

SEMI AUX026-1012
RESEARCH REPORT ON INTERLABORATORY STUDY TO
ESTABLISH PRECISION STATEMENTS FOR SEMI PV13, TEST
METHOD FOR CONTACTLESS EXCESS-CHARGE-CARRIER
RECOMBINATION LIFETIME MEASUREMENT IN SILICON WAFERS,
INGOTS, AND BRICKS USING AN EDDY-CURRENT SENSOR

The information in this Document has been furnished by the SEMI PV Analytical Test Methods Task Force, for informational use only and is subject to change without notice. The SEMI Standards Program is publishing this information as furnished by the group in the form of Auxiliary Information so that it may be referenced by the industry, as desired. **No material in this Document is to be construed as an official or adopted Standard.** SEMI assumes no liability for the content of this Document, which is the sole responsibility of the authors, nor for any errors or inaccuracies that may appear in this Document. SEMI grants permission to reproduce and distribute this Document provided that:

- (1) the Document is maintained in its original form, and
- (2) this disclaimer and the notice below accompany the Document at all times.

NOTICE: By publication of this Document, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned herein. Users of this Document are expressly advised that determination of any such patent rights or copyrights, and the risk of infringement of such rights, are entirely their own responsibility.

Copyright 2012 by SEMI (Semiconductor Equipment and Materials International, 3081 Zanker Road, San Jose, CA 95134). See above for information on limited rights for reproduction and distribution; all other rights reserved.

SEMI AUX026-1012

RESEARCH REPORT ON INTERLABORATORY STUDY TO ESTABLISH PRECISION STATEMENTS FOR SEMI PV13, TEST METHOD FOR CONTACTLESS EXCESS-CHARGE-CARRIER RECOMBINATION LIFETIME MEASUREMENT IN SILICON WAFERS, INGOTS, AND BRICKS USING AN EDDY-CURRENT SENSOR

1 Abstract

The goal of this study was to add a precision statement applicable to the SEMI PV13 standard based on an Interlaboratory Study (ILS). The study was planned and executed over the course of six months and included 23 labs from Europe, USA, and Asia. This final report includes a description of the study, data from the participating laboratories, and a resulting precision statement from the study. The statistical analysis and design of the study was based on ASTM E691-09, “Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method.”

2 Introduction

An Interlaboratory Study was conducted to establish a precision statement for SEMI PV13, Test Method for Contactless Excess-charge-carrier Recombination Lifetime Measurement in Silicon Wafers, Ingots, and Bricks using an Eddy-Current Sensor.

3 Test Method

The Test Method used for this Interlaboratory study (ILS) is SEMI PV13 and is currently under the jurisdiction of SEMI. To obtain a copy of this Standard, go to SEMI’s Web site, www.semi.org.

4 Participating Laboratories

The following laboratories and personnel participated in this ILS:

Applied Materials (Fei Yan)
3101 Scott Blvd., M/S 9153
P.O. Box 58039
Santa Clara, CA 95054

Arizona State University (Stanislav Gerasimenko)
Solar Power Laboratory
7700 South River Parkway
ASU Research Park
Tempe, AZ 85284

The Australian National University (Fiacre Rougieux)
E216 Building 32
School of Engineering
College of Engineering and Computer Science
The Australian National University
Canberra ACT 0200
Australia

Bosch Solar Energy AG (Thomas Roth)
Solar Energy (SE/ECC1)
Rober-Bosch-Str. 1
99310 Arnstadt
Germany

CiS (Kevin Lauer)
CiS Forschungsinstitut für Mikrosensorik und Photovoltaik GmbH
Konrad-Zuse-Str. 14
D-99099 Erfurt

ECN (Paula Bronsveld)
ECN-Solar Energy
Room 40.1.02
P.O. Box 1, Westerduinweg 3
NL-1755 ZG PETTEN
The Netherlands

Fraunhofer ISE (Johannes Giesecke)
Division Solar Cells – Development and Characterization
Fraunhofer-Institut für Solare Energiesysteme ISE
Heidenhorstrasse 2, 79110 Freiburg, Germany

Fraunhofer ISE (Jonas Haunschild)
Fraunhofer Institute for Solar Energy Systems
Emmy-Noether-Straße 2
79110 Freiburg, Germany

GT Advanced Technologies (Jamey Myers)
1600 Park 370 Place, Suite 2
Hazelwood, MO 63042

