New Methods Used to Evaluate Surface Corrosion Resistance

Gary Henrich, Swagelok Company, Solon, Ohio, USA

Electron Spectroscopy for Chemical Analysis (ESCA) and Auger Emission Spectroscopy are currently specified as analytical test methods of choice when evaluating corrosion resistant surfaces, typically stainless steels, in the semiconductor market. These two analytical techniques have been used routinely to study surfaces and to suggest their inherent corrosion performance. The neutral salt spray test is a commonly used test for quantifying the onset of general corrosion. However, two other competing methods, glow discharge optical emission spectroscopy (GD-OES) and electrochemical critical pitting temperature (CPT) can be used effectively to characterize the corrosion resistance of surfaces. GD-OES is a near-surface technique that is used for elemental depth profiling, oxide thickness measurements, surface contamination, or for bulk alloy analysis. Due to its broader depth profiling range GD-OES also provides more versatility for thicker applications such as electroplated surfaces, vapor deposited coatings, etc. The CPT test method is carried out in liquid medium, providing an exact temperature at which a surface begins to pit. Unlike the salt spray test, which may take several days to complete and is dependent on visual inspection, the CPT test method typically can be performed in 20 minutes. Using GD-OES and CPT in tandem can be used quantitatively to relate elemental differences in the surface layer with a material's corrosion resistance.

For more information, contact:
Gary Henrich
Swagelok Snow Metal Products
6060 Cochran Road
Solon, OH 44139
Ph: (440) 349-5657
Fax: (440) 349-5980
E-mail: gary.henrich@swagelok.com

Introduction

With the many advancements in coatings, surface treatments and modifications for enhanced wear, corrosion resistance or other unique properties, a need to characterize these surfaces in terms of their structure and corrosion performance has become more demanding. Specifically, for manufacturers of high purity (HP) and ultra-high purity (UHP) components serving the semiconductor industry this means compliance of wetted surfaces to SEMI F19-0304 standard. Properly passivated austenitic stainless steel surfaces conforming to the surface chemistry requirements appearing in SEMI F19-0304 (See Appendix A) will have low surface contamination from carbon, sulfur, phosphorous, silicon and nitrogen, and an enriched layer of chromium relative to iron as well as a minimum chromium oxide thickness. Meeting the requirements of this SEMI standard has been shown to have practical significance in HP and UHP applications.

Possessing the analytical capability to rapidly perform both quantitative elemental depth profiling and corrosion testing is valuable to all manufacturers of metal products where surface modifications or coatings are employed that render the surface more functional than their respective substrates. This analytical capability may be particularly appealing to HP and UHP manufacturers where there has been little choice in available analytical methodology. For example, the typical methods used to certify compliance with SEMI F19-0304 are either Auger Emission Spectroscopy (AES) or X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA). In the area of elemental depth profiling, GD-OES has, through technological improvements, evolved into a complementary, if not competing method, to AES. In recent years, improvements in GD-OES systems have driven it from primarily a bulk analytical technique to a powerful depth-profiling tool capable of resolving elemental differences within the first few molecular layers of the surface. As recently as 2000 it was introduced as a standard technique per ISO 14707, *Surface Chemical Analysis by GD-OES*.

For corrosion testing, the electrochemical critical pitting temperature (CPT) test (ASTM G 150) offers some advantages in terms of analysis time and quantification of data over existing pitting tests such as the ferric chloride immersion test (ASTM G 48) or cyclic potentiodynamic polarization (ASTM G 61), or to yet more popular corrosion tests such as the neutral salt spray (ASTM B 117). These two tests, GD-OES depth profiling and electrochemical CPT, will be described followed by one specific example of how these two techniques were used together effectively.

Glow Discharge Optical Emission Spectrometry (GD-OES)

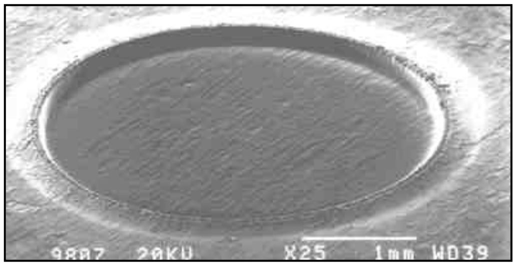
It is assumed that the reader has some previous knowledge of spectroscopy. The details of the glow discharge emission characteristics, instrument optics, alternate discharge sources, power supplies, sputtering parameters and data manipulation will not be explored here. However, a historical perspective followed by a basic understanding of the glow discharge principle and some practical matters regarding the technique will be given as well as a comparison to AES.

