



SEMI AUX034-0519
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MINORITY CARRIER DIFFUSION LENGTH MEASUREMENTS BY
SURFACE PHOTOVOLTAGE METHODS

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ROUND-ROBIN TESTING OF SAMPLE PREPARATION METHODS FOR MINORITY CARRIER DIFFUSION LENGTH MEASUREMENTS BY SURFACE PHOTOVOLTAGE METHODS

The auxiliary information content is result of "Round-Robin Testing of Sample Preparation Methods for Minority Carrier Diffusion Length Measurements by Surface Photovoltage Methods" which was divided into JEITA document EM3509 as related information section.

1 Objective

1-1 Round-robin testing was employed to ascertain the appropriate preparation conditions and the variance among participating laboratories.

2 Detail of experiment

2-1 Sample Specifications - plain-oriented (100) Czochralski (CZ) silicon wafers with diameters of 200 mm were used in the round-robin tests, as shown in Table 1. Laboratory B applied SC-1 cleaning to all samples to initialize the surfaces before shipping the samples to the other laboratories participating in the round-robin tests.

Table 1 : Samples Used in the Round-Robin Tests

	Conductivity type	Resistivity ($\Omega \cdot \text{cm}$)	Annealing
p-PW-L	P	1.8	No
p-PW-M	P	10	No
p-PW-H	P	20	No
p-H-M	P	10	Hydrogen
p-Ar-M	P	10	Argon
n-PW-L	N	1.5	No
n-PW-M	N	7	No
n-PW-H	N	9	No

2-2 Test Procedure

2-2.1 p-Type Samples - different preparations were performed on the samples in the sequence (a) to (d) below. After each surface treatment, the minority carrier diffusion length was measured by a surface photovoltage (SPV) method. The goals set out were to confirm the superiority of the conventional preparation practice and the method defined in this standard over SC-1 cleaning by comparing the results of (a) with those of (b) and (c); to compare the minority carrier diffusion lengths obtained with the conventional method and with the method defined in this standard using the results from (b) and (c); and to confirm the extent of internal sample change caused by the annealing in method (c) by comparing the results from (b) and (d).

(a) As-received - The minority carrier diffusion lengths were measured in the as-received samples, which had undergone SC-1 cleaning at Laboratory B.

(b) Conventional method (first repetition) - The samples were immersed for 2 minutes in a 5% hydrofluoric acid solution. Following this, the samples were rinsed for 10 minutes in ultrapure water and then dried in a

spin dryer. After being exposed to a cleanroom atmosphere for 24 hours, the minority carrier diffusion lengths of the samples were measured.

(c) HF + 2-step annealing - The samples were immersed for 10 minutes in a 5% hydrofluoric acid solution. Following this, the samples were rinsed for 10 minutes in ultrapure water and then dried in a spin dryer. Next, the samples were subjected to a 2-step annealing process (210°C for 5 minutes and 80°C for 30 minutes) with a hot plate in a cleanroom atmosphere. Once the first-step heat treatment was completed, either the samples were rapidly cooled by placing them on an aluminum plate at room temperature or the samples were transferred within seconds to the second-step heat treatment by preparing separate hot plates side by side for the first-step heat treatment and the second-step heat treatment. Once the second-step heat treatment was completed, the samples were rapidly cooled by placing them on an aluminum plate at room temperature. The minority carrier diffusion lengths of the samples were measured immediately after this processing was completed.

(d) Conventional method (second repetition) - The samples were immersed for 10 minutes in a 5% hydrofluoric acid solution. Following this, the samples were rinsed for 10 minutes in ultrapure water and then dried in a spin dryer. After being exposed to a cleanroom atmosphere for 24 hours, the minority carrier diffusion lengths of the samples were measured.

2-2.2 n-Type Samples - The samples underwent four surface treatments given in the sequence (a) to (d) below. The minority carrier diffusion lengths of the samples were measured after each surface treatment. The goals set out were to confirm the superiority of boiling with hydrogen peroxide over SC-1 cleaning by comparing the results of (a) with those of (b) through (d); and to ascertain the most appropriate standing time by comparing the results from (b), (c), and (d).

(a) As-received — The minority carrier diffusion lengths were measured in the as-received samples, which had undergone SC-1 cleaning at Laboratory B.

(b) H₂O₂ — Samples were boiled for 10 minutes in a 30% hydrogen peroxide solution at a temperature of between 70°C and 80°C. Following this, the samples were rinsed for 10 minutes in ultrapure water and then dried in a spin dryer. The minority carrier diffusion lengths of the samples were measured by SPV immediately after they were dried.