Insitut für Solarenergieforschung GmbH (ISFH) (Bianca Lim)
Am Ohrberg 1, 31860
Emmerthal, Germany

MEMC (Jesse Appel)
MEMC Electronic Materials, Inc.
501 Pearl Drive
P.O. Box 8 St. Peters, MO 63376-0008

MEMC (John Hilker)
MEMC Electronic Materials, Inc.
501 Pearl Drive
P.O. Box 8 St. Peters, MO 63376-0008

National Renewable Energy Lab (NREL) (Steve Johnston)
16253 Denver West Parkway
Golden, CO 80401

National University of Singapore (Ziv Hameiri)
Solar Energy Research Institute of Singapore (SERIS)
Block E3A, #06-01
7 Engineering Drive 1
Singapore 117574
SINGAPORE

Q-cells SE (Saioa Tardon)
OT Thalheim
Sonnenallee 17-21
06766 Bitterfeld-Wolfen
Germany

Sinton Instruments (James Swirhun)
4720 Walnut Street, Suite 102
Boulder, CO 80301

SolarWorld (Bjoern Seipel)
SolarWorld Industries America
25300 NW Evergreen Road
Hillsboro, OR 97124

Suniva (Rentian Xiong)
5765 Peachtree Industrial Blvd.
Norcross, GA 30092, USA

Sunpower (Roy Joseph Legaspi)
Sunpower Philippines Manufacturing Ltd.
100 East Main Ave., LTI,
Binan, Laguna, Philippines 4024

Tokyo University of Agriculture and Technology (Marwan Dhamrin)
2-24-16 Naka-cho, Koganei-shi
Tokyo 184-8588
Japan

University of Oxford (John Murphy)
Department of Materials
University of Oxford
16 Parks Road
Oxford
OX1 3PH
United Kingdom

Woongjin (Eunju Jang)
Woongjin Energy Co., Ltd
1316, Gwanpyeong-Dong
Yuseong-Gu, Daejeon
305-509 Korea

5 Test Sample Set Selection Considerations

There is no national laboratory that measures and certifies carrier lifetime; thus, selecting a sample set was quite difficult. Many common recombination-active defects that determine the carrier lifetime of a sample are not stable for long periods of time. Illumination can significantly change the recombination behavior of charge-carriers in commercial solar material. Defects such as boron-oxygen light-induced degradation and iron-boron are both unstable with illumination.

6 Description of Samples

For this study the following samples were chosen:

- i) N-type phosphorus doped semiconductor grade wafers (50 ohm-cm) with symmetric boron diffusions (50-100 ohms/square). The diffusion dominates the recombination behavior and remains stable under a variety of storage and shipping conditions. No passivating layer (such as oxide or nitride) was applied

so that lifetime remains stable over the timeline of the study. The wafer thickness of 210µm is close to the typical range of 180-200µm common in the PV industry, but still robust enough to be handled without significant risk of breakage during transport. Effective carrier lifetimes between 100 and 200 microseconds are representative of common industrial solar cell precursors. Samples Labeled A, B were of this type. Multiple samples were identically prepared by selecting wafers from the same batch and processing them with the same diffusion recipe. The wafers were processed by a photovoltaic laboratory.

- ii) Light-soaked bare CZ boron-doped (1.4 ohm-cm), polished “electronic-grade” wafers. CZ wafers often have high oxygen concentration, and therefore are susceptible to light-induced-degradation (LID). These samples were subjected to 20 hours of 1-sun illumination to fully activate the boron-oxygen complex responsible for this effect, yielding a stable bulk lifetime. These wafers had a resulting lifetime of approximately 2 microseconds which is comparable to bare solar wafers in production. Samples labeled C were of this type. Multiple identical samples were prepared by selecting adjacent wafers from the same ingot and uniformly illuminating them to achieve a stable lifetime.
- iii) Float zone (FZ) slugs of thickness 1.5 cm were chosen in order to simulate the measurement of Ingots and Bricks, as defined in the SEMI PV13 standard. Boron-doping of 1.5-2.5 ohm-cm was chosen to yield bulk lifetimes of 1-3 milliseconds. Samples were cut from the same ingot in order to ensure identical characteristics. The thickness of 1.5 cm was chosen to be 5 times the effective sensor sensitivity depth, which is exponential. These samples were labeled D and E. Float zone is an expensive crystal growth process and therefore is not common in production of commercial solar cells. The bulk lifetime of these samples is representative of commercial high-efficiency cells.