Historical Background of GD-OES

Although depth profiling by GD-OES is presented here as a relatively new technique, its roots stretch back to the mid-nineteenth century as the phenomenon of "cathodic sputtering", as it was called, was first observed in 1852 by W.R. Grove.[1] For many decades thereafter and well into the twentieth century work poured into various spectrometer designs as the area of atomic physics broadly captivated the research effort. However, gradually by the mid 1900's more work began in the area of applied spectroscopy and by 1947 the first GD device to be extensively used in spectrochemical analysis was introduced.[2] Within a decade GD was being used as an experimental tool for qualitative analysis of individual metals. A key milestone, the introduction of a direct current source known as the Grimm lamp in 1967, yielded quantitative results for individual elements. A collaborative effort between Grimm and H. Ritzl led to the introduction of the first GD-OES analytical instrument by 1978.[3] About the same time other US researchers including J.E Greene and J.M. Whelan, and Ancey *et al* in France, began reporting qualitative depth profiles. By 1972 C.J. Belle of Westinghouse Electric and J.D. Johnson of Spectrogram Corp. published the first quantitative depth profiles, but after much time and effort. Still, Belle and Johnson concluded their paper by recommending the technique to those 'who are concerned with electroplating, metalliding, vapour deposition or other processes at metal surfaces which protect, strengthen, and extend the usefulness of metals and metal alloys'.[4] Also in 1972 work by P. Boumans of Philips Research Laboratories, Netherlands reported a significant advancement - an equation for sputtering expressed in terms of current and potential.[5] The significance of Boumans' findings was that sputtering rates for individual elements in sample matrices had been established, and by the 1980's direct current source GD-OES became a popular technique in the metals industry. In 1988 a radio frequency source was introduced for non-conductive materials and by 1992 this feature was available on a commercially available instrument.[6] Over the last decade additional technological improvements mostly in the area of sputter control, and data manipulation have allowed the GD-OES technique to perform some analytical applications that were formerly only possible by surface chemical techniques like AES, XPS and secondary ion mass spectrometry (SIMS). Presently, quantitative depth profiling of conductive and nonconductive materials can be accomplished, depending on sample surface finish, with sub-nanometer resolution to depths of over 50 microns in a matter of minutes on a single burn.

GD-OES Operating Principle

As a hyphenated analytical technique, GD-OES relies on a glow discharge source for exciting sample atoms to produce their characteristic light emission and an optical emission spectrometer to resolve and quantify the line intensities within the resulting spectrum. The direct current source is commonly some variety of the original “Grimm lamp”. This device consists of a cathode block that is in intimate electrical contact with the sample, through which a highly negative potential is applied, while an evacuated tubular anode (6 – 12 torr) containing a trickle of argon gas flow is spaced precisely at a distance from the sample resulting in a discharge. This discharge, or glow, is essentially the result of neutral argon atoms becoming positively ionized in the controlled plasma inside the anode space. Charged argon ions progressively accelerate toward the negatively charged sample with enough velocity to sputter away, layer-by-layer, neutral sample atoms. As these neutral sample atoms drift into the plasma containing other high-energy argon atoms, atomic collisions cause the sample atoms to become excited. Upon relaxation to the ground state a characteristic photon of light is emitted from the sample atom, as in any emission technique. The light emission passes through a spectrally inert crystal (MgF_2) window and into the spectrometer where its intensity and wavelength are recorded. The sputtering process in GD-OES is quite controlled and continuous, producing a crater on the surface (Fig. 1[*]). Unlike other surface analytical methods that rely on cycling the sputter and spectroscopic analysis steps during the analysis, with GD-OES the material sputtered away is what produces the emission signal on a real-time basis. In addition, during analysis over a given time period, if the sputtering rate is known for individual analytes then atomic concentrations in the sample can be accurately calculated throughout the depth continuum.



