

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

Report 11-05710 rev 2

# 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 identified as **CSI-06**. Of particular interest was to establish whether the coupon met the Novellus Cleaning Specification (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

The aluminum coupon surface was covered with a thin  $\text{Al}_2\text{O}_3$  layer. Also found on the coupon surface were low to trace levels of  $\text{AlF}_3$  and/or Al oxyfluoride, organic fluorocarbon, organic N species, nitrate,  $\text{Ni}(\text{OH})_2$ , Ni metal, silicone/silicate,  $\text{SiO}_2$ , sulfate/sulfone, inorganic chloride, ZnO, Cu and Ca.

The levels of C, Cl, Ca, Si and S were within the Novellus Cleaning Specification. However, the levels of F were higher than the specification (<2%). No Fe or Na was detected on the coupon.

## DISCUSSION

1. The coupon surface was composed primarily of C, O and Al with low levels of N, F, Ni and Zn and trace levels of Si, S, Cl, Ca and Cu (see Table 1)

The levels of C, Cl, Ca, Si and S were within the Novellus Cleaning Specification. However, the levels of F were higher than the specification (<2%). No Fe or Na was detected on the coupon.

2. Al was found as higher levels of  $\text{Al}_2\text{O}_3$  and lower levels of Al metal and  $\text{AlF}_3$  and/or Al oxyfluoride (see Table 3). The fact that metallic Al is observed indicates that the  $\text{Al}_2\text{O}_3$  film thickness is less than the XPS information depth (~60-80Å) on this sample.
3. F was found as higher levels of inorganic fluoride/oxyfluoride and lower levels of organic fluorocarbon (see Table 4).

## DISCUSSION (cont'd)

4. The coupon surface contained low to trace levels of N (as higher levels of organic species and lower levels of nitrate), Ni (as higher levels of  $\text{Ni}(\text{OH})_2$  and lower levels of Ni metal), Si (primarily as silicone and/or silicate with possibly lower levels of  $\text{SiO}_2$ ), S (primarily as sulfate/sulfone with possibly low levels of sulfide), Cl (as inorganic chloride), Zn (likely as  $\text{ZnO}$ ), Cu and Ca.


The Cu chemical states were undetermined due to weak signals.

The Ca chemical states were undetermined due to its low levels and the minimum binding energy shifts associated with different forms of this element.

5. C was found primarily as hydrocarbon (C-C, C-H) with lower levels of carbon-oxygen functionalities and fluorocarbon and possibly inorganic carbonate (see Table 2). 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)

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

 <b>NOVELLUS</b> FIRST IN PRODUCTIVITY		Title: <b>SURFACE CLEANLINESS, PACKAGING, AND PROCESS SPECIFICATIONS</b>							Document Number:  <b>74-106348-00 Rev H</b>			
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

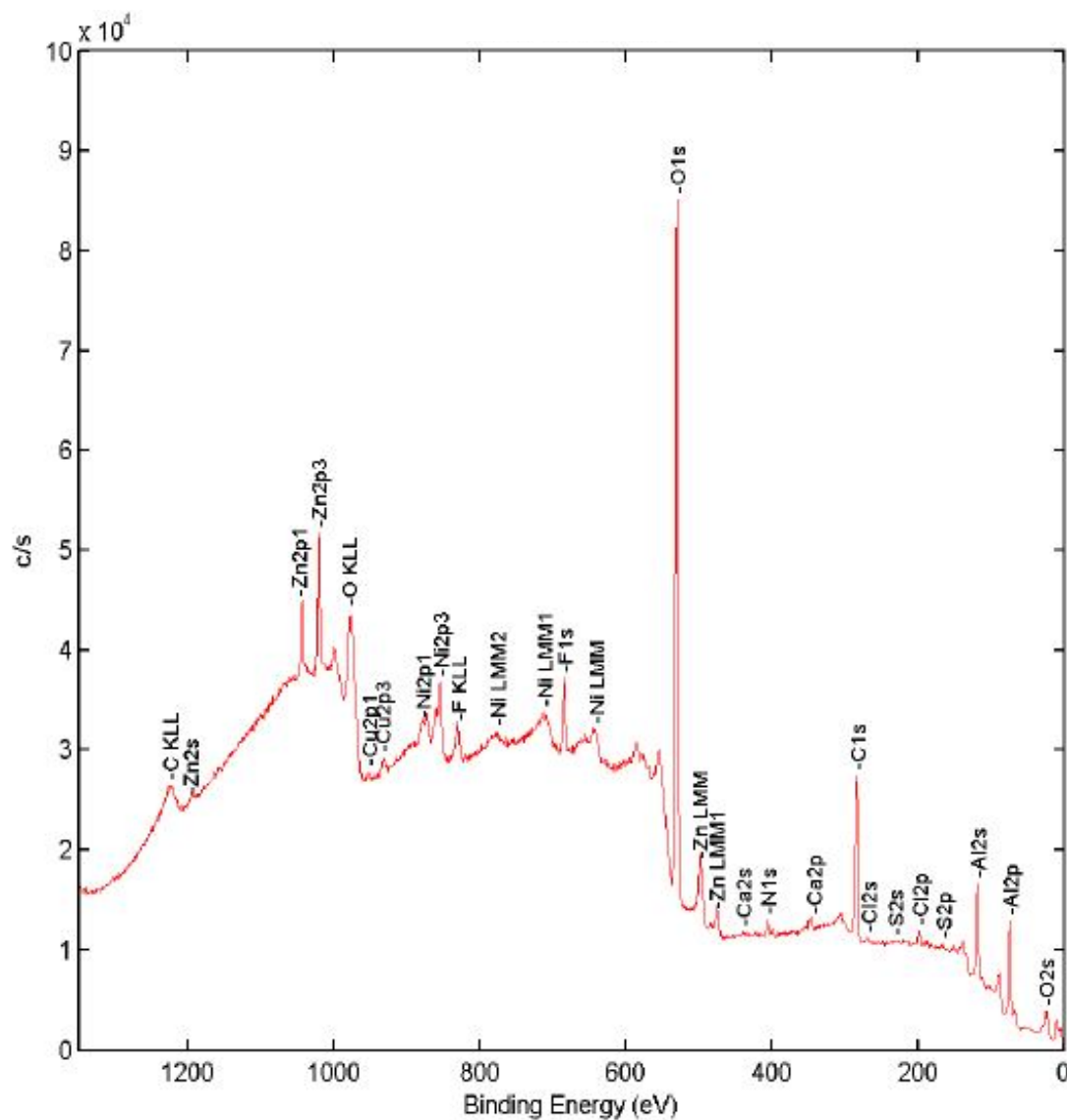
- Table 1 shows the atomic concentration in atomic% of the elemental composition.
- Individual spectrum is shown in Figure 1.