(c) H₂O₂ + 48-hour standing period — After completing (b) above, the samples were stored in a silicon-wafer shipping box and left in a cleanroom for 48 hours. After this time, the minority carrier diffusion lengths of the samples were measured.

(d) H₂O₂ + 100-hour standing period — After completing (c) above, the samples were stored in a silicon-wafer shipping container and left in a cleanroom for 100 hours. After this time, the minority carrier diffusion lengths of the samples were measured.

2-3 Measurement Conditions - Minority carrier diffusion length measurements were made with the Linear Photovoltage, Constant Photon Flux (LPVCPF) method, one of the SPV methods defined in SEMI MF391-02. The detailed measurement conditions are described by (a) to (d) below.

(a) Illuminating light wavelengths — seven wavelengths from 0.8 µm to 1.0 µm

(b) Lock-in amplifier time constant — 100 m seconds

(c) Correction for wafer-thickness effects on minority carrier diffusion length measurements — None

(d) Measurement points — Measurements were taken at 5 points on each reference sample (see Figure 1)

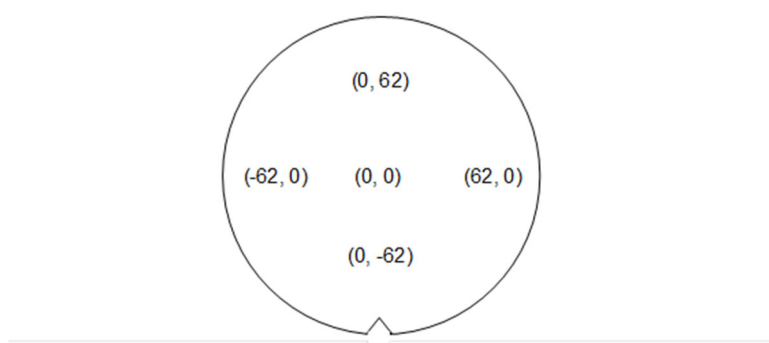


Figure1: Minority Carrier Diffusion Length Measurement Points Used in the Round-Robin Tests

2-4 Comments on the Timing of Preparations and Measurements - Laboratory B initialized all samples with SC-1 cleaning on October 20, 2004. One sample of each level (p-type: 5 levels x one sample = 5 samples, n-type: 3 levels x one sample = 3 samples) was distributed to each laboratory participating in the round-robin tests. Although the tests were conducted in parallel at each laboratory, each laboratory's test timing was slightly different, ranging from October 29 to December 25, 2004. As a result, variations were seen in the n-type sample "as-received" measurements among the laboratories. These variations are believed to be caused by the temporal changes that occur after SC-1 cleaning. This aspect is described in greater detail later.

3 Participating Laboratories - The laboratories listed (in alphabetic order) in (a) and (b) below took part in the round-robin tests.

(a) p-type sample tests - Komatsu Electronic Metals Co., Ltd., MEMC Japan Ltd., Shin-Etsu Handotai Co., Ltd., Sumitomo Mitsubishi Silicon Corporation, and Toshiba Ceramics Co., Ltd.

(b) n-type sample tests - Komatsu Electronic Metals Co., Ltd., MEMC Japan Ltd., Shin-Etsu Handotai Co., Ltd., and Toshiba Ceramics Co., Ltd.

4 Round-Robin Results

4-1 p-Type Sample Tests

4-1.1 Figure 2 indicates the SPV signals, taken from part of the measurement data, corresponding to the shortest illuminating light wavelength (0.8 μm) obtained using the LPVCPF method. Generally speaking, the SPV signals are larger in the samples after the conventional method and the HF + 2-step annealing method than in the as-received samples after SC-1 cleaning. At Laboratory E, however, the SPV signals from the samples after conventional processing were exceptionally small and, consequently, minority carrier diffusion lengths were impossible to measure at many measurement points.

4-1.2 Figure 3 shows the minority carrier diffusion length measurements found with SPV for each representative sample. Each point in the plot represents the average value of the 5 measurement points on each sample. Minority carrier diffusion lengths cannot be measured when the linear-regression calculation of the $\Phi_{\text{eff}}/\Delta V$ to α^{-1} relationship produces a poor correlation factor ($R^2 < 0.98$). The symbol (U.D.) is used in the diagram to indicate samples where measurements were not possible at one or more of the 5 measurement points. As mentioned above, (U.D.) occurred frequently in the measurements after conventional processing at Laboratory E and occurred in one instance at Laboratory B. This signifies the 24 hours standing time at room temperature after conventional preparation is often insufficient.

