

Company: Clean Sciences
Requestor: David Mortenson
From: Dr. Victor Chia

XPS Report 11-00318

XPS Analysis Report



Note: This analysis was outsourced to a partnering laboratory of Balazs



INTRODUCTION

The goal of this analysis was to determine the surface composition and chemistry of an aluminum coupon labeled as "Lot# 59163". Of particular interest was to establish whether the coupon met Novellus Cleaning Specifications (74-106348-00).

XPS was selected because of its surface sensitivity in the upper 5-10 nm of the sample surface. A survey scan was acquired to determine the elements present. This was followed by high resolution scans of the major elements to determine their oxidation/chemical states.

SUMMARY

Fluorine was out of specification for coupon Lot# 59163 with 4.1 atomic% compared to a spec of <2% for this element.

The aluminum coupon surface was covered with a thin Al_2O_3 layer. Also found on the coupon surface were low to trace levels of AlF_3 , Al oxyfluoride and/or organic fluorocarbon, SiO_2 , oxidized Fe species, sulfate, phosphate, inorganic chloride, Na, Mg, Ca and Cu.

The levels of C, Fe, Cl, Na, Ca, Si and S were within the Novellus Cleaning Specifications. However, the levels of F were higher than the specifications.

DISCUSSION

1. The coupon surface was composed primarily of C, O and Al with low levels of F and trace levels of N, Fe, Na, Mg, Si, P, S, Cl, Ca and Cu (see Table 1).
2. The levels of C, Fe, Cl, Na, Ca, Si and S were within the Novellus Cleaning Specifications. However, the levels of F were higher than the specifications (<2%).
3. Al was found as higher levels of Al_2O_3 and lower levels of Al metal and, based on the F levels and chemistry (see below), low levels of AlF_3 and Al oxyfluoride (see Table 4). The fact that metallic Al is observed indicates that the Al_2O_3 film thickness is less than the XPS information depth (~60-80Å) on this sample.
4. Curve-fitting of the F spectrum identified two component peaks. The lower binding peak was consistent with inorganic fluoride while the higher binding energy one was attributable to oxyfluoride and/or organic fluorocarbon (see Table 2).
5. The coupon surface contained trace levels of N (as organic species), Fe (as oxidized species), Si (likely as SiO_2), S (primarily as sulfate with possibly lower levels of sulfite), Cl (as inorganic chloride), P (as phosphate), Na, Mg, Ca and Cu. The Cu chemical states were undetermined due to weak signals.

DISCUSSION (cont'd)

6. The chemical states of Na, Mg and Ca were undetermined due to their low levels and the minimal binding energy shifts associated with different forms of these elements.
7. C was found primarily as hydrocarbon (C-C, C-H) with significantly lower levels of carbon-oxygen and carbon-nitrogen functionalities and fluorocarbon and/or inorganic carbonate (see Table 3). Most (possibly all) of the organic C, except fluorocarbon was likely attributable to adventitious C (i.e. C adsorbed from atmospheric exposure).

DISCUSSION (cont'd)

8. The results in Table 1 are compared to the Novellus cleanliness specification to determine if the coupons pass Class 3 cleaning classification.

 NOVELLUS FIRST IN PRODUCTIVITY	Title: SURFACE CLEANLINESS, PACKAGING, AND PROCESS SPECIFICATIONS	Document Number: 74-106348-00 Rev H Page 1 of 77
--	---	---

Cleaning Surface Specification	Analysis by ESCA given in At%	Carbon	Zinc	Chlorine	Fluorine	Sodium	Calcium	Silicon	Sulfur	Iron	Magnesium	Nitrogen
Cleaning Classification	Use Type											
Class 1	UHV	<30	<1	<1	<2	<.8	<.5	<1	<.5	<.5	<.5	<2
Class 2	UHV + Texturing											
Class 3	Vacuum and/or Atmosphere Clean											
Class 4	Cosmetic Clean	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Class 5	Cosmetic Clean (Wet Process Tools)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

RESULTS

Survey Analysis

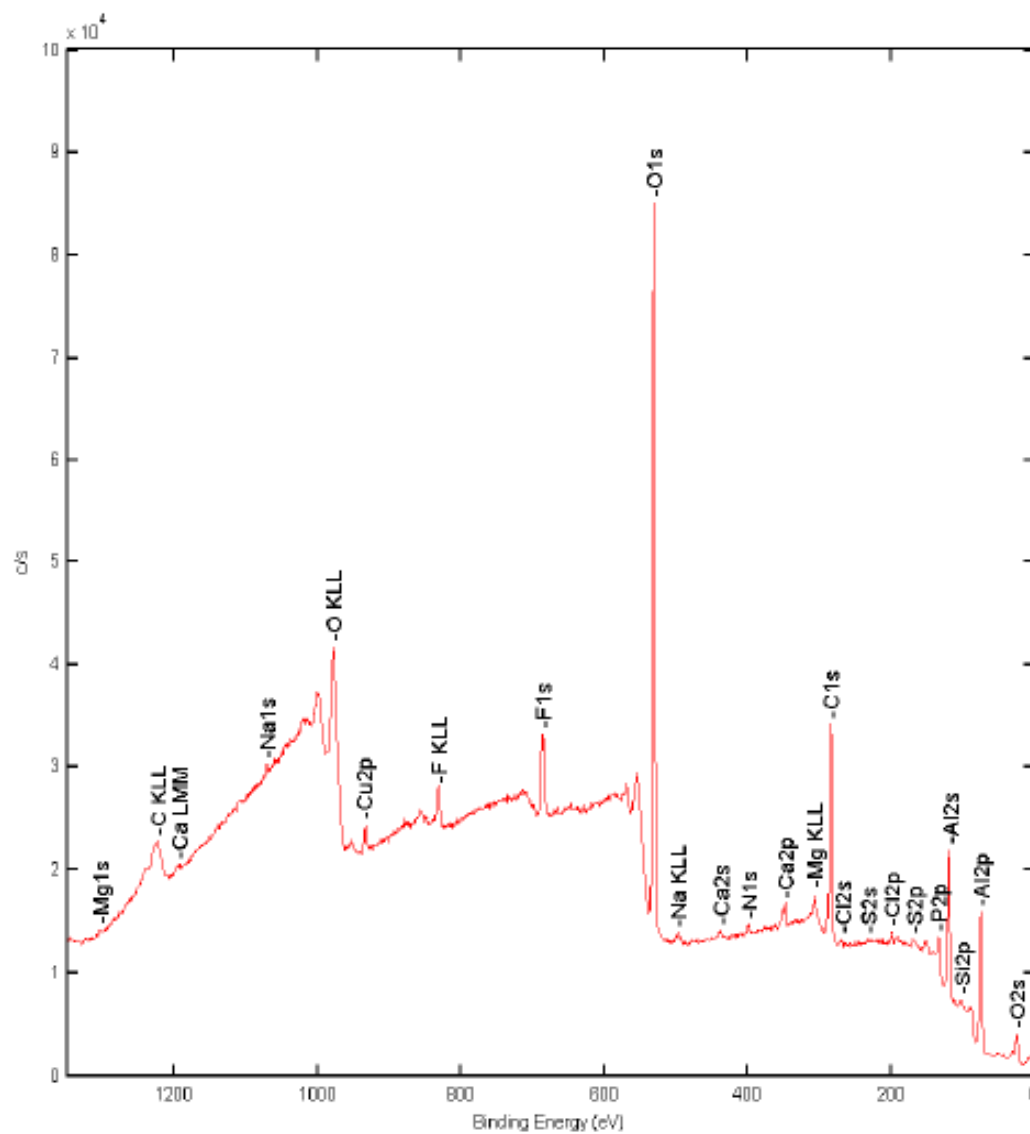
- Table 1 shows the atomic concentration in atomic% of the elemental composition.
- Individual spectrum is shown in Figure 1.