**Table 1: Survey data**

	C	N	O	F	Al	Si	S	Cl	Ca	Ni	Cu	Zn
CSI-06	26.2	1.1	40.8	4.1	21.9	0.3	0.3	0.5	0.4	2.2	0.2	2.0
NVLS Spec	<30	<2	NA	<2	NA	<0.1	<0.5	<1	<0.5	NA	NA	NA

- Normalized to 100% of the elements detected. XPS does not detect H or He.
- A dash line “-” indicates the elements is not detected.
- A less than symbol “<” indicates accurate quantification cannot be made due to weak signal intensity.
- A question mark “?” indicates species may be present at or near the detection limit of the technique.

Figure 1: Survey spectrum of **CSI-06**





## High Resolution Analysis

- Tables 2-4 present high resolution spectra of relative atomic percent of the components detected.

**Table 2: High resolution data of Carbon chemical state**

	C-C,C-H	C-O	C=O	O-C=O, COOH, fluorocarbon, carbonate
<b>CSI-06</b>	73	17	6	5

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 Aluminum chemical state**

	Al metal	Al <sub>2</sub> O <sub>3</sub>	AlF <sub>3</sub> , Al oxyfluoride
<b>CSI-06</b>	8	82	10

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 Fluorine chemical state**

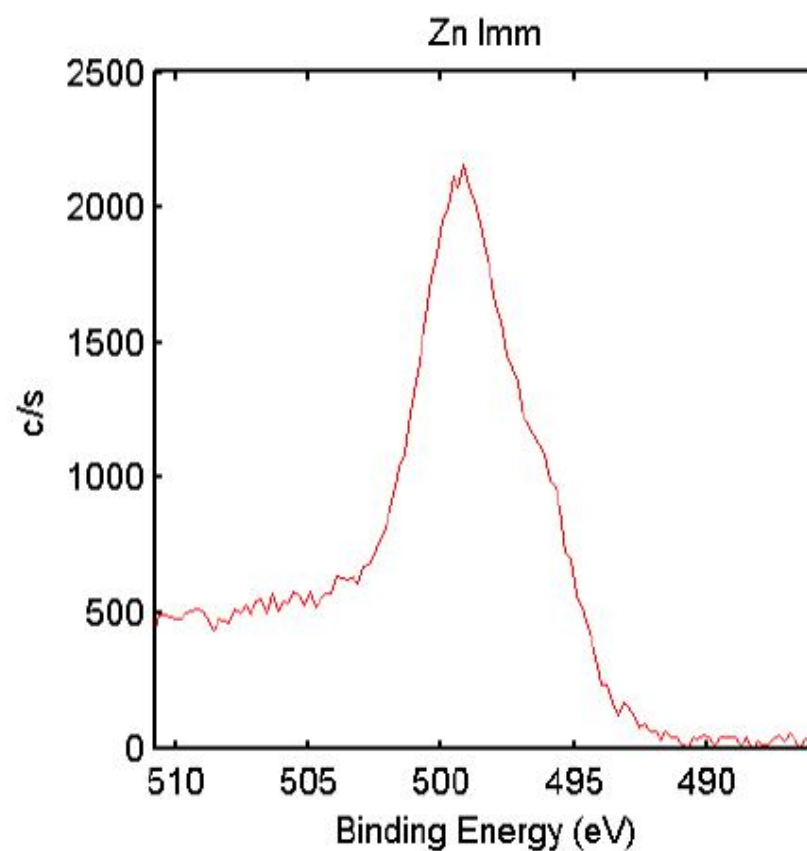
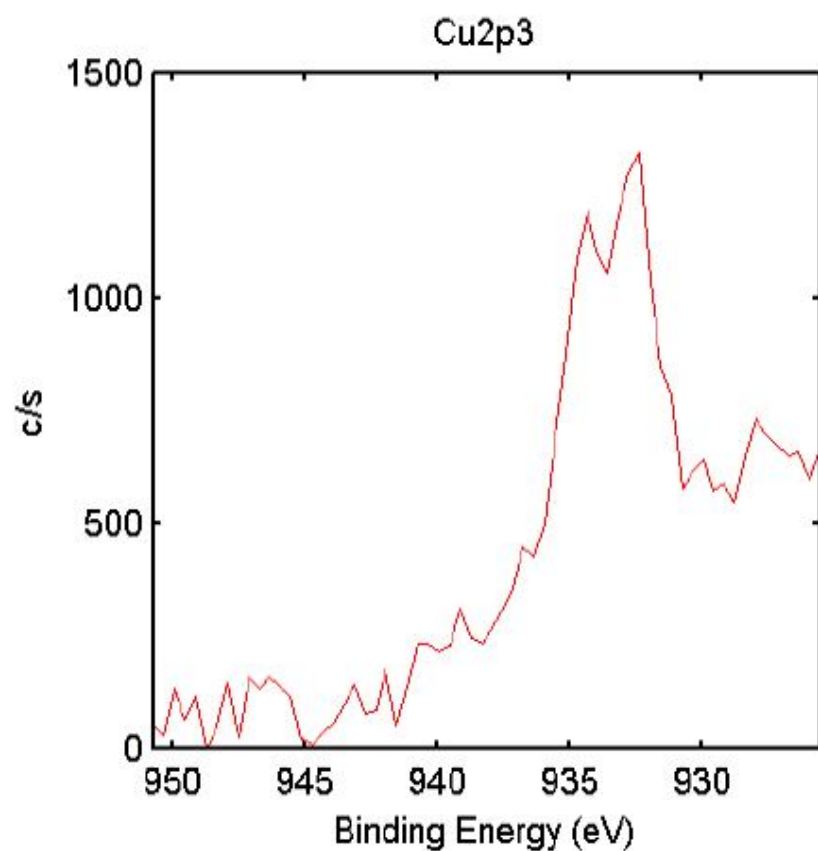
	Fluoride/oxyfluoride	fluorocarbon
CSI-06	79	21