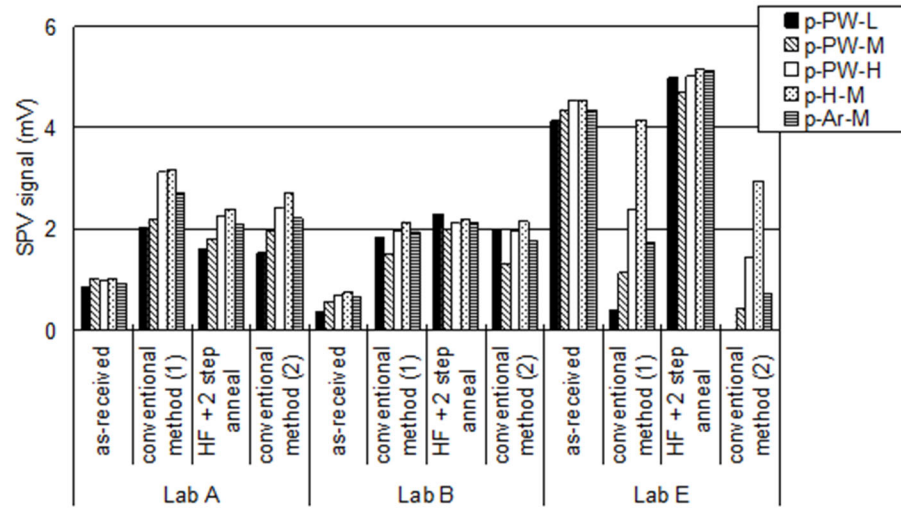


Figure 2 : SPV Signals (at wafer center) in p-Type Samples after Each Surface Treatment — Illuminating Light Wavelength: 0.8 μ m

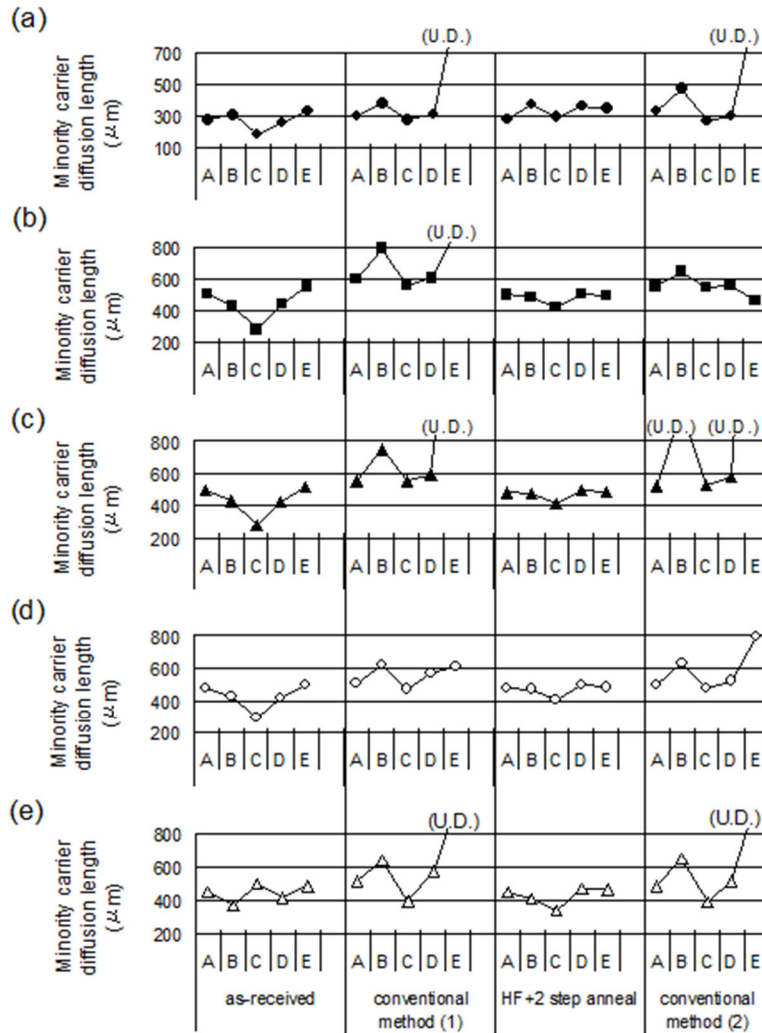


Figure 3: Minority Carrier Diffusion Length Measurements after Each Surface Treatment — Average of the 5 Measurement Points. (a) p-PW-L (b) p-PW-M (c) p-PW-H (d) p-H-M (e) p-Ar-M