Table 1: Survey data

	C	N	O	F	Na	Mg	Al	Si	P	S	Cl	Ca	Cu	Fe
Sample	26.3	0.5	39.1	4.1	0.2	0.2	26.2	0.7	0.9	0.4	0.4	0.4	0.3	0.2
Novellus Spec	<30	<2	NA	<2	<0.8	<0.5	NA	<1	NA	<0.5	<1	<0.5	NA	<0.5

- a) Normalized to 100% of the elements detected. XPS does not detect H or He.
- b) A dash line “-” indicates the elements is not detected.
- c) A less than symbol “<” indicates accurate quantification cannot be made due to weak signal intensity.

Figure 1: Survey spectrum of Coupon Lot# 59163



High Resolution Analysis

- Table 2-4 present high resolution fluorine, carbon and aluminum relative atomic percent of the components detected.

Table 2: High resolution data of Fluorine chemical state

	Fluoride	oxyfluoride and/or fluorocarbon
Sample	47	53

Note: Values in this table are percentages of the total atomic concentration of the corresponding element shown in Table 1

Table 3: High resolution data of Carbon chemical state

	C-C,C-H	C-O, C-N	O-C=O	Fluorocarbon, carbonate?
Sample	80	15	3	2

Note: Values in this table are percentages of the total atomic concentration of the corresponding element shown in Table 1

High Resolution Analysis

Table 4: High resolution data of Aluminum chemical state

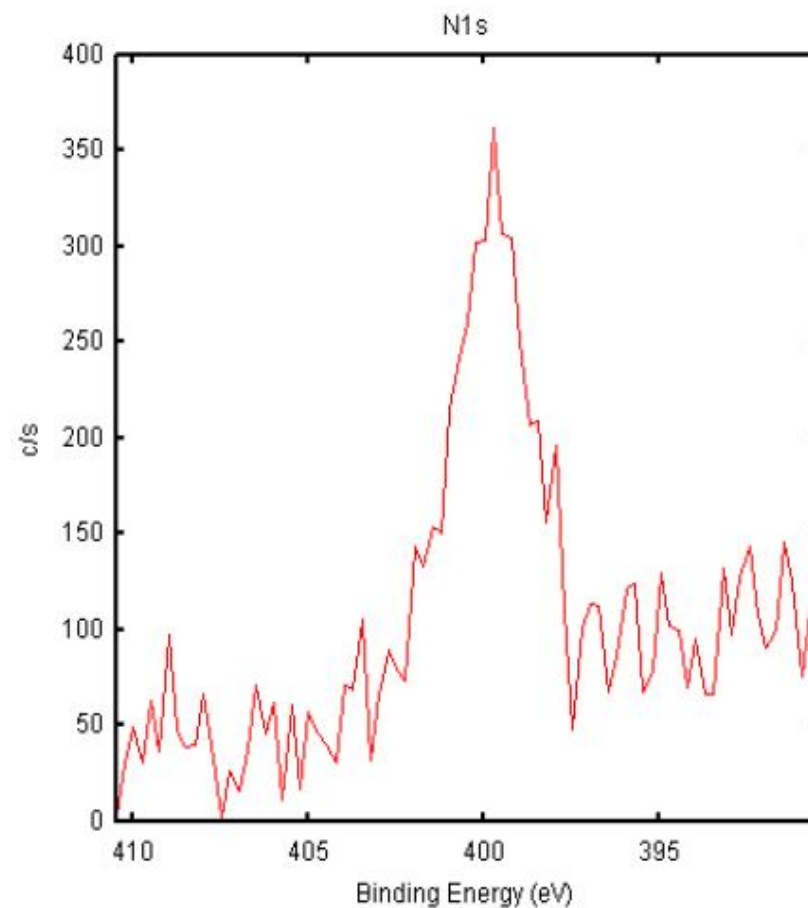
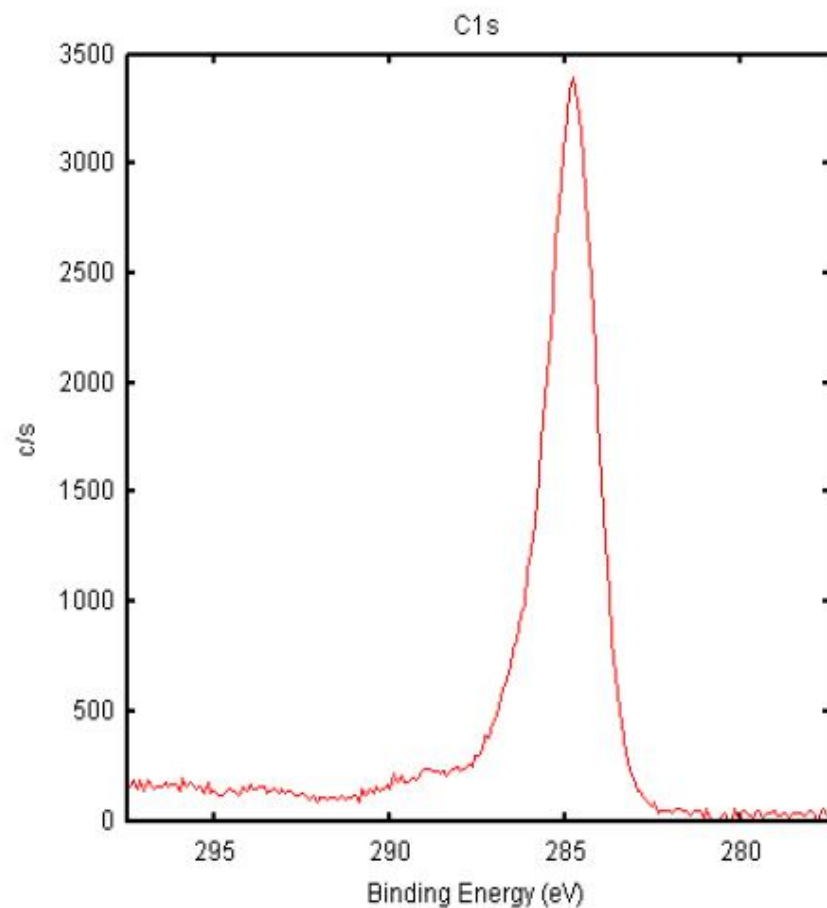
	Al metal	Al ₂ O ₃	AlF ₃ , Al oxyfluoride
Sample	26	55	19

Note: Values in this table are percentages of the total atomic concentration of the corresponding element shown in Table 1

- High resolution spectra are shown in Figures 2-12.