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

- High resolution spectra for **CSI-06** is shown in Figures 2-11.

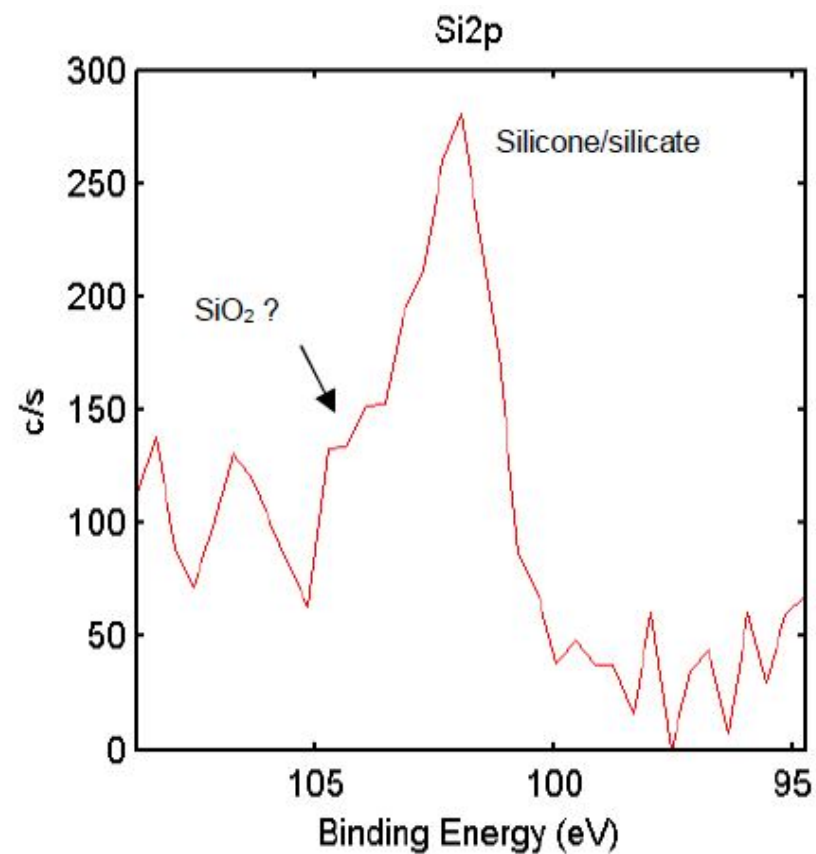
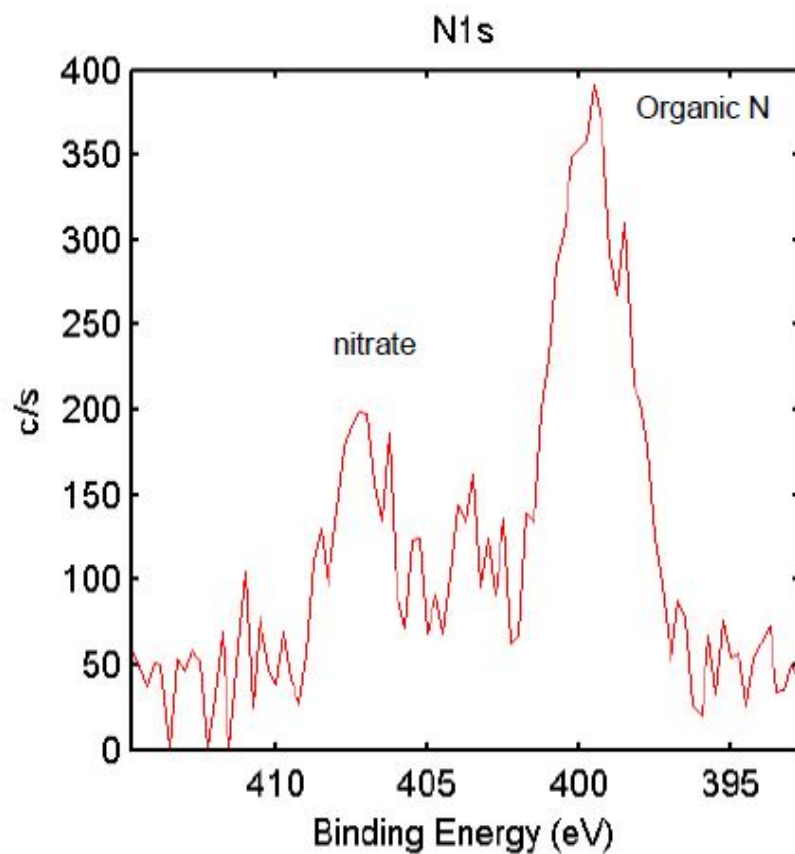
## High Resolution Analysis of CSI-06