No samples were selected from the 10-100 microsecond range due to stability concerns for the defects that cause these lifetimes.

7 Interlaboratory Study Instructions

The Interlaboratory study was conducted in two different parts: wafer and bulk.

For the wafer portion of the study, a pilot round (as suggested by ASTM E691-09) was first conducted in order to ensure that the participating laboratories have working, calibrated instruments. The participants were sent the following instructions for the pilot round:

The study will consist of two parts. The first part (Pilot Run) will include the measurement of two samples to verify that the instruments are working properly. A set of calibration wafers is included to be used only if recalibration is required. After completing this pilot run, the full scale study will begin.

Pilot Run Instructions

The shipment will contain the following:

1. 2 wafers to be tested (Labeled A1, A2, A3 or C1, C2, C3)
2. A set of 4 conductance sensor calibration wafers – these should only be used if the measured values of the first wafers are out of specification.
3. A USB flash drive with the latest WCT software update and installation instructions.

After installing the software update, and entering the correct calibration values for your WCT-120, measure each of the wafers. The input parameters (type, resistivity, thickness) are given on the wafer cases. As the wafers are bare, the optical constant should be 0.7.

A1, A2, A3: Measure in both QSS and Transient mode. Specified MCD = $1E15\text{ cm}^{-3}$

C1, C2, C3: Measure in QSS mode. Specified MCD = $2E14\text{ cm}^{-3}$

Save and email the Excel measurement files for each sample to james@sintoninstruments.com. The measurement values will be confirmed by email as within specification and then you will send the wafers to the next participant in the Round Robin using the included shipping documents and instructions.

If the measurement is not within specification you will be instructed to recalibrate the instrument using the included calibration set.

After verifying data was present in the required ranges as well as instrument functionality in the pilot round, the participants were sent the following instructions:

This is the second part of the SEMI Round Robin Study. This round consists of measuring 3 wafers over the course of 3 days. Two of the wafers will be measured in both transient mode and QSS mode, while the third wafer will be measured only in QSS mode.

Round Robin Instructions

The shipment will contain the following:

1. 3 wafers to be tested. (Labeled Ax, Bx, Cx)

The input parameters (type, resistivity, thickness) are given on the wafer cases. As the wafers do not have an AR coating, the optical constant should be 0.7. Please measure the wafers one time per day for three days.

Ax, Bx: Measure in both QSS and Transient mode. Specified MCD = $1E15\text{ cm}^{-3}$

Cx: Measure in QSS mode. The polished side of the wafer should be facing up. Specified MCD = $2e14\text{ cm}^{-3}$

Save and email the Excel measurement files for each sample to james@sintoninstruments.com.

The participating laboratories were given the sample doping and thickness, as these are inputs to the measurement analysis software.

For the bulk (1.5cm slug) study, there were not enough samples available to conduct a pilot run, so only a single round was conducted. The following instructions were sent out to the participants:

The study will consist of one round. A set of calibration wafers is included to be used only if recalibration is required.

The shipment will contain the following:

1. 2 slug samples to be tested. (Labeled A1, A2, A3 or C1, C2, C3)
2. A set of 4 conductance sensor calibration wafers – these should only be used if the measured values of the slug samples are out of specification.
3. A USB flash drive with the latest BCT software update and installation instructions. This software update requires Microsoft Office 2007 or 2010.

After installing the software update, and entering the correct calibration values for your BCT, measure each of the wafers. The input parameters (type, resistivity) are given on the sample cases.

A1, A2, A3: Measure in Transient mode. Specified MCD = $1E15\text{ cm}^{-3}$

C1, C2, C3: Measure in Transient mode. Specified MCD = $1e15\text{ cm}^{-3}$

Save and email the Excel measurement files for each sample to james@sintoninstruments.com. The measurement values will be confirmed by email as within specification and then you will send the wafers to the next participant in the Round Robin using the included shipping documents and instructions.

The instructions state that “measurement values will be confirmed” after they are sent to the coordinator. This “confirmation” consisted of verifying that for Round 1 the instrument sensor calibration was within normal specification (by checking sheet resistance) and for Round 2 that the required data range was available in the measurement.

8 Description of the Test Equipment

The Lifetime measurement instruments used for this study are primarily the Sinton Instruments WCT-120, BLS-I, and BCT-400. Two participant labs used previous models of the equipment: the BCT-210 and BCT-350. Product specifications are available in the Appendix.

