Background Statement for SEMI Draft Document 5715A
Revision to SEMI F77-0703 (Reapproved 0310), TEST METHOD FOR ELECTROCHEMICAL CRITICAL PITTING TEMPERATURE TESTING OF ALLOY SURFACES USED IN CORROSIVE GAS SYSTEMS

with title change to:

TEST METHOD FOR ELECTROCHEMICAL CRITICAL PITTING TEMPERATURE TESTING OF STAINLESS STEEL SURFACES USED IN CORROSIVE GAS SYSTEMS

Notice: This background statement is not part of the balloted item. It is provided solely to assist the recipient in reaching an informed decision based on the rationale of the activity that preceded the creation of this Document.

Notice: Recipients of this Document are invited to submit, with their comments, notification of any relevant patented technology or copyrighted items of which they are aware and to provide supporting documentation. In this context, “patented technology” is defined as technology for which a patent has issued or has been applied for. In the latter case, only publicly available information on the contents of the patent application is to be provided.

Background
This document is due for five year review. The document was reviewed and revisions were made throughout the document in response to comments received from the previous ballot.

NOTICE: This Document was completely rewritten. Per the Procedure Guide (December 2014) ¶3.5.1.1 a complete rewrite is appropriate when the use of underlines for additions and strikethroughs for deletions would be excessive.

Ballot Adjudication Information*

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<tr>
<th>Task Force Review</th>
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*This meeting’s details are subject to change, and additional review sessions may be scheduled if necessary. Contact the task force leaders or Standards staff for confirmation.

Telephone and web information will be distributed to interested parties as the meeting date approaches. If you will not be able to attend these meetings in person but would like to participate by telephone/web, please contact Standards staff.
1 Purpose

1.1 The purpose of this Test Method is to determine the relative resistance to pitting corrosion of the wetted surfaces of components intended for use in corrosive gas distribution systems for semiconductor manufacturing. This Test Method is an adaptation of ASTM G150 and is intended to differentiate between alloy compositions or processes that may affect the corrosion performance of the wetted surfaces.

1.2 Detailed information on the method is found in ASTM G150, and it is recommended that the user have a copy of ASTM G150 for application of this Test Method.

2 Scope

2.1 This Test Method describes a procedure, based on the electrochemical critical pitting temperature (CPT), which is used to rank the pitting corrosion resistance of wetted surfaces of tubing or test coupons of representative finished surfaces intended for use in corrosive gas systems. Pitting corrosion is believed to be a major corrosion failure mode in semiconductor gas delivery systems, particularly in components and tubing welded and exposed to corrosive gases and moisture.

2.2 This Test Method is an adaptation of ASTM G150. The adaptation describes a method for performing the test method on coupons or wetted surface sections cut from gas supply system components such as tubing. It is an aqueous immersion method.

2.3 The test method is reproducible and provides a metric (critical pitting temperature) in addition to a qualitative (visual) evaluation of corrosion resistance.

NOTICE: This standard does not purport to address safety issues, if any, associated with its use. It is the responsibility of the users of this standard to establish appropriate safety health practices and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 Only analysts familiar with the instrumentation and technique should use this Test Method.

3.2 The test conditions of this Test Method do not simulate actual service in a corrosive gas supply system. Thus the test results may not correlate to relative corrosion resistance in a specific corrosive gas or corrosive gas supply system.

3.3 The Critical Pitting Temperature (CPT) is valid only in a range of 10°C to 95°C. A CPT result greater than 95°C is not considered to be valid since it is approaching the boiling point of the solution. A critical pitting temperature (CPT) below 10°C shall only be reported as <10°C and may be an indication of crevice corrosion, which renders the test invalid.
3.4 Since alloy composition and surface parameters can affect the results of the test, all variables other than the one being tested must be fixed during the test in order to obtain reproducible and comparable results.