**Figure 2: High resolution and chemical state assignments**



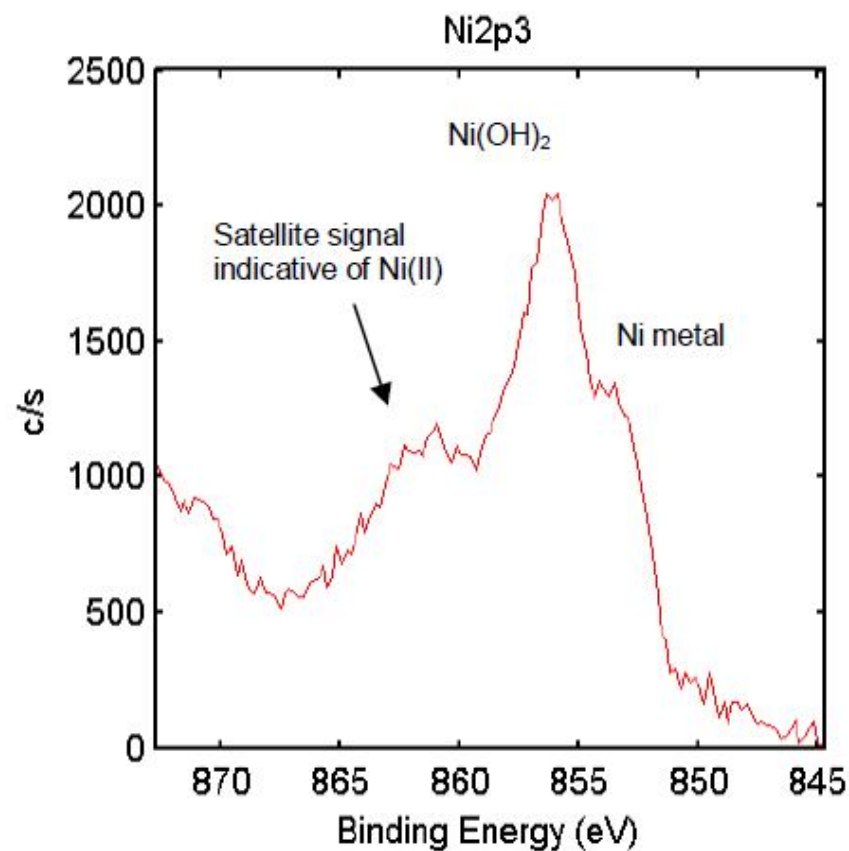
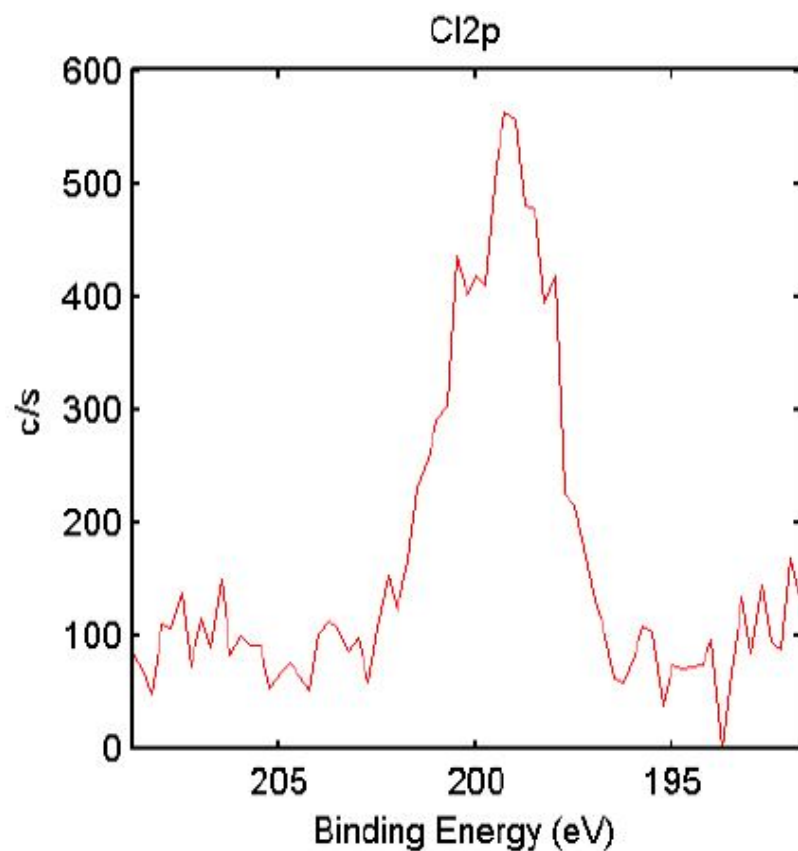
## High Resolution Analysis of CSI-06