9 Data Report Method

Each laboratory sent Excel measurement result files by email to the ILS coordinator. Data was then compiled by copying and pasting by the ILS coordinator.

10 Statistical Data Summary/Discussion

The statistical evaluation of the data was completed according to ASTM E691-09, “Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method.”

According to the ASTM document, the statistical analysis has 3 purposes, “to determine whether the collected data are adequately consistent to form the basis for a test method precision statement, to investigate and act on any data considered to be inconsistent, and to obtain the precision statistics on which the precision statement can be based.”

First, the dimensionless h- and k-values are calculated from the measurement data. The h-value is a metric for the consistency of within-laboratory results. The k-value is a metric for between-laboratory consistency. The h- and k-values are compared to critical values which are found in the ASTM E691 document, and depend on the number of labs and number of measurements taken by each lab for each sample. These critical values are used to determine if a lab or sample is an outlier and should be corrected or removed from the study.

All data and analysis is presented in Appendix 2, tables 1-14. The h- and k- statistics were calculated for each of the samples for each of the measurement modes (Quasi-Steady-State, Transient) and measurement outputs (Lifetime, Jo). All data were accepted as being within (or very close to within) the critical h- and k-values except for the exceptions described below.

In the wafer study, it was found that Lab 14 had very poor within lab repeatability (k value = 12.8 for sample A, QSS). This instability is likely due to a hardware failure and therefore data from this lab was excluded.

In the bulk portion of the study, two outliers occurred – Labs 17 and 19. It was found that the maximum illumination intensity in these instruments was below the specification. This hardware problem caused the measured values to significantly under-report the lifetime. One of the Labs (17) was designated as an outlier by the h-k test, but the other lab (19) was not. Precision data is presented after removing these two from the analysis.

For a study-wide view of all of the h- and k- statistics, Figures 1 through 6 show the entire set of h- and k statistics grouped by laboratory, as well as the critical limits.

The pilot round of test data can be used as a recalibration of the wafer instruments’ illumination sensors, per SEMI PV13 9.4.1.1. This recalibration of the reference cell was performed in software analysis by the ILS coordinator without the assistance of the study participants – the raw data was re-analyzed using a new illumination sensor calibration. The illumination sensor data is not required for transient-mode measurements. Therefore this only changes the results for the QSS-mode data on wafers. This data is presented as a separate precision statement in Appendix 3.

10 wafer sample sets were prepared and sent in parallel. As measured at one site, the samples were identical with a relative standard deviation of approximately 2-3% between samples. No correction for differences between sample sets was made in this study, since these differences are comparable to the within-lab repeatability. Therefore a part of the variation between laboratories is due to non-identical samples.

APPENDIX 1: Instrument Parameters

Sinton Instruments WCT-120

Lifetime measurement range	100 ns to greater than 10 ms
Measurement modes	QSSPC, transient, generalized
Resistivity measurement range	3-600 (undoped) ohms/square
Light Bias Range	0-50 suns
Calibrated injection range	1e13 - 1e16 cm-3
Illumination Spectrum	Xenon with IR-pass filter
Sensor area	40-mm diameter
Sample Size	40-210mm
Wafer thickness range	0.001 -2 cm
Environment	20-25C
Power	100-240v AC 50/60 Hz