*** Figure 1 – Sputter crater from argon ion beam on sample surface.**

GD-OES Analysis

Quantitative depth analysis by GD-OES is not a difficult operation. Though instrument pre-calibration to different classes of alloys is required, once accomplished, the instrument simply needs to be warmed up and the multi-element calibration curves verified against check standards to compensate for instrument drift. Check standards should be alloys within the approximate elemental range of the sample to be tested. Next the sample is held in position such that the area of interest is exposed to the argon plasma. Sample analysis can take just a few seconds to a few minutes normally. However, depending on the depth of analysis and the material being analyzed longer run times of up to 30 minutes may be required.

---

[*] Reprinted courtesy of LECO Corp.

Practical Considerations Using GD-OES

In bulk analysis mode over 70 elements may be theoretically determined, though most GD spectrometers are built practically to analyze about 60 in depth mode with good sensitivity. Spectral lines used in GD-OES may range from the 119 nm chlorine line deep within the ultraviolet to the oxygen line at 777 nm in the upper visible region. The anode diameter can vary from 1 to 10 mm, offering some flexibility to match the sample size. Concentration ranges for individual elements vary according to their emission intensities, but are generally at the single ppm level.

Most of the limitation when performing a depth profile is inherent in the sample. Ideally, the sample surface should be flat and smooth. Irregular surfaces cause problems, either resulting in a loss of vacuum or compromising the anode to cathode distance, which both cause the discharge to short out. Excessively rough surfaces are also undesirable, resulting in "smeared" elemental depth profiles. However, GD-OES accuracy is not compromised with a moderate degree of surface roughness. The data in Table 1[*] were obtained in bulk analysis mode and show the relationship of elemental composition and observed vacuum versus surface finish of a flat specimen. As the surface roughness increased there was only a negligible loss of vacuum and the elemental compositions remained virtually identical. That data clearly shows that moderate surface roughness is quite tolerable. However, if depth plots of the roughest surfaces had been done, they would have produced rather noisy profiles. The point here is that for the most discreet surface analyses the sample surface should be as smooth as possible. For atypical specimens there are mounting and fixturing tricks that do allow the analysis of curved surfaces, sintered metals, wires and even powders, but generally speaking a flat, dense surface is much easier to analyze. When performing process optimization studies that involve GD-OES it is often advantageous to use flat coupons. On smooth coupons, accurate depth scans to within 5 – 10 angstroms of the surface are possible.

[*]Table 1 – Surface finish versus composition and vacuum reading in GD-OES

Element	[*]BS81N Certified	BS81N slurry polished	BS81N 320 grit carbide	BS81N 180 grit alumina	BS81N 80 grit alumina	BS81N 80 grit + scratches
Cr	19.72	19.5	19.2	19.5	19.4	19.4
Ni	8.42	8.25	8.29	8.25	8.27	8.3
Mo	0.36	0.369	0.373	0.369	0.361	0.354
Mn	1.83	1.89	1.89	1.88	1.9	1.88
Si	0.56	0.549	0.545	0.552	0.555	0.553
Cu	N/A	0.241	0.241	0.242	0.243	0.244
Vacuum (Torr)		11.069	11.107	11.261	11.261	11.145

---

[*] BS-81 N is a certified alloy standard from Brammer Standard Company

[*] BS 81N is a certified alloy standard from Brammer Standard Company

Comparison to AES

Though depth profiling by GD-OES and AES yield similar data there are some important differences that are summarized in Table 2. AES, being an electron beam technique has advantages of being able to focus on small surface features, depending less on surface geometry and offering some chemical bonding information, though limited. In this regard, XPS offers a distinct advantage to either AES or GD-OES. XPS provides both elemental compositional and the chemical state of the surface constituents since its signal is derived from core electrons rather than outer shell electrons, as with AES. The energy of a photoemitted core electron is a function of binding energy and is characteristic of the element from which it was emitted.[7] Perhaps the chief advantage of AES (and XPS) is the ability to analyze the first few molecular layers making it a true surface technique. With GD-OES, the first few milliseconds of analysis are taken up in plasma stabilization. The primary advantages of GD-OES are faster depth profiling rates, greater dynamic depth range, lower initial cost of equipment, and generally less analytical skill required to perform the analysis. Still, oxide thickness data from thirteen 316L SS coupons run by both GD-OES and AES, shown in Table 3 and plotted in Figure 2, compared favorably. GD-OES showed a slight positive bias of 3.3 Angstroms, and the correlation coefficient, r^2, of paired data was approximately 0.89.

