defects can change their electrical and optical activity and it is important to consider this mechanism when investigating these types of changes.

Recently, the use of InGaAs cameras instead of Si CCDs has enhanced the range of detectable wavelengths into the near IR allowing for the imaging of radiative transitions associated with sub-bandgap energy levels, provided that the band-to-band emission is removed using appropriate filters[7]. While this provides information about the intensity of the DBL, precisely determining the energy of the emitted photons requires spectroscopic techniques. Cathodoluminescence spectroscopy studies of defect band emission in Si have identified several common levels and provided insights into their probable origin[8, 9]. However, there has not been conclusive work detailing the origin of the sub-bandgap energy levels. The EBIC technique has been used extensively to study the nature of various extended defects in Si[10, 11]. The temperature dependence of EBIC contrast can also be used to reveal information about the origin of various sub-bandgap energy levels[12].

II. Experimental

A series of adjacent wafers cut from a mc-Si ingot were selected and processed to various levels of completion. This work focused on the step in which the SiN_x:H ARC is applied. The wafers studied before and after the ARC application both experienced the same texturing, P-diffusion, and phosphosilicate glass (PSG) removal processes. A NIR InGaAs Camera (320 x 256 pixels) was used for DBL imaging. The excitation source was 4 30W 810nm laser diodes that provided the intensity of approximately 1 sun. The band-to-band emission was filtered using RG1000 Schott glass filters. CL spectroscopy was performed on a JEOL 5800 SEM at a specimen temperature of 15K. EBIC analysis was performed on the same JEOL 5800 SEM, while using a stage cooled with liquid nitrogen capable of achieving temperatures near 80K.

III. Results

Fig. 1 shows an example of the intensity reversal of DBL. Figures 1a and 1b are the same region before and after the ARC step, respectively. Note the center of 1a where the bright spot (high intensity) changes to a darker spot (lower intensity) in 1b, this will be referred to as region 1. The opposite effect can be seen in 1c and 1d, which represents region 2.

The regions where the intensity reversal was observed were isolated and CL spectroscopy and spectroscopic imaging were performed. The images in Fig. 2-5 represent a) band-to-band emission, b) defect band emission, and c) photon energies of the two analysis regions before and after ARC application. The monochromatic images in a and b represent

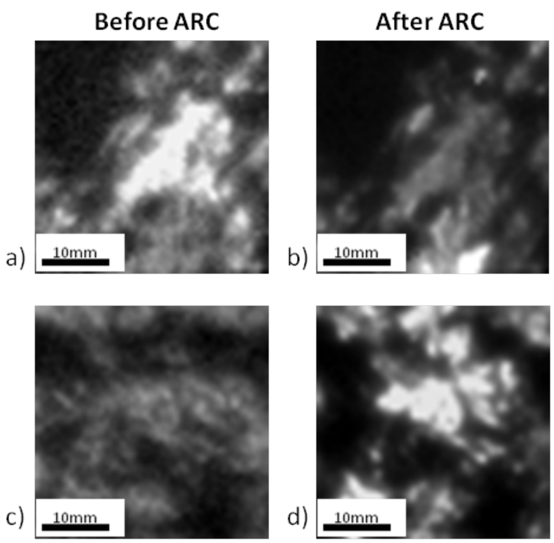

Fig. 1. Defect-band PL images of intensity reversal.

emission of 1.1eV 0.83ev signifying the band-to-band and defect band luminescence respectively. The photon energy maps (c) represent a 200meV energy window centered at 0.95eV and the coloration is interpreted as blue, indicating higher energy photon emission, and red, indicating lower energy emission. The positions where the spectra in Fig. 6 and 7 were taken are marked in Fig. 2-5, with circles where the circle color corresponds to the spectra color. The defect luminescence in region 1, before ARC, has reduced intensity and contains a peak at approximately 0.83eV, in contrast to the spectra from the bulk that contains only the band-to-band transition peak. After the ARC is applied, there is a change in the DBL as shown in the bottom two spectra in Fig. 6b. Defect 1 (red) has a broad peak at approximately 0.87eV that has higher intensity than the band-to-band peak. Defect 2 (blue) contains the 0.83eV peak (as does the bulk spectra in black) as well as a broad peak at approximately 1.00eV. The spectra of region 1 before and after the ARC application are fundamentally different than the region 2, as shown in Fig. 7, where the spectra do not change before (a) and after (b) the ARC step. The defect luminescence is essentially the same as the bulk luminescence, except that the intensity is decreased.

The EBIC images in Fig. 8 show the defect contrast at 300K and 80K for region 1, region 2, and a reference region. There is a similar change in defect contrast, from 300K to 80K in both regions 1 and 2, as the contrast of all the defects increases. The only apparent difference is that in region 2, there appears to be a higher density of current-limiting features.