Figure 3: High resolution and chemical state assignments



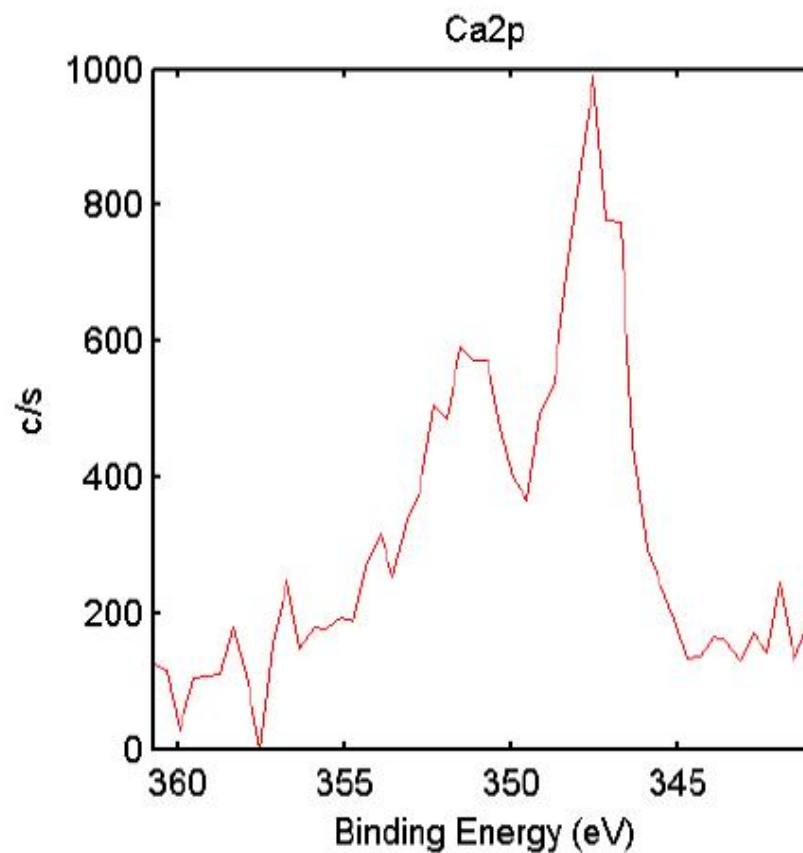
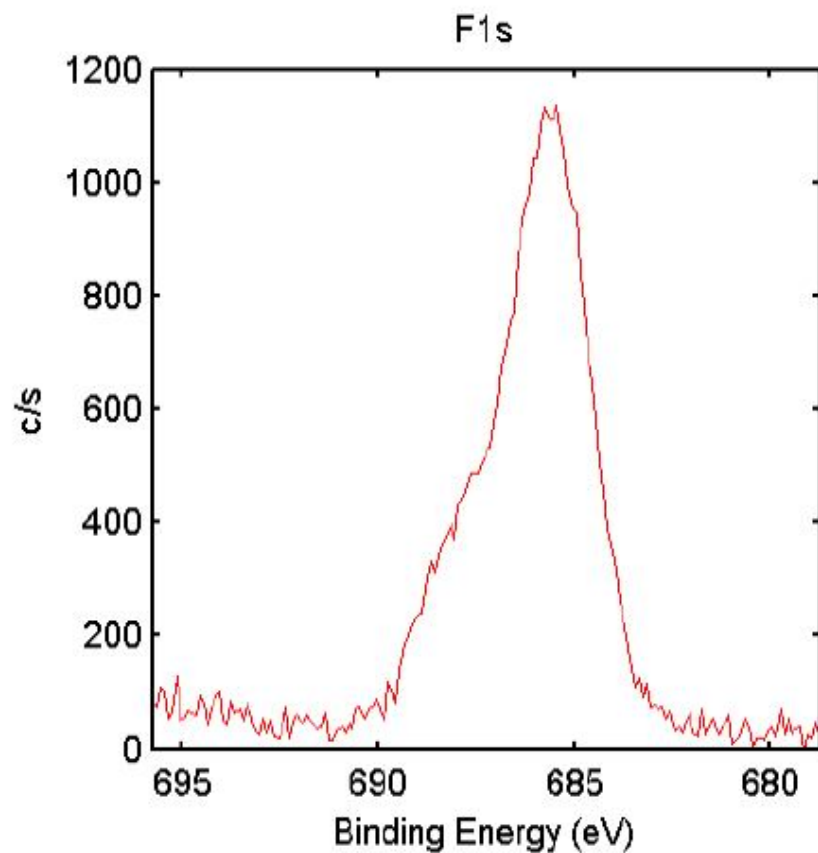
## High Resolution Analysis of CSI-06