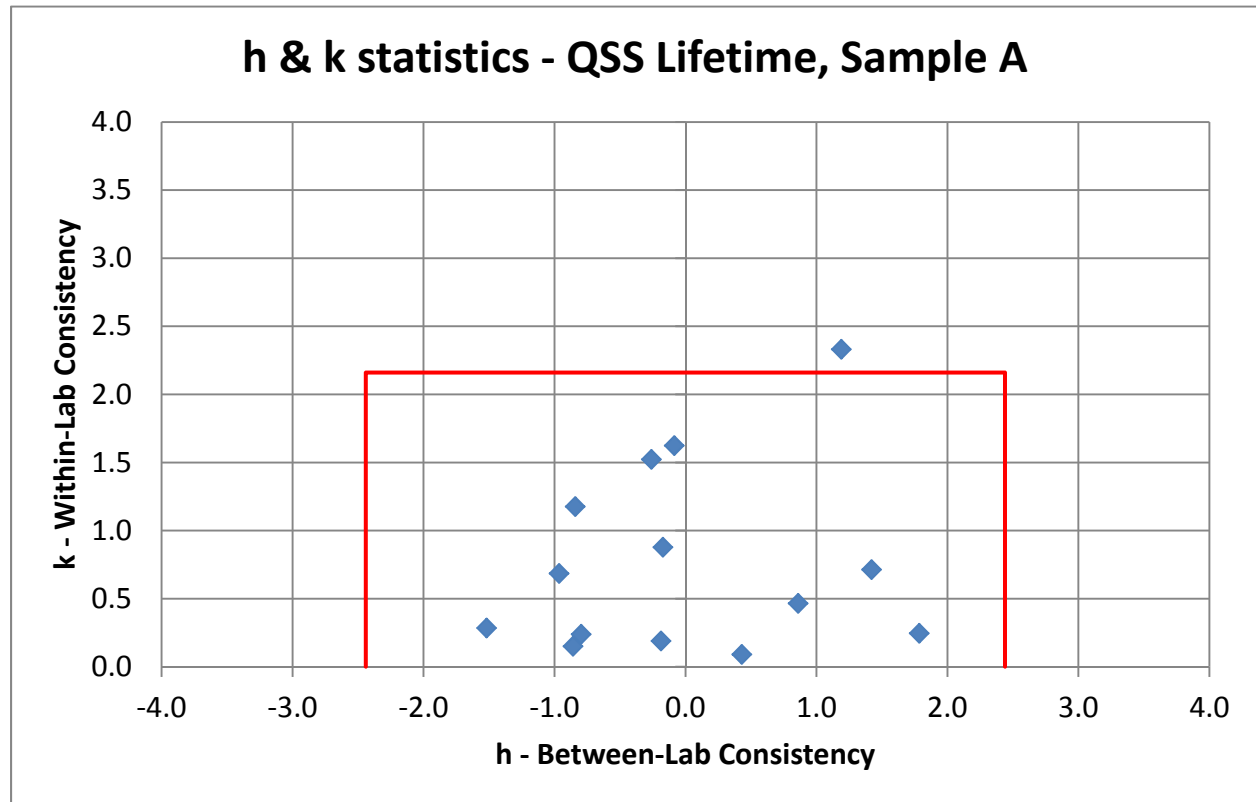
Sinton Instruments BCT-400/BLS-I

Lifetime measurement range	100 ns to greater than 10 ms
Measurement modes	QSSPC, transient, generalized
Resistivity measurement range	.05-300 ohm-cm
Light Bias Range	0-50 suns
Calibrated injection range	1e13 - 1e16 cm-3
Illumination Spectrum	Xenon with IR-pass filter
Sensor area	45mm x 15mm
Sample Size	flat to 15cm curved bricks/ingots
Environment	20-25C
Power	100-240v AC 50/60 Hz

APPENDIX 2: ILS Data

Table 1 : Sample A, QSS mode measurement, Lifetime (μs)

Lab	Test Results		A_QSS	Mean	Std Dev	d	h	k
	1	2	3					
1	138.55	139.3	139.24	139.030	0.3403	-2.8071	-0.1865	0.1889
2	119.13	119.53	118.3	118.987	0.5123	-22.8505	-1.5183	0.2843
3	137.91	138.35	141.46	139.240	1.5800	-2.5971	-0.1726	0.8769
3.1	134.08	140.31	139.38	137.923	2.7440	-3.9138	-0.2601	1.5230
4	169.3	168.25	168.54	168.697	0.4427	26.8595	1.7847	0.2457
5	126.25	130.07	131.2	129.173	2.1180	-12.6638	-0.8415	1.1755
6	156.48	157.07	165.67	159.740	4.2001	17.9029	1.1896	2.3311
7	128.75	129.29	128.69	128.910	0.2698	-12.9271	-0.8590	0.1498
8	164.88	161.75	163.03	163.220	1.2849	21.3829	1.4208	0.7131
9	143.02	136.44	142.19	140.550	2.9259	-1.2871	-0.0855	1.6239
10	154.84	153.72	155.77	154.777	0.8381	12.9395	0.8598	0.4652
11	130.4	129.35	129.82	129.857	0.4294	-11.9805	-0.7961	0.2384
12	129.05	126.5	126.37	127.307	1.2339	-14.5305	-0.9655	0.6848
13	148.31	148.51	148.11	148.310	0.1633	6.4728	0.4301	0.0907
14	105.78	157.22	152.02	138.340	23.1211	-3.4971	-0.2324	12.8327



Note: Lab 14 h,k data not displayed because k=12.83 is too large to be displayed.