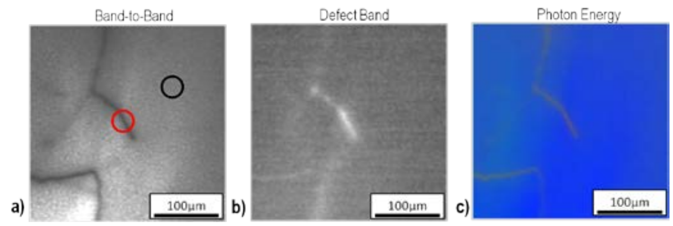

Fig. 2. CL spectral images showing the a) band-to-band, b) defect-band , c) photon energy maps for region 1 before ARC application.

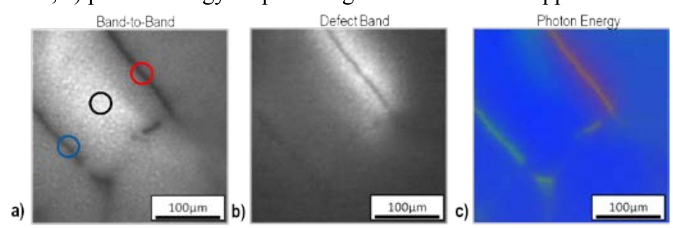

Fig. 3. CL spectral images showing the a) band-to-band, b) defect-band , c) photon energy maps for region 1 after ARC application.

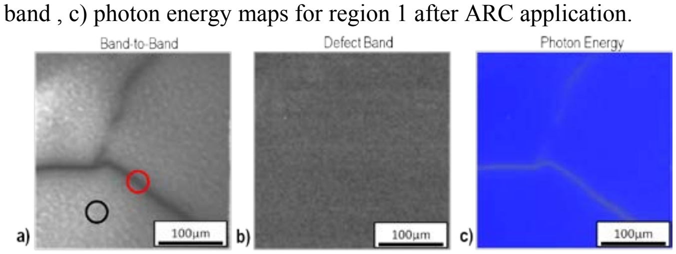

Fig. 4. CL spectral images showing the a) band-to-band, b) defect-band , c) photon energy maps for region 2 before ARC application.

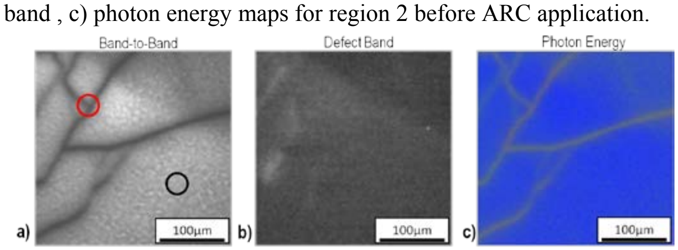

Fig. 5. CL spectral images showing the a) band-to-band, b) defect-band, c) photon energy maps for region 2 after ARC application.

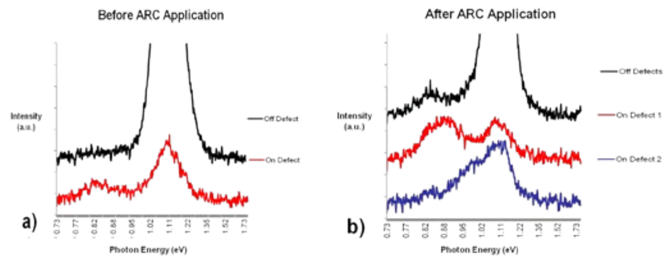

Fig. 6. a) CL spectra from region 1 before (Fig. 2) and b) after ARC application (Fig. 3).

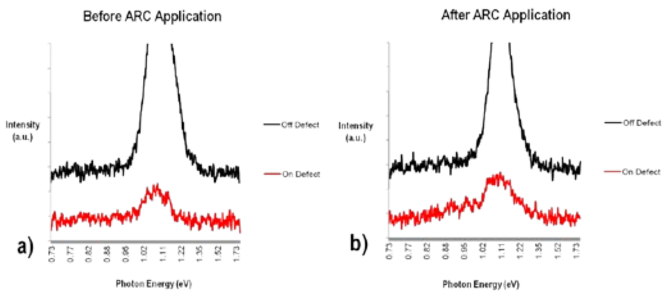

Fig. 7. a) CL spectra from region 2 before (Fig. 4) and b) after ARC application (Fig. 5).

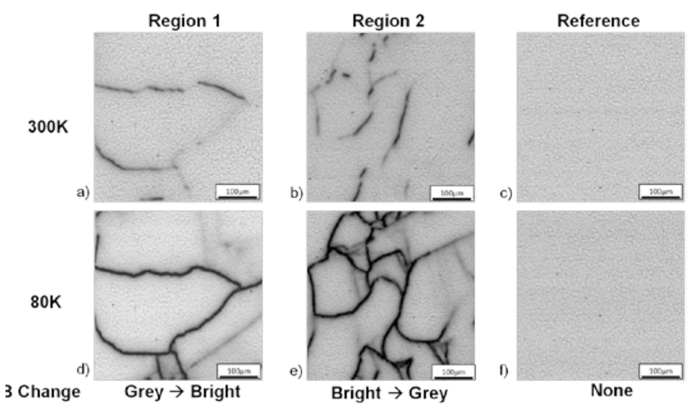

Fig. 8. Room temperature EBIC images (a-c) and images of the same regions at 80K (d-f).