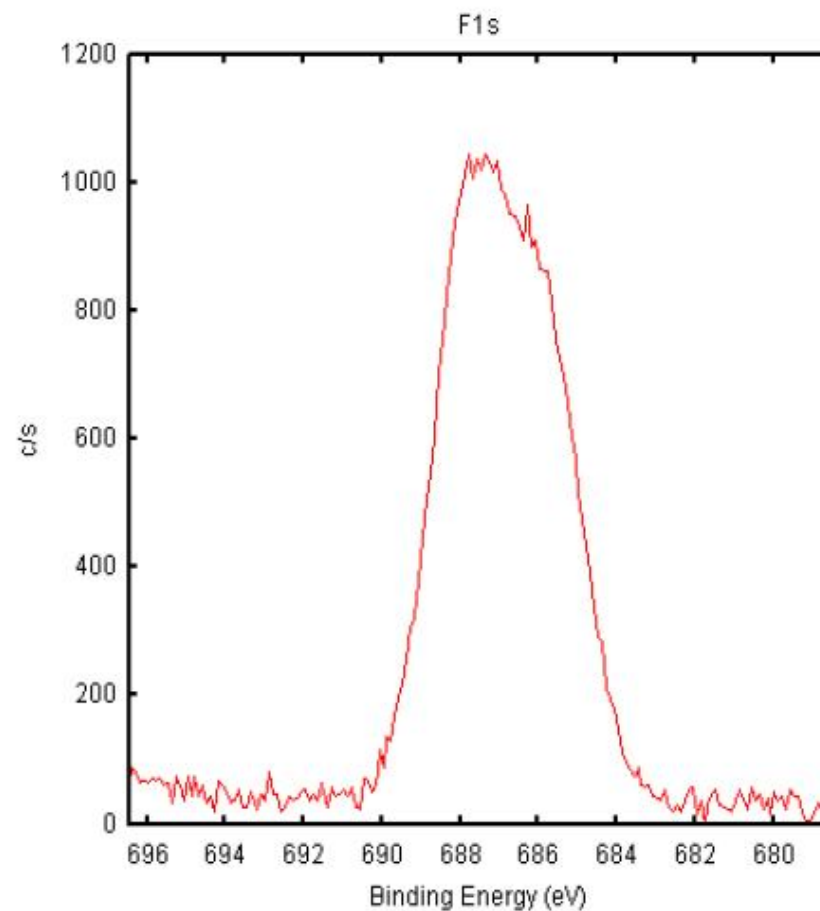
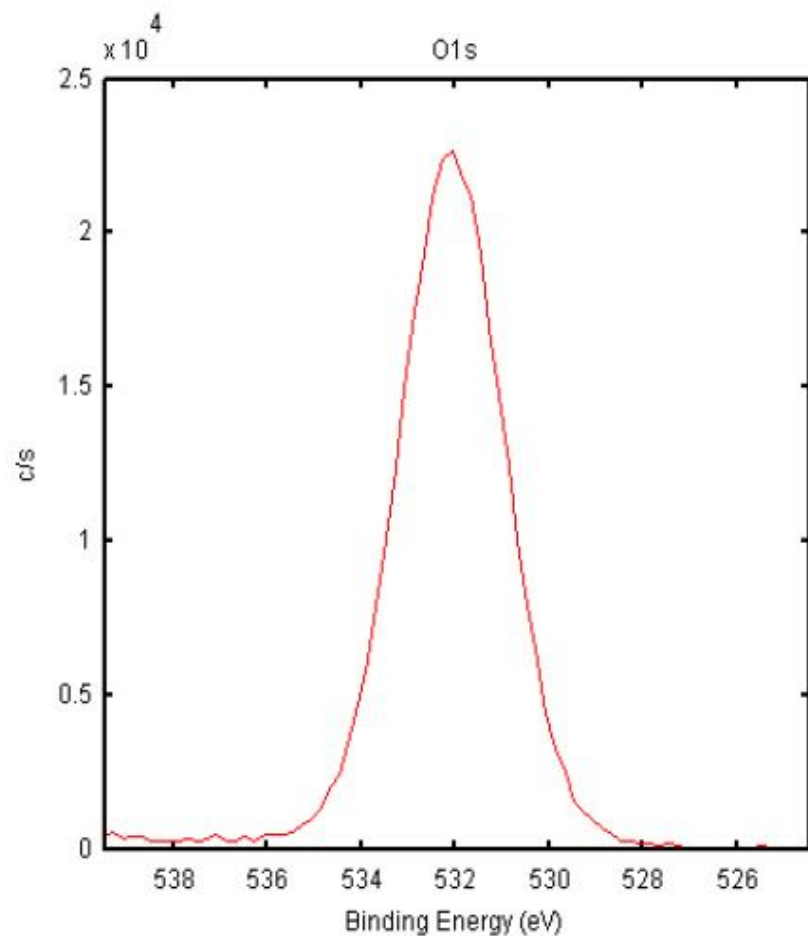
High Resolution Analysis of **Coupon Lot# 59163**