4-1.3 Figure 4 plots the variance among the laboratories in 2 sets of minority carrier diffusion length measurements - in the as-received state and after applying the HF + 2-step annealing preparation method. The variance in measurements after the conventional method is not given here because of the frequent U.D. measurements. Although the SPV signals were small in the as-received samples, the variance among laboratories was large. The CV value among the laboratories for the HF + 2-step annealing measurements was within 13%. This value also includes variances caused by the use of different measuring instruments and variations between the wafers.

4-1.4 To verify to what extent changes occur within samples due to the annealing treatment in the HF + 2-step annealing preparation method, the minority carrier diffusion length after the conventional method (first repetition) was compared with the minority carrier diffusion length after the conventional method (second repetition). Figure 5 indicates the results of this comparison. Data values from Laboratory B and Laboratory E, where U.D. measurements occurred frequently, are not included in this diagram. The 2 sets of results show good correspondence, but the minority carrier diffusion lengths after the conventional method (second repetition) were slightly shorter, with an average change of about 4%.

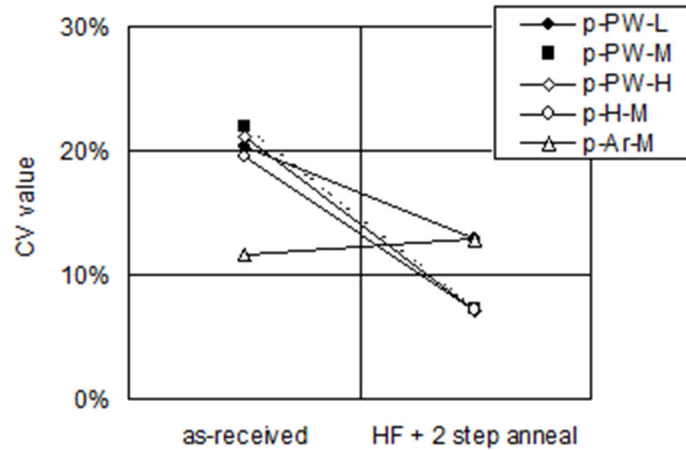


Figure 4: Inter-laboratory Variance in Minority Carrier Diffusion Lengths in the As-Received and after HF + 2-Step Annealing

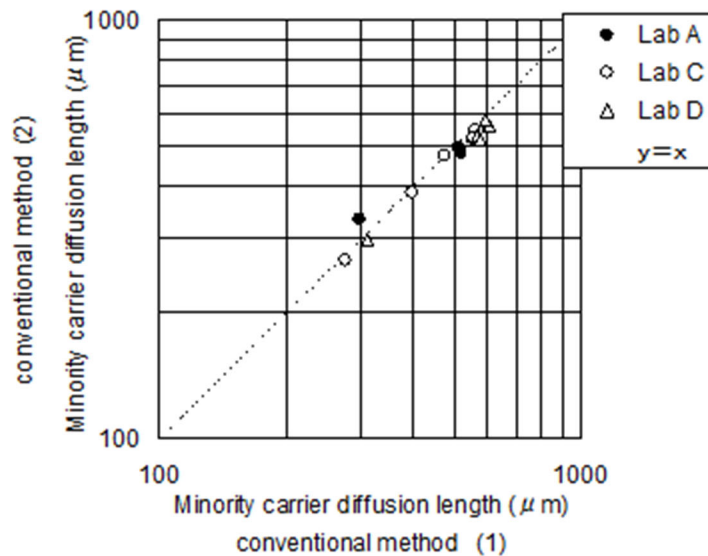


Figure 5: Comparison of Minority Carrier Diffusion Lengths after Conventional Preparation (first repetition) and after Conventional Preparation (second repetition) — Each Plotted Value is the Average of the 5 Measurement Points

Next, Figure 6 compares minority carrier diffusion lengths between the conventional method (first repetition) and the HF + 2-step annealing method. Each ratio was calculated with the measurement after the conventional method (first repetition) as the denominator and the measurement after HF + 2-step annealing as the numerator. The ratios for Laboratory B and Laboratory E used a different denominator: the sample's diffusion length measurement one month after performing the conventional method (second repetition). Differences between the conventional method and the HF + 2-step annealing method were generally contained in a range of about 20%. Except for the p-PW-L sample, it is believed the cause of the shortening minority carrier diffusion lengths after HF + 2-step annealing is due to the continuing decrease in minority carrier diffusion length measurements after the conventional method (first repetition) even beyond a standing period of 24 hours after HF treatment, as shown in Figure 2.