IV. Discussion

The spectra collected from regions 1 (low to high DBL) and region 2 (high to low DBL) show fundamental differences in the radiative transitions associated with the defects. Defects in region 1 before the ARC step emit photons of 0.83eV which is slightly higher in energy than the D1 band associated with dislocations in silicon[13]. This peak is not present in the bulk of region 1 before the ARC application. Defects in region 1 after the ARC application display multiple luminescence signatures (Fig. 6b). One defect contains a peak at 0.87eV, which has been associated with D2 band in silicon that has a higher intensity than the band-to-band transition peak. Another defect exhibits a shallow peak at 1.00eV (D4), as well as the 0.83eV identified in the defect before the ARC step. It is important to note that the bulk signature after the ARC step also contains this 0.83eV peak. In one study, an increase in defect band intensity was found to correspond with hydrogen treatment, but the origin of the increase was not determined[14]. What is clear is that the ARC application step has altered the defect luminescence in region 1 and created pathways for more sub-bandgap radiative transitions. Defects in region 2 before and after the ARC application do not show any peaks other than the band-to-band peak, which decreases in intensity. This is interesting, as the DB PL shows high intensity before the ARC step. However, the detector for CL is sensitive to approximately 0.79eV and the detector used for PL is sensitive to approximately 0.72eV. This suggests a transition corresponding to emission with energy below 0.79eV but above 0.72eV. This needs to be investigated further. The EBIC images do not provide any further understanding the of DBL intensity reversal at this time. However, the interpretation of thorough measurements of the defect contrasts will provide information about the presence and alteration of the various energy levels active in the recombination process.

V. Summary

This study investigates the DBL intensity reversal based on the variation in CL spectra obtained before and after ARC application in two regions. The SiN_x:H coating is reacting with defects in such a way that more sub-bandgap energy levels are involved in radiative transitions during the recombination process in the region where DB PL is decreased after the ARC step. However, in the region where the DB PL increases the ARC coating may be passivating deep level defects where the transitions involved are not visible to the detector. It is currently unclear whether the origin of the change in DBL intensity is related to the H in the SiN_x:H ARC or the temperature associated with ARC deposition. A thorough investigation of the character of these defects may reveal the nature of their behavior during the ARC application step, and this will be the focus of future work on this topic.

Acknowledgment

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] T. Trupke, R. A. Bardos, M. C. Schubert et al., “Photoluminescence imaging of silicon wafers,” Applied Physics Letters, vol. 89, no. 4, pp. 044107-3, 2006.

[2] S. Johnston, F. Yan, K. Zaunbracher et al., Imaging Study of Multi-Crystalline Silicon Wafers Throughout the Manufacturing Process: Preprint.

[3] I. Périchaud, “Gettering of impurities in solar silicon,” Solar Energy Materials and Solar Cells, vol. 72, no. 1-4, pp. 315-326, 2002.
[4] R. Lüdemann, “Hydrogen passivation of multicrystalline silicon solar cells,” Materials Science and Engineering B, vol. 58, no. 1-2, pp. 86-90, 1999.
[5] A. G. Aberle, “Overview on SiN surface passivation of crystalline silicon solar cells,” Solar Energy Materials and Solar Cells, vol. 65, no. 14, pp. 239-248, 2001.
[6] R. Krain, S. Herlufsen, and J. Schmidt, “Internal gettering of iron in multicrystalline silicon at low temperature,” Applied Physics Letters, vol. 93, no. 15, pp. 152108-3, 2008.
[7] F. Yan, L. National Renewable Energy, U. Colorado State et al. "Defect-band emission photoluminescence imaging on multi-crystalline Si solar cells preprint," http://purl.fdlp.gov/GPO/gpo11163.
[8] V. Higgs, E. C. Lightowlers, S. Tajbakhsh et al., “Cathodoluminescence imaging and spectroscopy of dislocations in Si and Si[sub 1 - x]Ge[sub x] alloys,” Applied Physics Letters, vol. 61, no. 9, pp. 1087-1089, 1992.
[9] W. Lee, “Cathodoluminescence study of dislocation-related luminescence from small-angle grain boundaries in multicrystalline silicon,” Appl. Phys. Lett., vol. 94, no. 11, pp. 112103, 2009.
[10] A. Jakubowicz, “On the theory of electron-beam-induced current contrast from pointlike defects in semiconductors,” Journal of Applied Physics, vol. 57, no. 4, pp. 1194-1199, 1985.
[11] T. Sekiguchi, B. Shen, T. Watanabe et al., “EBIC study on the electrical activity of stacking faults in silicon,” Materials Science and Engineering: B, vol. 42, no. 1-3, pp. 235-239, 1996.
[12] V. Kveder, M. Kittler, and W. Schroter, “Recombination activity of contaminated dislocations in silicon:A model describing electron-beam-induced current contrast behavior,” Physical Review B, vol. 63, no. 11, pp. 115208, 2001.
[13] N. Drozdov, “Recombination radiation on dislocations in silicon,” JETP letters, vol. 23, no. 11, pp. 651-653, 1976.
[14] T. Sekiguchi, and K. Sumino, Cathodoluminescence study on dislocations in silicon: AIP, 1996.