Figure 2: High resolution and chemical state assignments



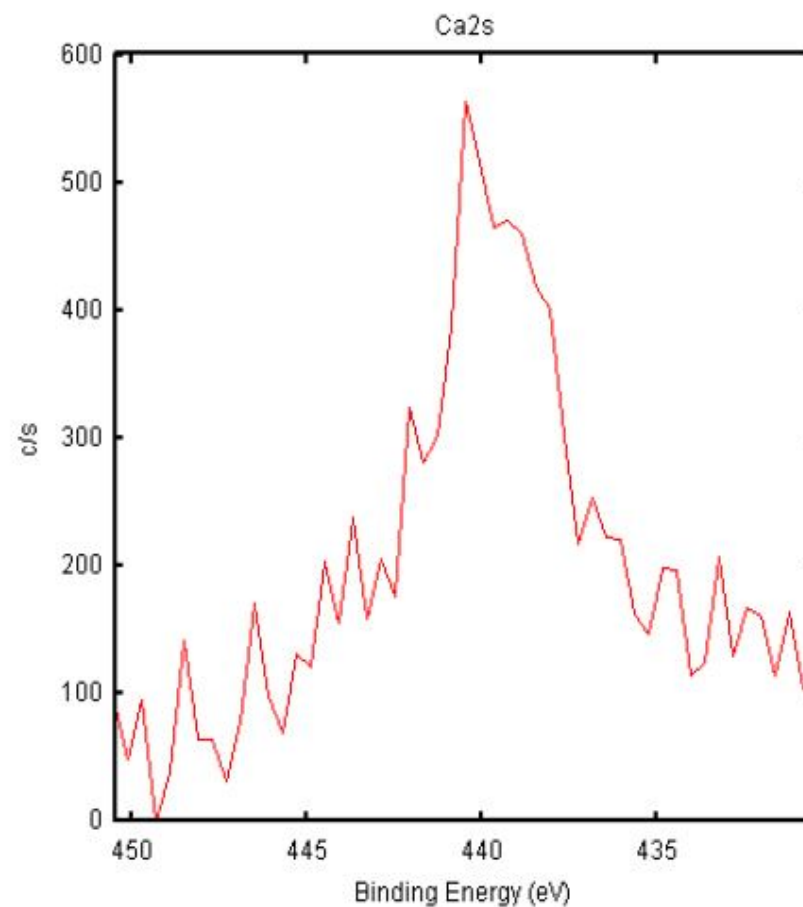
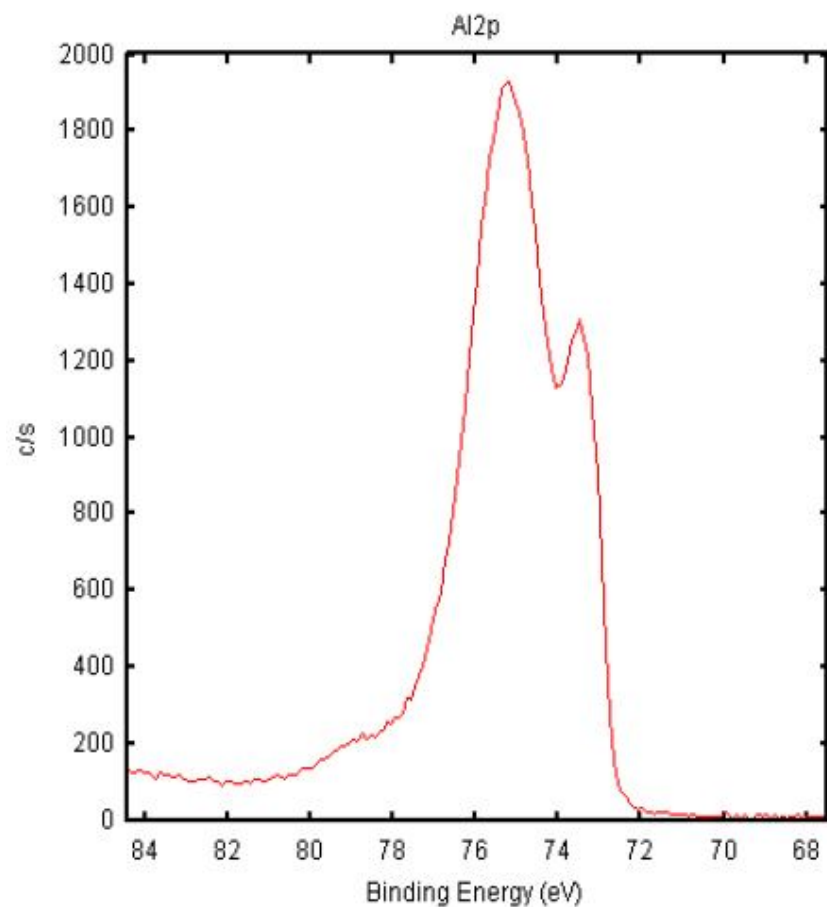
High Resolution Analysis of **Coupon Lot# 59163**

Figure 3: High resolution and chemical state assignments



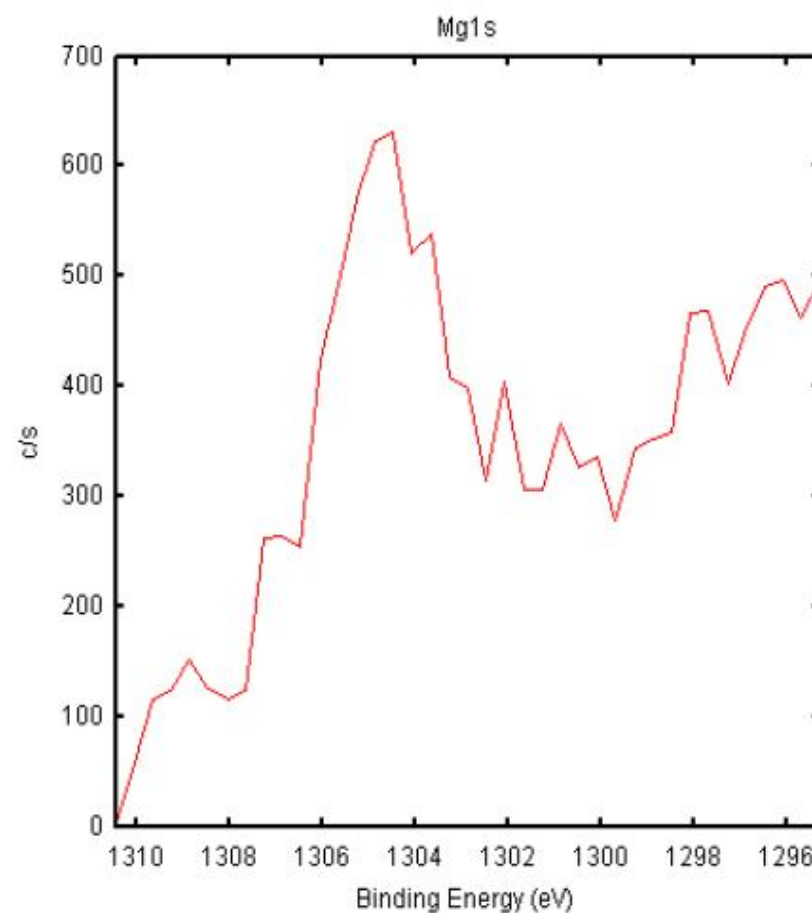
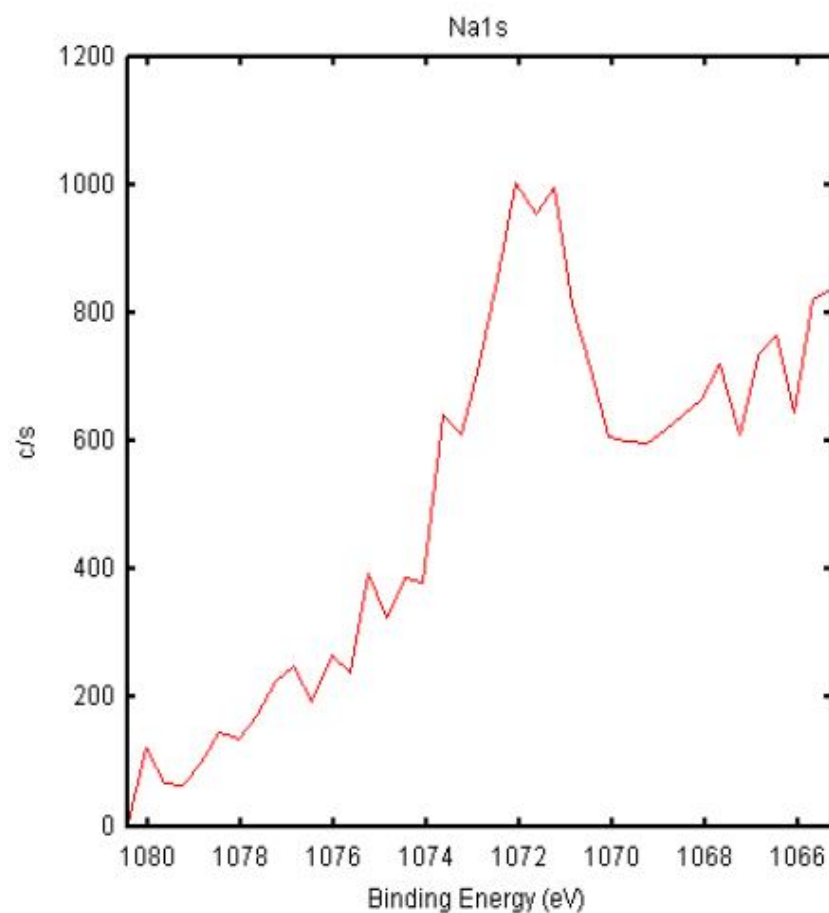
High Resolution Analysis of **Coupon Lot# 59163**