Figure 4: High resolution and chemical state assignments



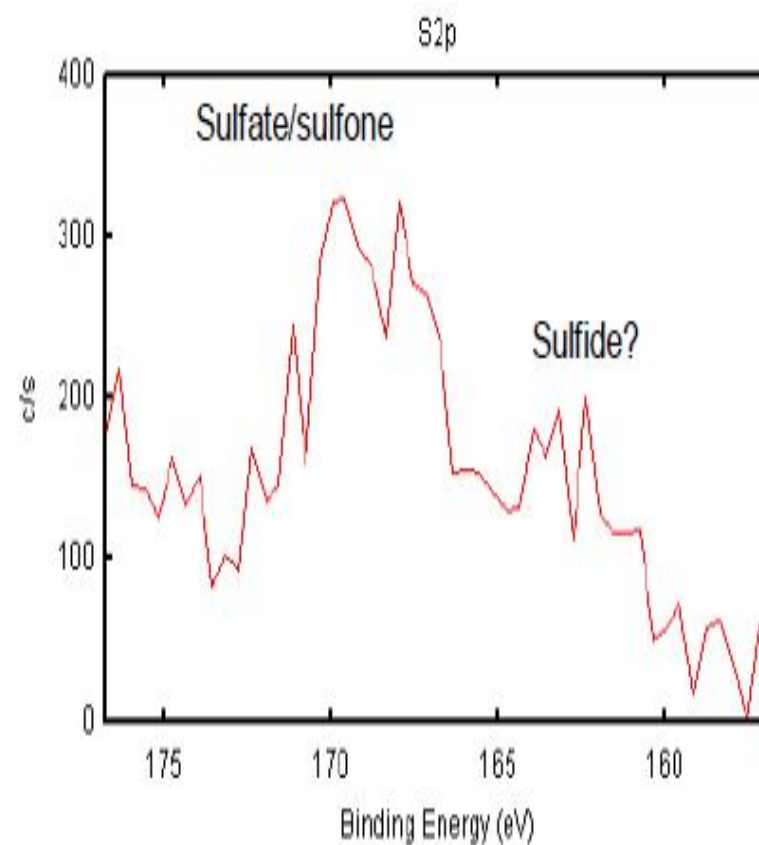
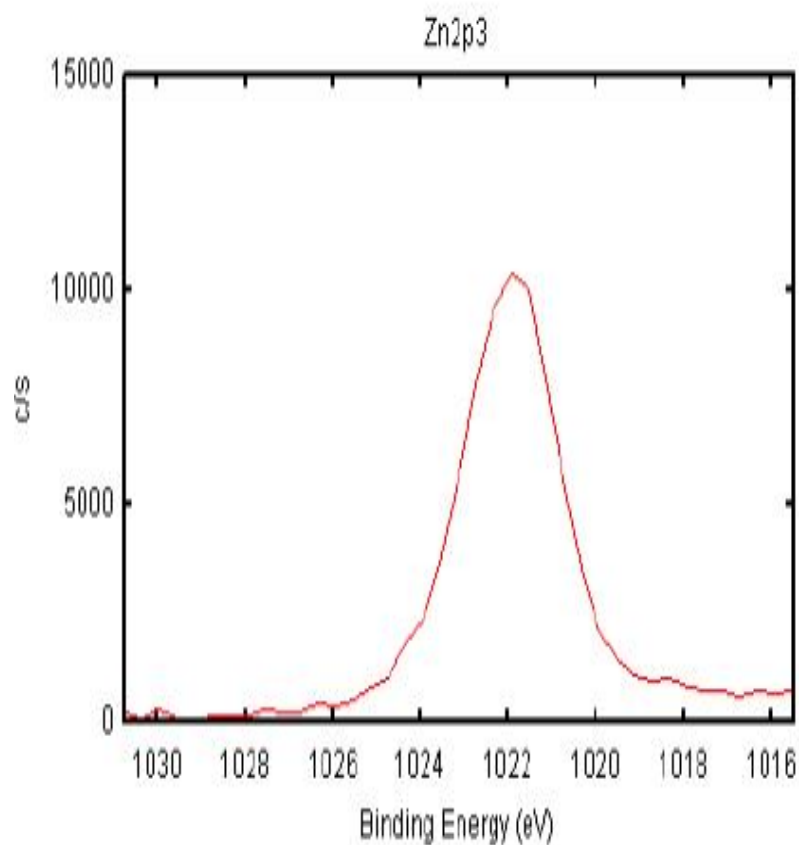
## High Resolution Analysis of CSI-06

Figure 5: High resolution and chemical state assignments



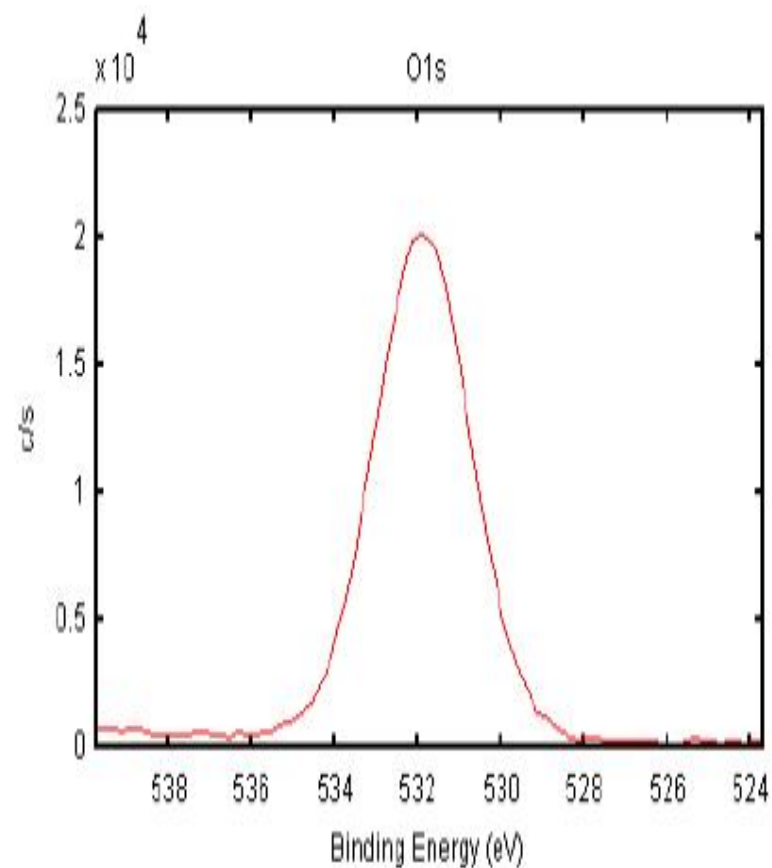
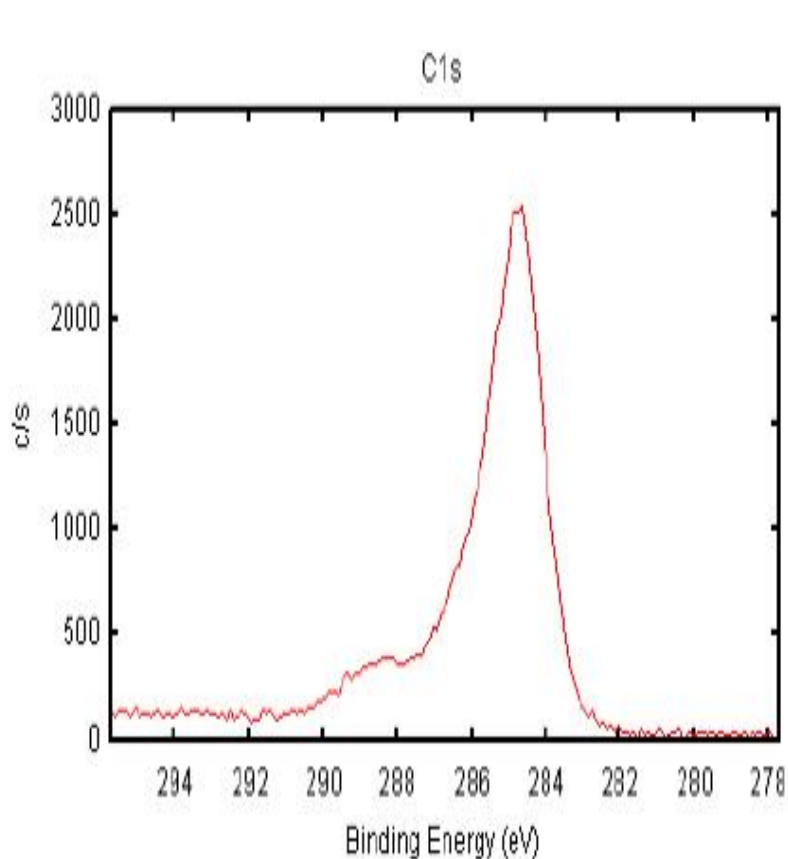
## High Resolution Analysis of CSI-06