4 Referenced Standards and Documents

4.1 SEMI Standards
SEMI F19 — Specification for the Surface Condition of the Wetted Surfaces of Stainless Steel Components

4.2 ASTM Standards
ASTM G3 — Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

NOTE 1: Unless otherwise stated, the sign conventions used in this test method are in agreement with ASTM G3, and the terminology relating to corrosion and corrosion testing is as defined in ASTM G15.

5.1 Abbreviations and Acronyms
5.1.1 CPT — Critical Pitting Temperature
5.1.2 M — Molar Concentration
5.1.3 mV — Millivolts
5.1.4 µA/cm² — Microamperes per square centimeter
5.1.5 OCP — Open Circuit Potential
5.1.6 SCE — Saturated Calomel Electrode

5.2 Definitions

5.2.1 Crevice Corrosion — Corrosion at a cavity between adjoining pieces or at the edge of a seal or masking paint. The chemical mechanism of crevice corrosion is similar to that of pitting, the cavity being a “pre-formed” pit. As corrosion is initiated at the cavity, the critical temperature for crevice corrosion is always lower than the critical pitting temperature.

5.2.2 Critical Pitting Temperature (CPT) — the lowest temperature at which stable propagating pitting occurs on the test surface under the specified test conditions, as indicated by a rapid increase beyond a specified limit of the measured anodic current density of the test surface.

5.2.3 Flushed Port Cell — A type of CPT test cell that utilizes a porous seal against the test specimen through which deionized water is flushed to avoid crevice corrosion at the edge of the seal. This is illustrated and described in ASTM G150. These cells are commercially available.

5.2.4 Luggin Probe — A capillary ended tube that holds the reference electrode. The capillary end is filled with the test solution and situated close to the test specimen so that the reference electrode senses the solution potential at this open tip. Also known as a Luggin-Haber capillary.

5.2.5 Open Circuit Potential — The potential between the test specimen and the counter electrodes with no electrical connection.

5.2.6 pitting — corrosion of a metal surface, confined to a point or small area, that takes the form of cavities.

5.2.7 SCE Reference Electrode — Saturated Calomel Electrode (SCE), a standard reference electrode based on the reaction between elemental mercury and mercury chloride.

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5.2.8 *wetted surface* — surfaces of a component in contact with the contained fluids.

6 Summary of Method

6.1 The test method measures the critical pitting temperature (CPT) by using a potentiostatic technique and a temperature scan. The test is performed in an electrochemical cell in a 1 M NaCl aqueous electrolyte solution. The test specimen is polarized to a constant anodic potential, typically 700mV for stainless steel, and the temperature scanned at a rate of 1°C/minute, beginning at 0°C. The current is measured by means of a potentiostat/galvanostat instrument. The CPT is the temperature at which the current density increases above 100 µA/cm² for 60 seconds. Pitting is confirmed by visual or microscopic observation of the specimen after testing, as shown in Figure 1.

![Figure 1](image)

**Examples of Pitting on Type 316 Stainless Steel after a Pitting Potential Test in 1 M NaCl. (11× Magnification)**

7 Possible Interferences

7.1 Specimens must be examined after testing to confirm pitting. A possible interference is failure by crevice corrosion in which case the test is considered invalid. Crevice corrosion can occur at the seal of the test specimen to the test apparatus or at the edge of the masking media. The crevice corrosion sites exist at the boundaries of the area exhibiting pitting and can be identified by a straight edge resulting from the masking. Figure 2 gives an example of the typical morphology of crevice corrosion sites from a pitting potential test performed on type 316 stainless steel using masked edges. Crevice corrosion also has a critical temperature which is always less than the CPT. The critical crevice corrosion temperature for AISI 316L is less than 10°C. Test results for AISI 316L less than 10°C achieved by the use of this Test Method are likely due to crevice corrosion and are considered invalid.
Figure 2
Examples of Crevice Corrosion (Dashed Circles) on Type 316 Stainless Steel after a Pitting Potential Test in 1 M NaCl. Magnification 11X

8 Apparatus

8.1 The apparatus necessary to determine the CPT consists of a test cell, a potentiostat and potential measuring instrument, a current measuring instrument and recorder, a temperature controller and recorder, and a specimen holder. Specifications for this equipment are described in ASTM G150.