Figure 4: High resolution and chemical state assignments



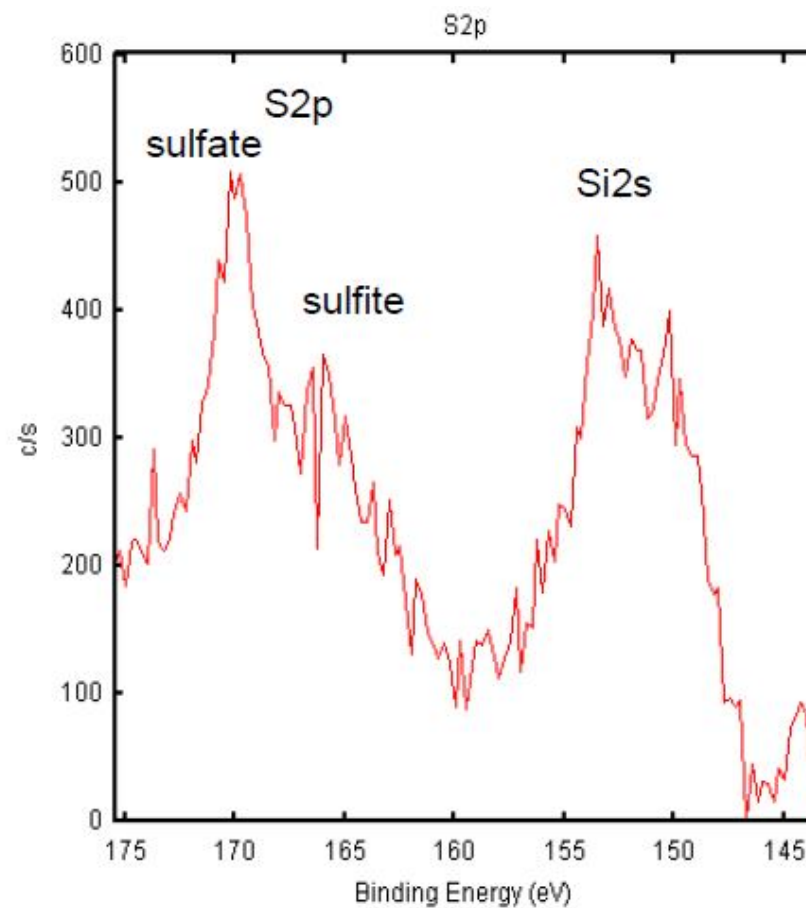
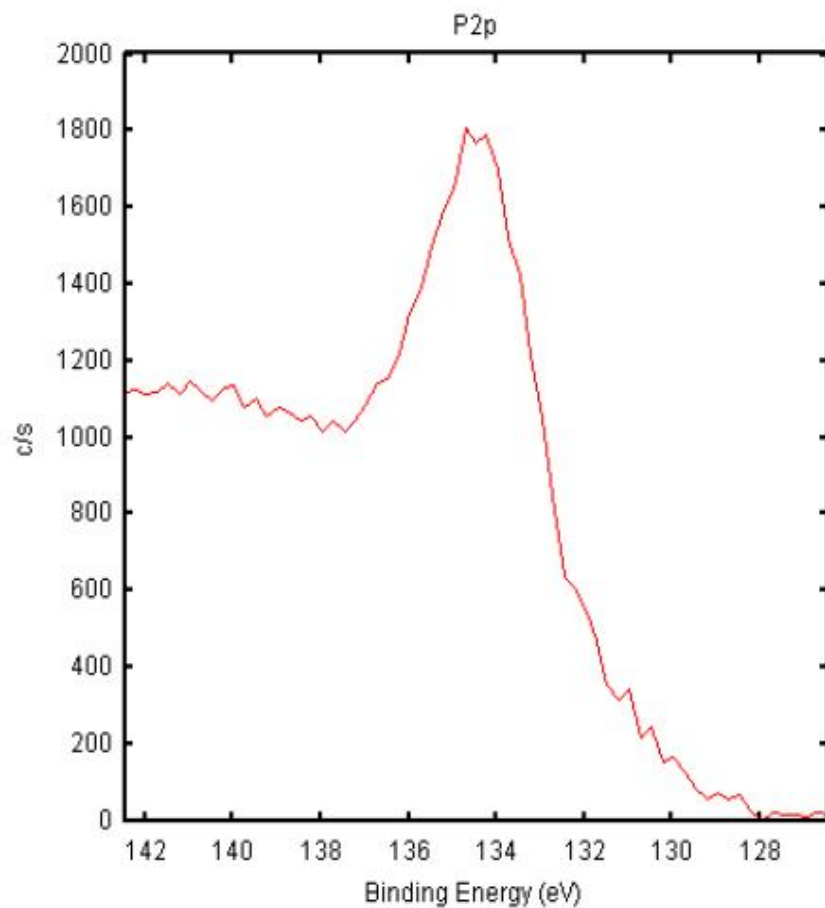
High Resolution Analysis of **Coupon Lot# 59163**