Table 2 – Summary of differences in depth profiling by GD-OES and AES

Attribute	GD-OES	AES
Elementals determined	metals, metalloids, rare earths, most nonmetals and H	All elements except H
Signal derivation	photon emission	electron emission
Beam diameter	2 – 10 millimeters	0.1 – 1 micrometers
Spatial resolution	fair	excellent
Detection limit	Most elements 1 –10 ppm	Most elements ~0.1%
Sputter rate	Typically, 2 – 10 nm / sec.	1 nm / sec
Sputter depth per single analysis event	Up to 100 micrometers	2-3 nanometers
Analysis time	Seconds to minutes	Minutes to hours
Sample surface	Ideally flat	Any
Sample size	Ideally > $1cm^2$	Microscopic
Spectral mapping	No	Yes
Additional chemical information	No, only element type	Yes, limited bonding information
Chamber evacuation	No vacuum in chamber, but moderate vacuum on glow source	Entire instrument under high vacuum

Table 3 – Comparison of GD-OES to AES for surface oxide depth on 316L SS

GD-OES	Auger	bias
22.6	18.5	4.1
24.6	20.5	4.1
25.3	21	4.3
26.6	21	5.6
28.2	22.5	5.7
28.4	24.5	3.9
28.6	25	3.6
29.2	25	4.2
29.8	26	3.8
30	29.5	0.5
31.1	31.5	-0.4
33.7	33.5	0.2

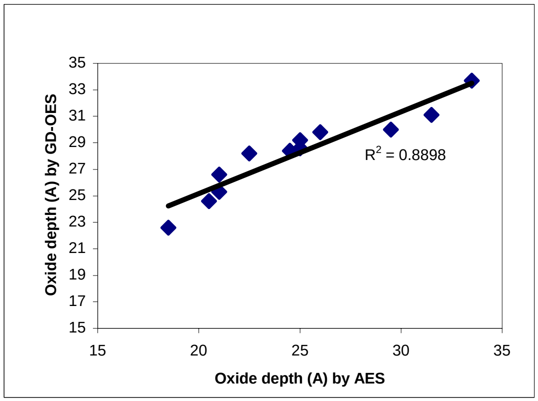


Figure 2 - AES versus GD-OES for oxide

Applications

We have used the quantitative depth-profiling feature of GD-OES on a variety of samples over the course of a few years and have found that it is a convenient, valuable analytical tool. Some of the applications have included:

- Characterization of the chromate layer on zinc over steel electroplate
- Characterization of the passive oxide layer on 316 SS
- Optimization of an electropolishing and passivation process
- Plating bath activation studies
- Contamination issues
- Nitrogen and carbon diffusion profiles

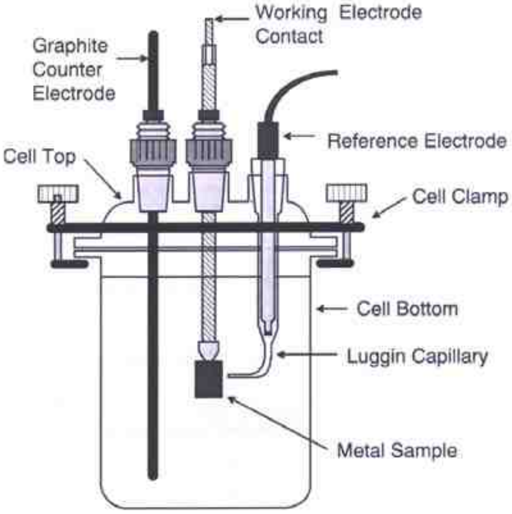
Electrochemical Critical Pitting Corrosion Test

The electrochemical CPT, as described in ASTM G 150 is a relatively new method, first published by ASTM in 1997. This test grew out of a desire to provide rapidly what takes several hours or days by immersion pitting tests. CPT results generally provide the same sort of information as lengthier potentiostatically controlled pitting corrosion tests such as ASTM G 61 (potentiodynamic polarization), where the pitting potential is determined or ASTM G 48 (ferric chloride immersion) where weight loss is measured. Typically austenitic stainless steel samples can be evaluated in less than 20 minutes by electrochemical CPT. Superaustenitics and exotic alloys that are inherently more corrosion resistant may take 60 – 90 minutes to test.