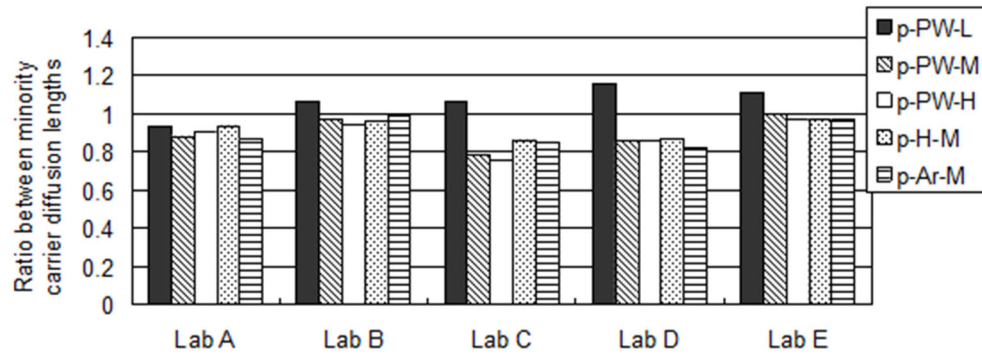


Figure 6: Comparison of Minority Carrier Diffusion Lengths Between Conventional Preparation (first repetition) and HF + 2-step Annealing (For laboratories B and E only, the sample measurements one month after the conventional preparation (second repetition) are compared with measurements after HF + 2-step annealing)

4-2 n-Type Sample Tests

4-2.1 Figure 7 indicates the SPV signals, taken from part of the measurement data, corresponding to the shortest illuminating light wavelength (0.8 μm) obtained using the LPVCPF method. After hydrogen peroxide processing, the longer the standing time, the larger the SPV signals. There was no pattern at all in the measurements of the as-received samples, with some laboratories recording the strongest signals among the tested references and others recording the weakest signals. This disparity can be accounted for by the different times the laboratories took between the pre-distribution SC-1 cleaning and the sample measurements. For example, Laboratory E took measurements 12 days after SC-1 cleaning, but laboratories B and D took measurements after a 47-day interval. This phenomenon is thought to be the result of a temporal change similar to that seen after hydrogen peroxide processing.

4-2.2 Figure 8 shows the minority carrier diffusion length measurements found with SPV in each reference sample level. Each point in the plot represents the average value of the 5 measurement points on each sample. Samples with one or more measurement point having a poor correlation factor ($R^2 < 0.98$) are marked in the diagram with (U.D.). U.D. measurement points were found in the as-received samples. As explained above, the shorter the interval between SC-1 cleaning and measurements, the smaller the SPV signal. The U.D. occurrences finally disappeared when the samples were given a standing time of 100 hours after hydrogen peroxide processing.

4-2.3 Figure 9 illustrates the variance among the laboratories' measurements 100 hours after hydrogen peroxide processing. The CV value among the laboratories was within 13%. This value includes variances caused by the use of different measuring instruments and variations between the wafers.

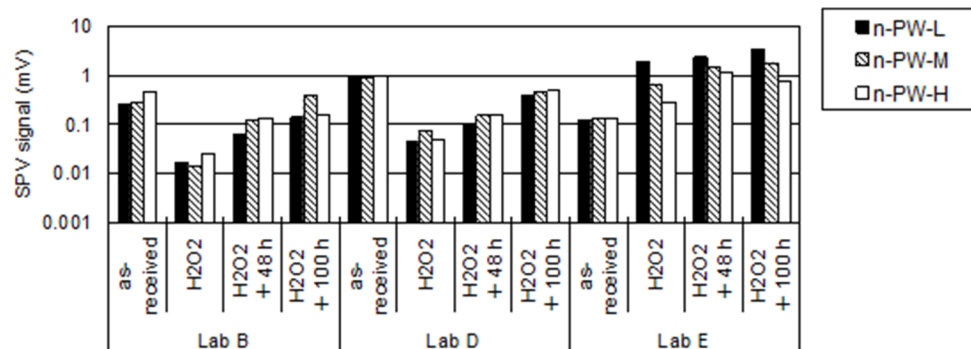


Figure 7: SPV Signals (at wafer center) in n-Type Samples after Each Surface Treatment — Illuminating Light Wavelength: 0.8 μm