8.2 The choice of test cell is dependent on the type of test specimen.

8.2.1 The test cell for flat specimens is a flushed-port cell described in Appendix X2 of ASTM G150.

8.2.2 The test cell can be modified for testing tubular specimens. The modified test cell consists of a 2 Liter glass beaker cut to 11.5 cm (4.5 inches) high and capped with a polyethylene cover. There are three electrodes, consisting of the test specimen, an SCE reference electrode inserted in a Luggin probe, and two graphite rods as the counter electrode. See Figure 3 for the modified test cell set-up.

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8.3 Instruments shall be routinely calibrated in accordance with manufacturer recommendations to assure proper performance.

9 Test Specimens

9.1 Test specimens are required to be representative of a product or process lot. Sampling shall be per agreement between component supplier and purchaser.

9.2 Sample preparation should preferably be done by the component manufacturer. The sample(s) are to be cleaned and packaged per the manufacturer’s standard final cleaning and packaging procedures.

9.3 If sample preparation is done by a party other than the manufacturer, the sample(s) may be cleaned by degreasing with a suitable detergent, rinsing in deionized water, followed by ethanol or similar solvent, and air drying. After degreasing, the specimen must be handled with clean gloves, soft clean tongs, or equivalent preventive measures, to avoid surface contamination. If the sample(s) are not to be analyzed immediately they should be packaged by wrapping in clean metal foil or sealing in cleanroom quality nylon bags. If sample preparation is done by a party other than the manufacturer this shall be stated in the report narrative and the analytical results are not to be interpreted as indicative of the manufacturer’s quality of cleaning and packaging procedures. A note to this effect shall be included in the reported results.

9.4 After preparation, samples should be analyzed promptly, with allowance for shipping times and queuing time at the analyst.

9.5 Flat specimens shall be sized and shaped to conform to the requirements of the flushed port cell as described in ASTM G150. Alternatively a flat specimen may be tested in the modified test cell described in § 8.2.2, using the masking outlined in § 9.7.

9.6 Tubing specimens shall consist of 5.0 cm (2.0 inches) length of tubing sectioned axially. Other types of components that do not have a suitable flat surface per 9.5 shall be sectioned to expose the surface of interest to the test solution. The cut surfaces shall be smoothed sufficiently to be effectively masked per § 9.7.
9.7 All specimens should be masked to isolate the test to the surface of interest only. This can be accomplished by masking with a non-reactive lacquer, which can be baked to ensure optimum adhesion. Alternately, plater’s tape can also be used, leaving 0.63 cm (0.25 inch) uncovered at the end for electrical contact.

9.8 The finish of the surface to be tested shall be consistent with the requirements of the surface roughness and surface defects of the intended specification grade (GP, HP, or UHP) of SEMI F19. Since surface finish can affect the CPT results, surface finished should be done as consistently as possible within a sample set. Details of the surface finishing process, parameters and characterization should be provided in the test report as outlined in ¶ 15.

9.9 A minimum of 3 specimens shall be tested, and preferably 5 or more to obtain statistical significance in the testing results.

9.10 The minimum test area is 1 cm². This minimum test area is required for both flat specimens and tubing specimens. Certain types of components may not have sufficient test area to meet this requirement. This should be noted in the test report and the calculated test area reported.

10 Reagents And Materials

10.1 Reagent grade chemicals and deionized water shall be used in the preparation of test solutions.

10.2 The 1 M chloride test solution is prepared by dissolving 58.45 grams sodium chloride (NaCl) in deionized water to a total solution volume of 1 Liter. The solution can be made up in bulk and stored in a sealed container for one month at room temperature.

10.3 Due to the different process gases used by the semiconductor industry such as HCl, HBr, Cl₂, BCl₃, HF, WF₆ etc., another test solution to represent the particular anion of the process gas which may impart different pitting characteristics may be used (e.g., 1 M NaBr, or 1 M NaF). The results obtained with other test solutions will not be considered indicative of CPT in chloride media.