CPT Operating Principle

Since a pitting corrosion event is influenced by type and concentration of electrolyte medium, temperature, and changing electrochemical potential applied to the system, controlling any two of these variables can be used to obtain the third. When studying the corrosion resistance of a metal, in essence the first barrier of protection is the passive layer. Being able to precisely measure a variable that relates to the momentary breakdown of this film and initial pitting of the substrate is an excellent method to assess surface integrity.

ASTM G 150, a corrosion method relevant to stainless steels of up to 6% molybdenum, describes the potential independent CPT using a potentiostatic technique while scanning temperature.[8] Specimens may be tested within a standard electrochemical cell as detailed in Figure 3[*] and pictured in Figure 4. Not shown in Figure 3 is a surrounding heating mantle and internal cooling coils for maintaining temperature. The specimen is suspended in a 1 M NaCl electrolyte solution in such a way as to eliminate the possibility of crevice corrosion. This can be either accomplished through the use of a specialized specimen holder (Figure 5) or by painting all non-critical metal surfaces of the specimen and immersed electrical connections with an insulating lacquer. It is extremely important that the probability of crevice corrosion be eliminated, as this will invalidate the test.



*** Figure 3 - CPT Cell Configuration**

The initial temperature of the bath is set at 0°C (32°F) and the specimen is immersed, then anodically polarized to a potential estimated to be above the pitting potential range and held at this potential throughout the test. A potential of 700 mV versus SCE has been

---

[*] Reprinted courtesy of Gamry Instruments, Inc.

found to be suitable for most stainless steels.[9] Essentially the purpose of the anodic polarization is to hold the specimen in a passive state so that any breakdown of the passive layer is a significant event and solely the result of temperature change, not shifting potential. By use of a heating mantle and temperature scan software, the electrolyte is slowly heated at a rate of 1°C/minute (1.8°F/min.). The current flow is monitored throughout the temperature scan by use of a Luggin capillary type reference electrode positioned very close to the specimen being measured. The CPT is defined as the temperature at which the current increases rapidly, which for practical reasons is defined as the temperature at which the current density exceeds 100 µA/cm^2 (645 µA/in^2) for 60 seconds[10], as shown in Figure 6. Visual confirmation of pitting only on the critical surface and not under lacquer or in seal areas confirms the validity of the test result.