Figure 5: High resolution and chemical state assignments



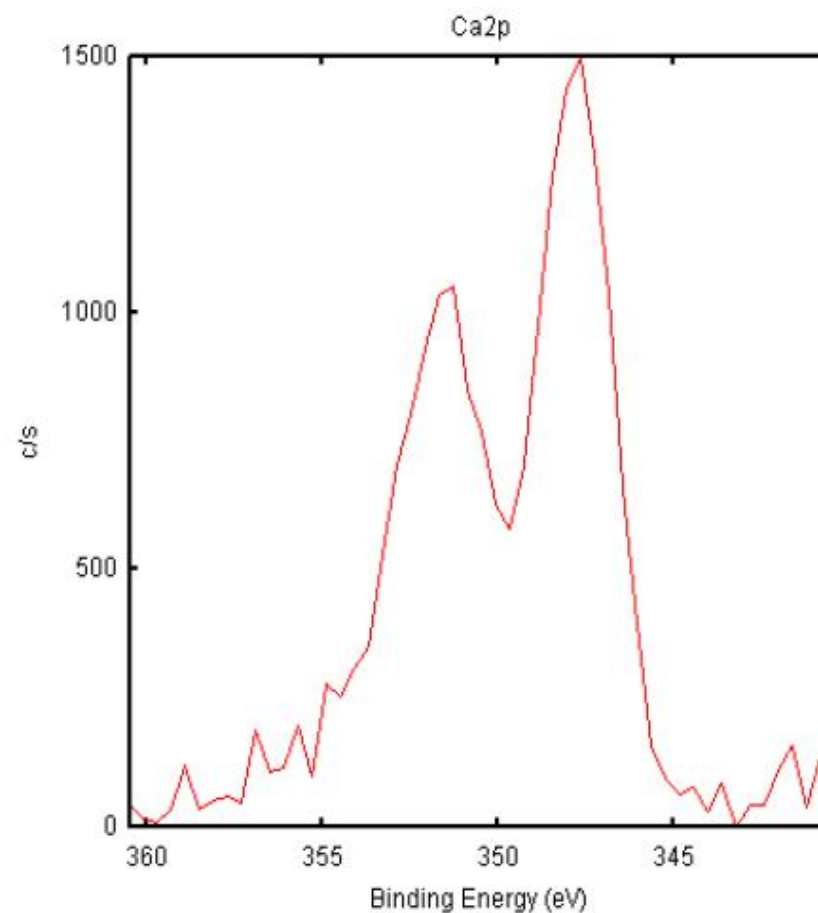
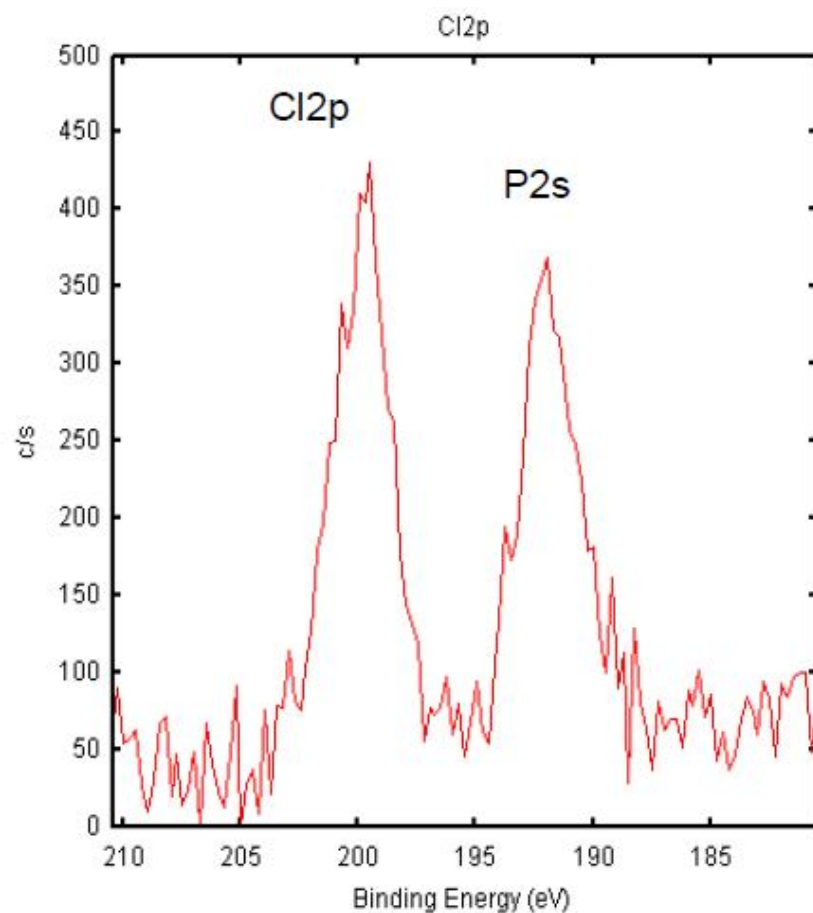
High Resolution Analysis of **Coupon Lot# 59163**

Figure 6: High resolution and chemical state assignments



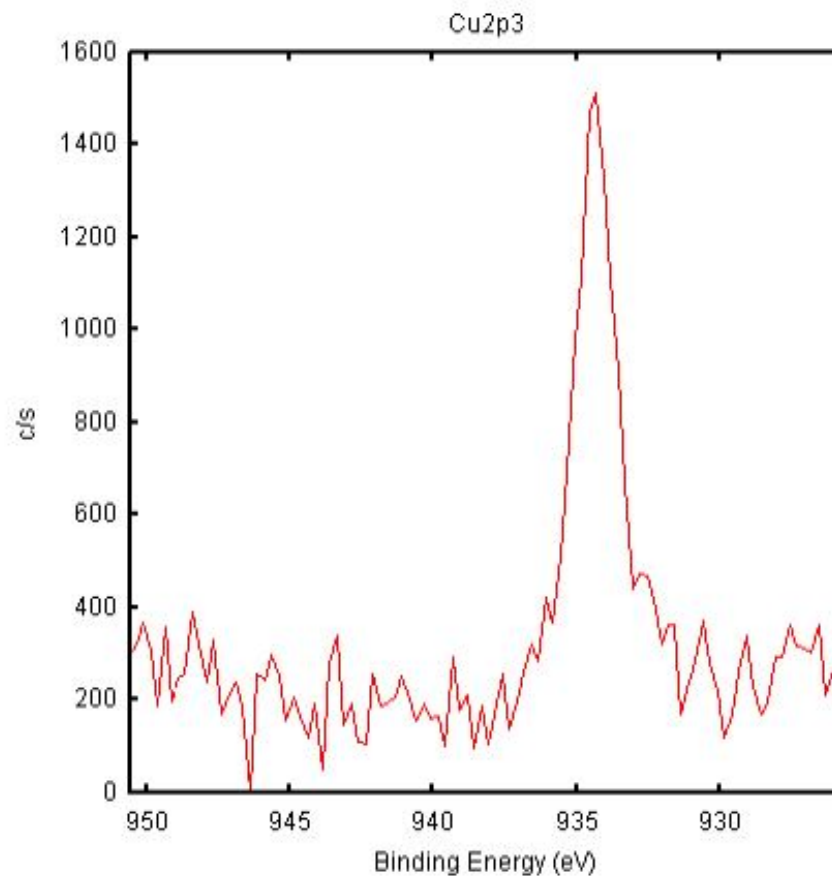
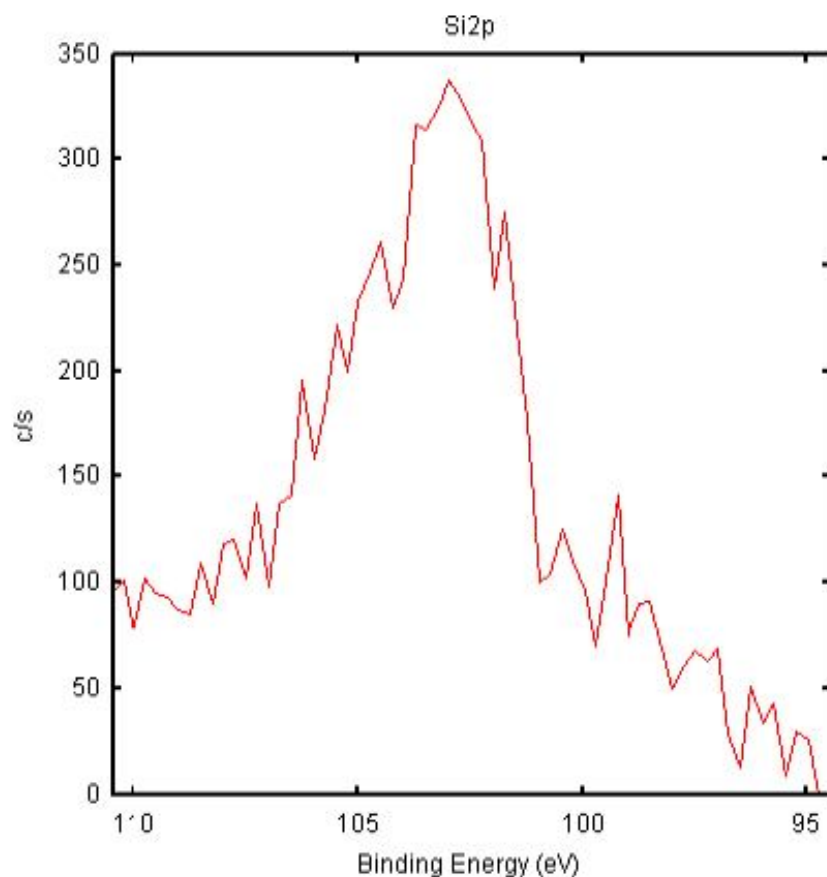
High Resolution Analysis of **Coupon Lot# 59163**