**Figure 6: High resolution and chemical state assignments**



## High Resolution Analysis of CSI-06

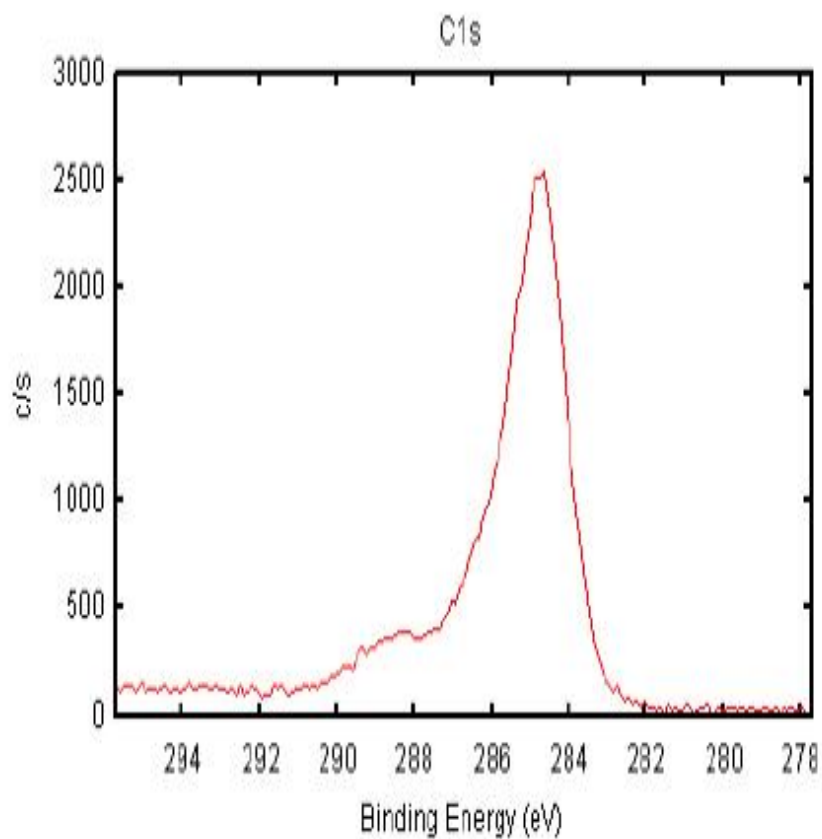
**Figure 7: High resolution and chemical state assignments**