Figure 4 - Standard CPT CellCPT Cell

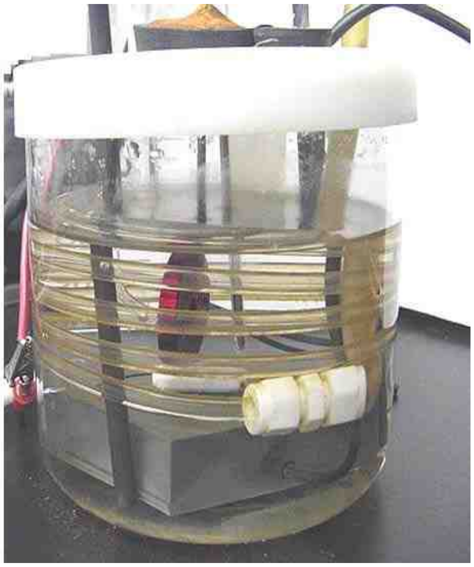


Figure 5 - Flat Specimen (Avesta Type) CPT Cell

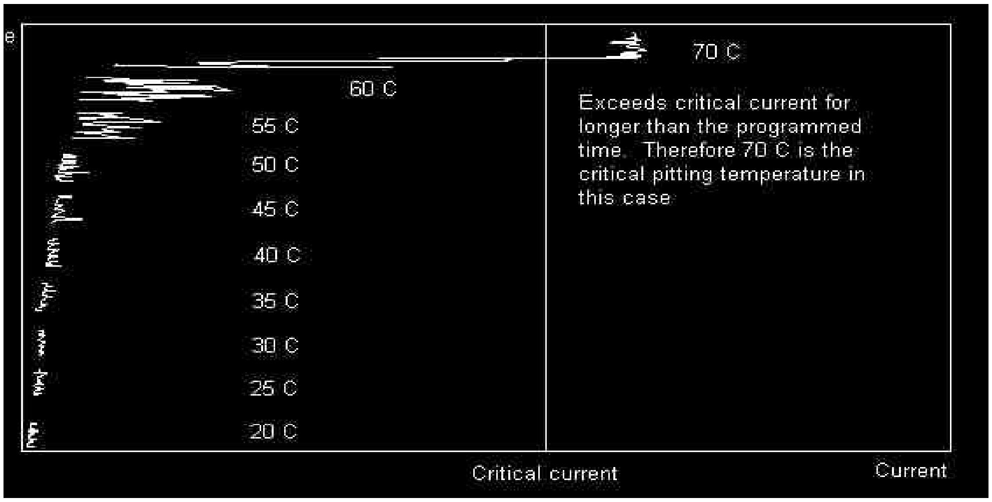


*Figure 6 – Typical Current -Temperature plot showing CPT**

Practical Considerations with Electrochemical CPT

As mentioned previously, crevice corrosion events must be eliminated from the test by proper masking. Another common factor that must be controlled carefully is tuning the temperature controller, so that the potentiostat temperature scan is in synchrony with the actual temperature controller. A departure from this relationship will result in increasingly erroneous CPT values as the temperature scan proceeds. Fortunately, this correction is usually only required during set up. Our experience has also shown that as the CPT increases the precision generally decreases. This is especially true in the case of high grade stainless steels where the CPT often exceeds 60°C (140°F) can be overcome by increasing the number of sample replicates.

Applications

ASTM G 150 has been used successfully for various material studies including:

- Weld corrosion susceptibility of 316L SS [11, 12], Duplex 2205 and 2507
- Bulk elemental composition of 316 SS[13] versus corrosion resistance
- Electropolishing and Passivation processes evaluations

Using GD-OES and Electrochemical CPT Together

An excellent example of how GD-OES surface analysis and electrochemical CPT were used together is a study we conducted on the corrosion resistance of electropolished (EP) and passivated VIMVAR 316L SS. The material chemistry is shown in Table 4.

---

[*] Reprinted courtesy of ACM Instruments

Table 4 - Composition of 316L SS Studied

Cr	Ni	Mo	Mn	Si	C	S	Al	N	P	Fe
17.8	13.5	2.66	0.29	0.11	0.019	0.007	0.004	0.003	0.002	Balance

Two types of electropolishing baths and three different passivation baths were studied. Flat disk coupons were prepared representing a typical machined surface. "Machined only" and "Machined + EP only" (no passivation) and "Machined and Passivated only" (no EP) coupons were also included as controls.

Experimental

GD-OES depth scans of the oxide layer were performed in triplicate on each coupon with three coupons per condition using a LECO 850-A GDS. Sample burns of 10-15 seconds produced depth profiles within the desired range of 0.5 –50 nm. The atomic concentrations of Fe, O, C, Cr, Ni, P and S were plotted across the depth range of 0.5 – 10 nm. Oxide thickness, Cr/Fe ratio at 1 nm, Cr/Fe ratio maximum, carbon depth and atomic percent of near surface phosphorus were determined from the depth plots. Details on these analytical parameters may be found in Appendix B.

For CPT analysis five samples per condition were tested to increase precision. Non-critical surfaces were masked with a non-conductive lacquer. The analysis was performed using a Gamry PC4 potentiostat equipped with Gamry CPT 110 critical pitting temperature software. The GD-OES and CPT data are shown in Table 5.

Table 5 – Surface Chemical and Corrosion Data

	GDOES					
Surface Treatment	Oxide Depth (A)	Cr/Fe (@ 10 A)	Cr/Fe (max)	C (A)	P max (%)	Avg. CPT (^{o}C)
MF	33.3	0.98	1.27	9.40	2.37	23.7
MF+ P1	31.7	1.82	1.92	8.52	1.10	24.8
MF + P2	46.3	0.66	1.29	11.17	2.30	22.5
MF + P3	37.3	1.60	1.63	7.57	2.05	21.7
EP 1 only	36.2	1.43	3.14	7.84	6.35	22.3
EP 2 only	49.1	0.40	1.30	5.60	1.70	21.2
EP 2 + P1	38.0	1.60	1.90	4.70	1.20	33.6
EP1 + P1	23.9	3.44	3.51	6.00	0.81	29.4
EP 1+ P1	28.4	2.82	3.19	5.51	1.77	25.0
EP1 + P2	29.0	2.49	3.45	6.68	1.78	25.7
EP1 + P2	29.5	2.30	3.07	7.03	1.45	25.2
EP1 + P3	36.0	0.97	3.38	8.70	7.70	17.1
EP1 + P3	51.8	0.69	3.28	5.81	8.59	19.0