Figure 7: High resolution and chemical state assignments



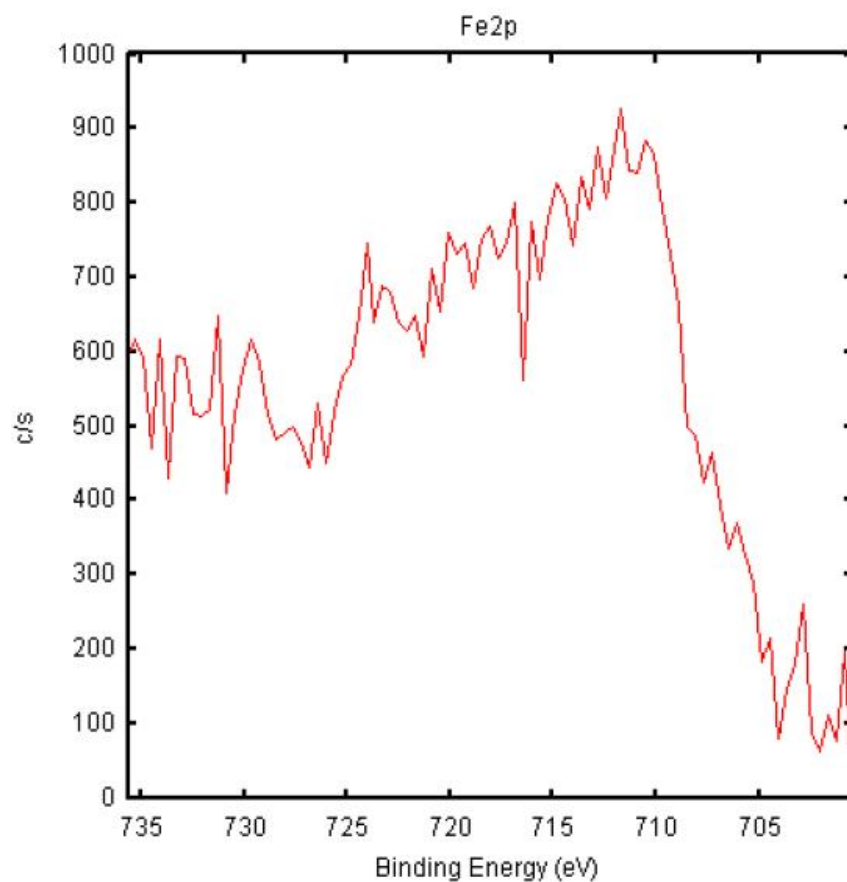
High Resolution Analysis of **Coupon Lot# 59163**

Figure 8: High resolution and chemical state assignments



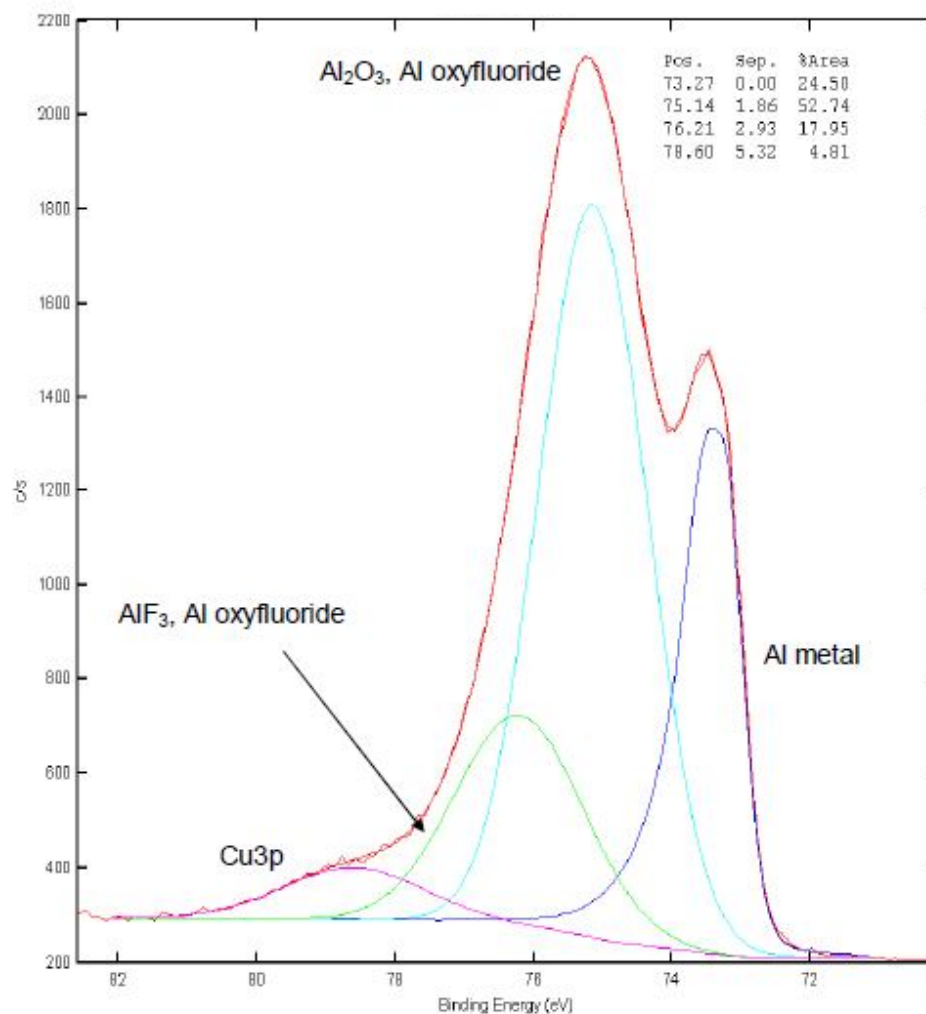
High Resolution Analysis of **Coupon Lot# 59163**