11 Applied Potential

11.1 The standard anodic potential commonly used for most stainless steels is 700 mV versus SCE at 25°C.

12 Procedure

12.1 Mount the specimen in the test cell specimen holder per the test cell design or manufacturer's instructions for a flat specimen in the flushed port cell, or held vertically such that the test area specified in Paragraph 9.10 will be fully exposed to the test solution for specimen to be tested in the test cell of Paragraph 8.2.2.

12.2 Place the test specimen, the counter electrodes, the reference electrode and the other components in the empty test cell. The reference electrode should be placed in a Luggin probe. The Luggin probe tip should be placed as close to the sample as possible without interfering with the stir bar. The temperature probe should be touching sample (masked section only).

12.3 Turn on temperature controllers and set at −2°C.

12.4 Fill the test cell with 800 ml of the test solution chilled to ≤ 2°C. Ensure that the specimen, electrodes and other components are properly positioned in the cell and test solution.

12.5 Connect the electrodes to the potentiostat and data recording device and the connections for temperature measurement and control. Let the system cool and stabilize at 0 ± 1°C for a minimum of 10 minutes.

12.6 Record the open circuit potential (OCP) of the test specimen shortly before the test is begun.

12.7 Set the data acquisition for electrode current and solution temperature. The sampling rate shall correspond to a minimum of two measurements every minute to follow solution temperature and the variation of the current on the test specimen.

12.8 Apply the constant anodic potential to the test specimen. The potential shall be applied for 60 ± 5 seconds before the temperature ramping is initiated.

12.9 The temperature is then ramped at 1°C/minutes.

12.10 Continue measuring the temperature until the CPT has been determined or the maximum required temperature is reached. The CPT is determined when the current density reaches 100 μA/cm² and remains above
this level for a minimum of 60 seconds. Terminate the test and data acquisition after either of these limits has been reached.

12.11 When test is completed, remove the specimen and rinse with DI water.

13 Visual Examination of Test Specimen

13.1 Examine the test area of the specimen under an optical microscope at 20X magnification. Confirm the existence of pits and the absence of crevice corrosion, as indicated by the absence of pits touching the masked-off or lacquered area (see § 7.1 and Figure 2). Any crevice corrosion observed on the specimen after testing means that the test results are invalid and must be discarded.

14 Data Analysis

14.1.1 Determine critical pitting temperature. The critical pitting temperature is the temperature at which the current density exceeds 100 μA/cm² for at least 60 seconds. Figure 4 shows an example of a temperature vs. current density scan. In this particular example, the critical pitting temperature was determined to be 18°C.

![Figure 4](image)

**Figure 4**  
Current Density as a Function of Temperature. The Critical Pitting Temperature is the Temperature at Which the Current Density Exceeds 100 μA/cm² for at Least 60 Seconds.

15 Reporting Results

15.1 Information required in the test report.

15.1.1 Test specimen identification

15.1.1.1 Manufacturer

15.1.1.2 Part number (if applicable).

15.1.1.3 Lot number
15.1.1.4 Specification Grade per F19 or surface processing history (e.g., mechanical polish, electropolish, passivation).

15.1.1.5 Welded specimens must be identified and the welding process specified.

15.1.1.6 Tubing diameter for tubing samples.

15.1.2 Test identification number and date of test.

15.1.3 Type of test cell and test solution volume.

15.1.4 Test solution chemistry and concentration, if other than specified in Paragraph 10.2.

15.1.5 Critical pitting temperature (CPT). CPTs below 10°C shall only be reported as below 10°C.

15.1.6 The scatter or deviation in the CPT values based on multiple runs if available

15.2 It is recommended that the data from the CPT test should be presented graphically also. An example is shown in Figure 4.

16 Related Documents

16.1 SEMI Standards

SEMI F20 — Specification for 316L Stainless Steel Bar, Forgings, Extruded Shapes, Plate, and Tubing for Components Used in General Purpose, High Purity and Ultra-High Purity Semiconductor Manufacturing Applications

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