MF = Mechanically Finished; P1, P2, P3 = Passivated, by different processes
EP = Electropolished, by different processes

Results

A typical GD-OES depth profile plot for this experiment is shown in Figure 7. The plot demonstrates that GD-OES can reveal key features within the thin passive oxide layer. For example, the enrichment of chromium relative to iron at about 0.002 micrometers is clearly distinguishable, as are other minor elemental constituents. The dominant oxide layer within the top 0.004 micrometers of the surface is easily quantified by this technique.

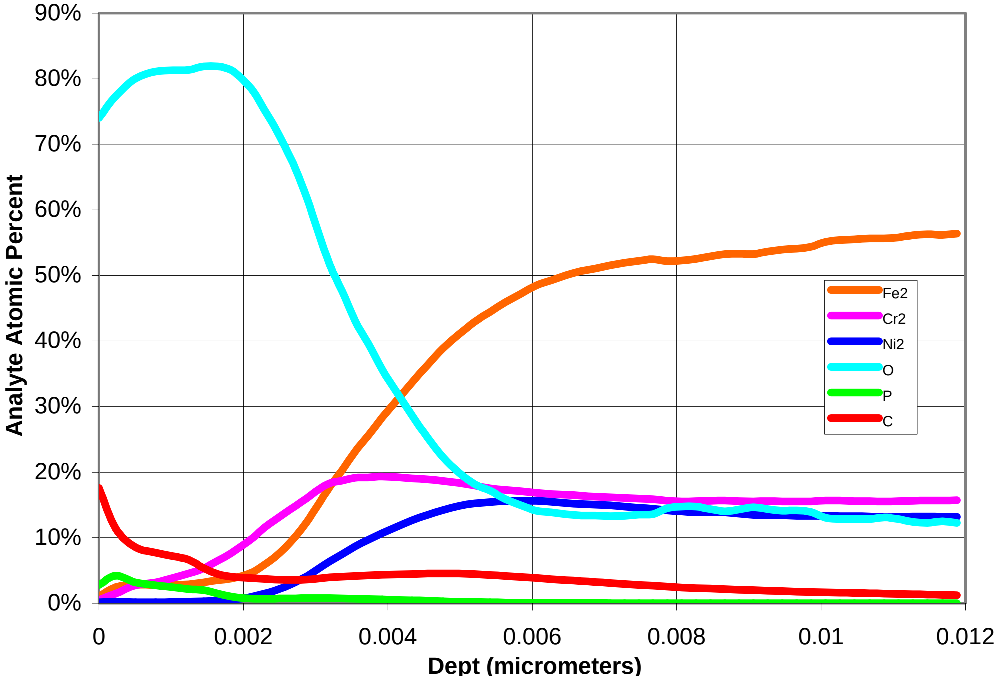


Figure 7 - Typical GD-OES depth profile of electropolished and passivated 316L stainless steel

Although strong individual correlations between individual surface elements and CPT were not clearly evident in the raw data, collectively distinct patterns were found indicating that EP process 1 (EP1) was superior to EP2. And among the passivation processes used on EP1, the CPT data showed P1 imparted the best pitting resistance. Interestingly, the surfaces most chromium enriched (high Cr/Fe max) were not always positively correlated with superior corrosion resistance. Similarly, a direct correlation between oxide thickness and CPT was lacking. However, it was evident that when the surface was free of other residual contaminants, notably P, C, Si, and S (latter two elements not shown in this report) then and only then did the effect of those intuitively “good” markers for corrosion resistance (high Cr/Fe ratios and oxide thickness) relate well to the CPT. These findings were supportive in material selection as well as optimization of cleaning, electropolishing and passivation processes.

Conclusion

GD-OES has a long history as a spectroscopic analytical technique for metal analysis, but its use as a serious depth-profiling tool has been limited to the last few decades. More recently it has proven to be a practical tool for near surface analysis and we have found it to yield results comparable to AES in much less time. Likewise, the electrochemical CPT test, per ASTM G-150 for stainless steels, is a rapid, reliable method for evaluating pitting resistance of metals. When split samples were analyzed by both GD-OES and electrochemical CPT, very useful information was obtained. Through carefully controlled experiments with standardized coupon samples, the GD-OES technique for depth profiling and electrochemical CPT for quantification of corrosion resistance can together yield data for optimizing processes that affect the passive layer of 316L SS.