Figure 9: High resolution and chemical state assignments



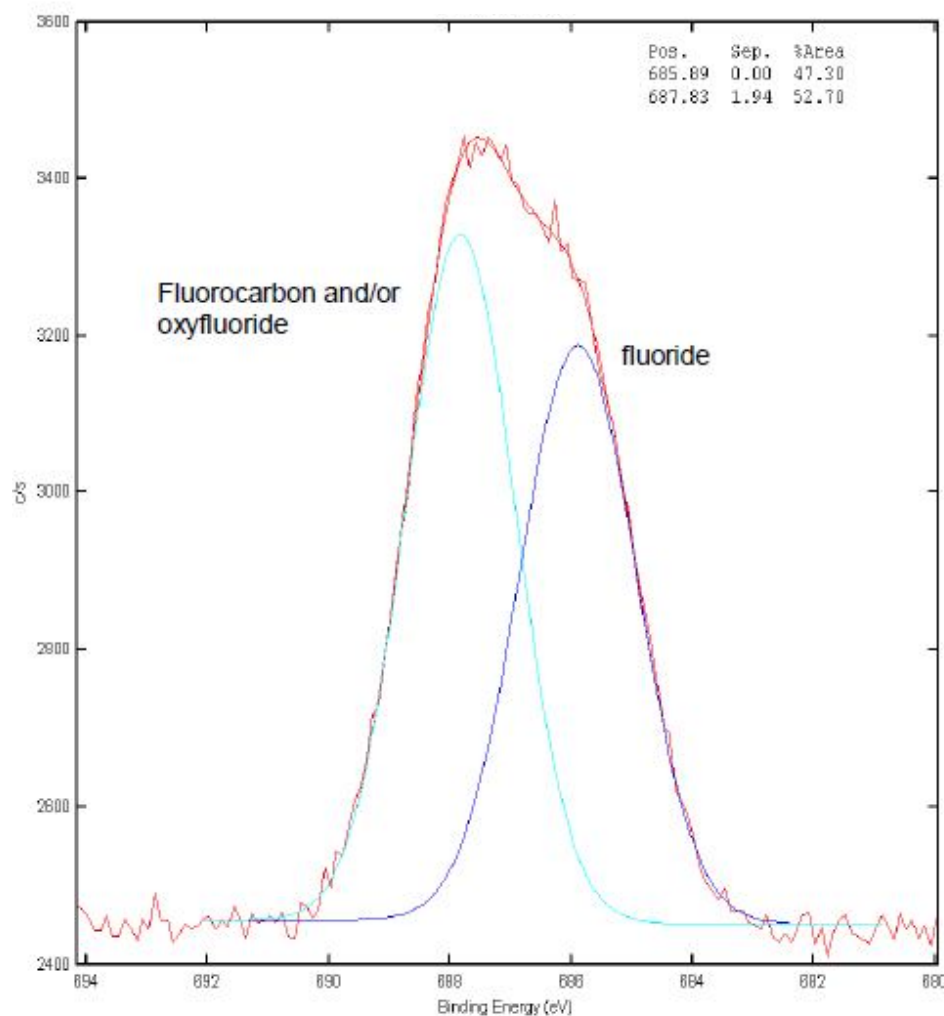
High Resolution Analysis of **Coupon Lot# 59163**

Figure 10: High resolution and chemical state assignments



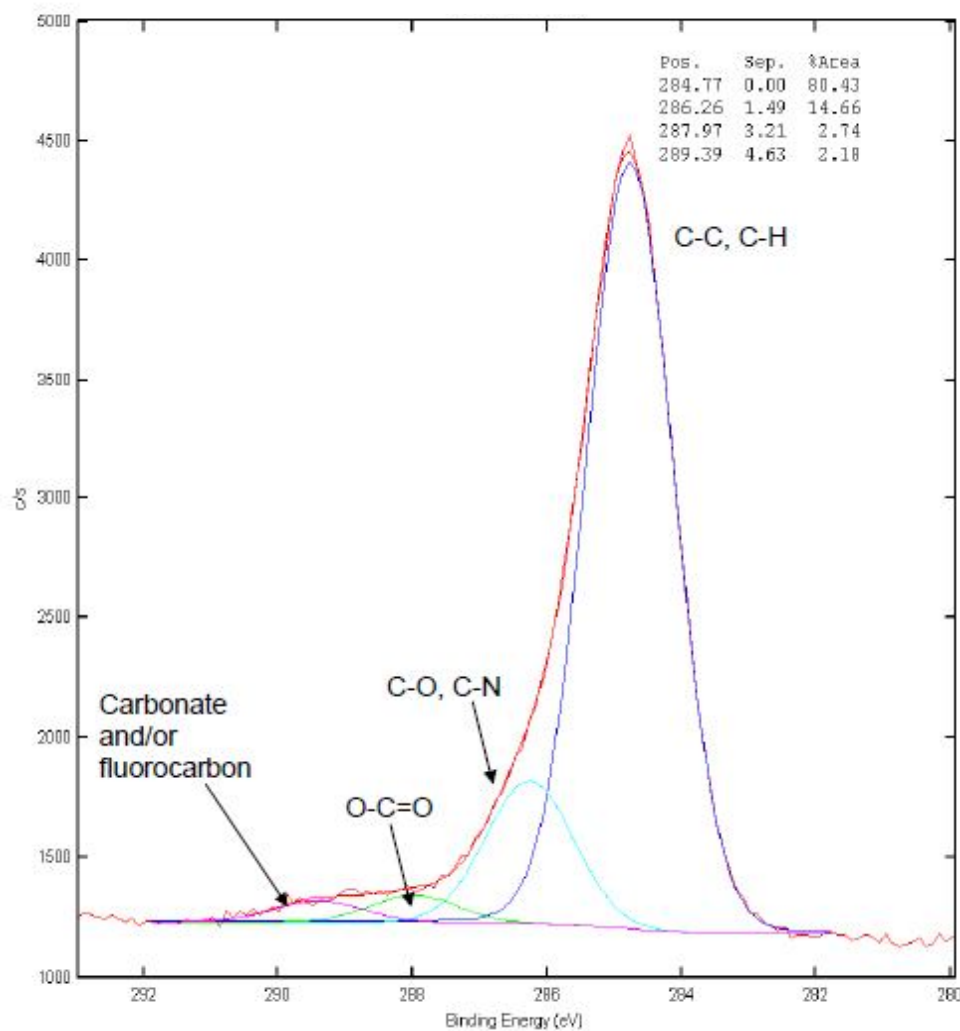
High Resolution Analysis of **Coupon Lot# 59163**

Figure 11: High resolution and chemical state assignments



High Resolution Analysis of **Coupon Lot# 59163**

Figure 12: High resolution and chemical state assignments



APPENDIX A

XPS data is quantified using relative sensitivity factors and a model that assumes a homogeneous layer. The analysis volume is the product of the analysis area (spot size or aperture size) and the depth of information. Photoelectrons are generated within the X-ray penetration depth (typically many microns), but only the photoelectrons within the top three photoelectron escape depths are detected. Escape depths are on the order of 15-35 Å, which leads to an analysis depth of ~50-100 Å. Typically, 95% of the signal originates from within this depth.

Analytical Condition

Instrument	PHI Quantum 2000
X-ray source	Monochromated Al-k _α 1486.6eV
Acceptance Angle	±23°
Take-off angle	45°
Analysis area	1400μm x 300μm
Charge Correction	C1s 284.8 eV

APPENDIX B

XPS does not detect H or He. Values given are normalized to 100% using the elements detected. Detection limits are approximately 0.05 to 1.0 atomic %. High resolution scans were obtained from the major elements of interest to determine their chemical states. Chemical state assignments for a given element have been made by consulting reference data from the literature. The atomic concentrations provided can typically be reproduced for major constituents of sample surfaces to better than $\pm 10\%$. For elements present at levels below 10 at% down to the detection limit of $\sim 0.05 - 0.5$ at% the uncertainty in the reproducibility of the results can be significantly larger.