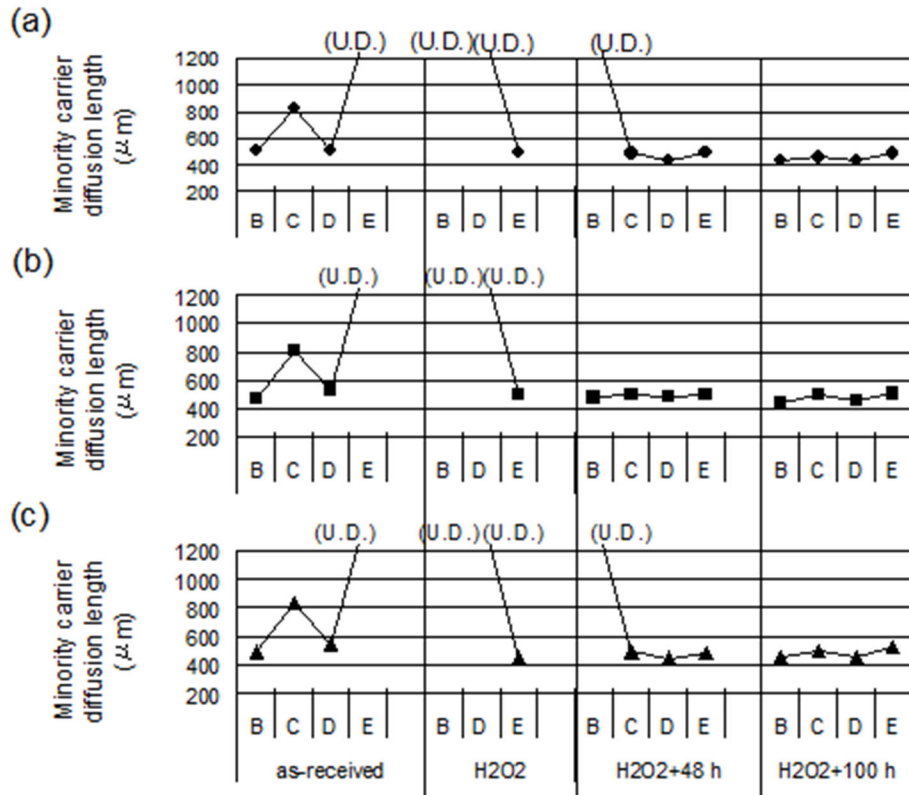


Figure 8: Minority Carrier Diffusion Length Measurements in n-Type Samples after Each Surface Treatment-Average of the 5 Measurement Points. (a) n-PW-L (b) n-PW-M (c) n-PW-H

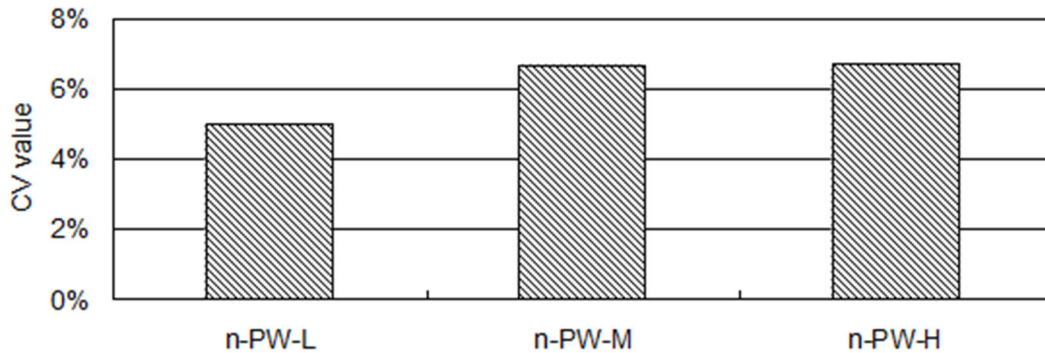


Figure 9: Inter-laboratory Variance in Minority Carrier Diffusion Lengths in the As-Received Samples and after H_2O_2 + 100-Hour Standing Time



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