References

[1,2,3,4,5,6,] Payling, Jones and Bengston, *Glow Discharge Optical Emission Spectrometry*, John Wiley & Sons, NY, USA, 1997, pgs 12-19

[7] Hanke and Bayha, *Surface Characterization for Optimizing Electropolishing for Medical Devices,* Materials Evaluation and Engineering, Minneapolis, MN, USA and MCP Corp., Charlotte NC, USA, no date available.

[8,9,10] ASTM, Philadelphia, PA, ASTM *Annual Book of Standards 2001, Wear and Erosion; Metal Corrosion*, Volume 03.02, Standard Test Method for Electrochemical Pitting Temperature Testing of Stainless Steels, G 150-99, 2001, pg 650.

[11] B. DeForce, S. Collins, P. Williams, *Role of Surface Composition on the Corrosion Resistance of Electropolished 316L Stainless Steel*, Swagelok Company, Solon OH, USA.

[12] B. DeForce, S. Collins, P. Williams, *Role of Manganese in the Corrosion of Welded 316L Stainless Steel,* Swagelok Company, Solon, OH, USA.

[13] S. Collins and P. Williams, *Weldability and Corrosion Studies of AISI 316L Electropolished Tubing,* Swagelok Company, Solon OH, USA.
Note: Referenced Swagelok publications available at www.swagelok.com

Appendix A - Surface Chemistry Requirements Per SEMI F19-0304 for HP and UHP Materials

SEMI F19-0304, "*Specification for the Surface Condition of the Wetted Surfaces of Stainless Steel Components*," defines the acceptable ranges of values for surface analysis figures of merit for wetted surfaces intended for use in semiconductor applications.

High Purity Grade HP	Ultra-High Purity Grade UHP
Cr/Fe and CrOX/FeOX ratios ≥ 1.0; oxide thickness t ≥ 1.5 nm (t ≥ 15 Å).	Cr/Fe ratio ≥ 1.5 and CrOX/FeOX ≥ 2.0; oxide thickness t ≥ 1.5 nm (t ≥ 15 Å).
Adsorbed Carbon contamination shall be <30 atomic percent, declining to base levels within 1.5 nm (15 Å) of the initial surface. Sulfur (S), Phosphorous (P), Nitrogen (N) and Silicon (Si) shall be < 2 atomic percent on the initial surface. All other contaminants shall be < 1 atomic percent.	Adsorbed Carbon contamination shall be <30 atomic percent, declining to base levels within 1.5 nm (15 Å) of the initial surface. Sulfur (S), Phosphorous (P), Nitrogen (N) and Silicon (Si) shall be < 2 atomic percent on the initial surface. All other contaminants shall be < 1 atomic percent.

Appendix B – Surface Parameters Measured in Electropolishing / Passivation Study

- **oxide thickness (A):** the full width at half maximum (FWHM) of the oxygen peak. For high purity and ultrahigh purity surfaces, SEMI F19-0304 requires a minimum oxide thickness of 15 Ǻ, and also indicates that an oxide thickness above 60 Ǻ may describe a mechanically polished surface with high carbon contamination.
- **Cr/Fe ratio at 10 (A):** the ratio of Cr to Fe at 10 Ǻ is a measure of both chromium enrichment in the oxide, and the cleanliness of the surface (minimization of contaminants such as C or P).
- **maximum Cr/Fe ratio:** this measure is determined by finding the location in the oxide with the largest difference between Cr and Fe, and taking the ratio of the two values. It is also a measure of chromium enrichment in the oxide, and in general is at least equal to (and more often greater than) the Cr/Fe ratio at 10 Ǻ.
- **carbon layer thickness (A):** the full width at half maximum (FWHM) of the carbon peak. SEMI F19-0304 states (paragraph 6.6.1): "Adsorbed Carbon contamination shall be < 30 atomic percent, declining to base levels within 15 Angstroms of the initial surface." This parameter measures surface cleanliness, with lower values indicating a cleaner surface.
- **maximum phosphorus (%):** The height of the phosphorus peak in at.%. This measure indicates how well cleaned the surface is after mechanical finishing or electropolishing.