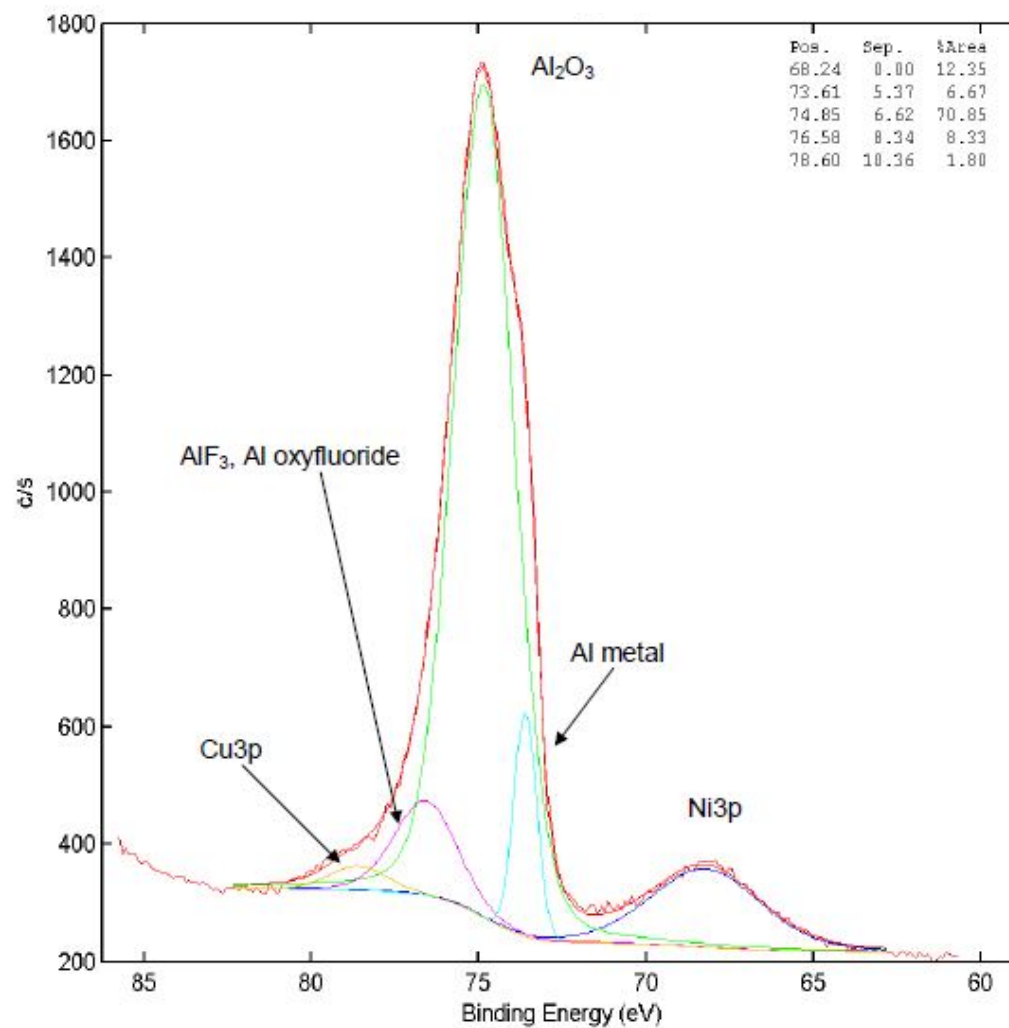
## High Resolution Analysis of CSI-06

**Figure 8: High resolution and chemical state assignments**



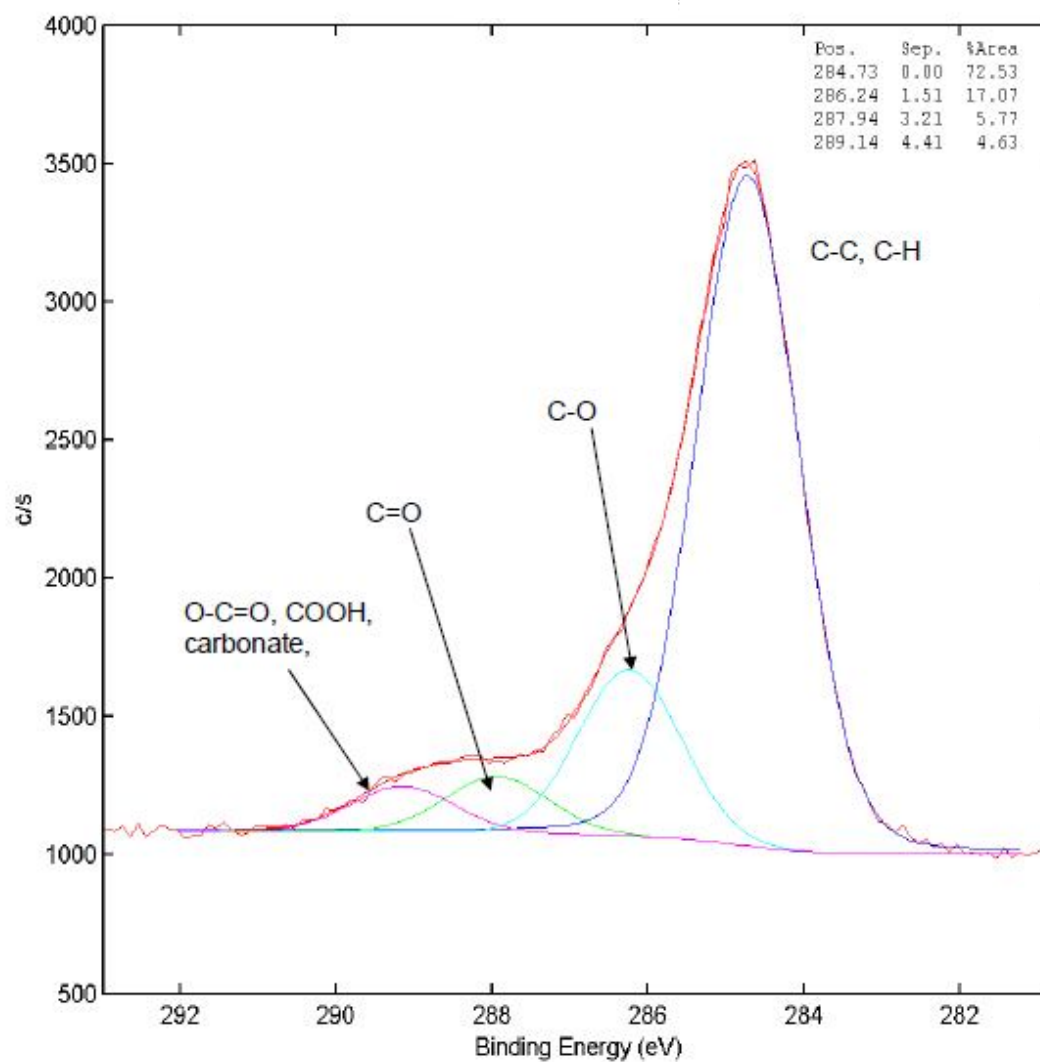
## High Resolution Analysis of CSI-06

Figure 9: High resolution and chemical state assignments



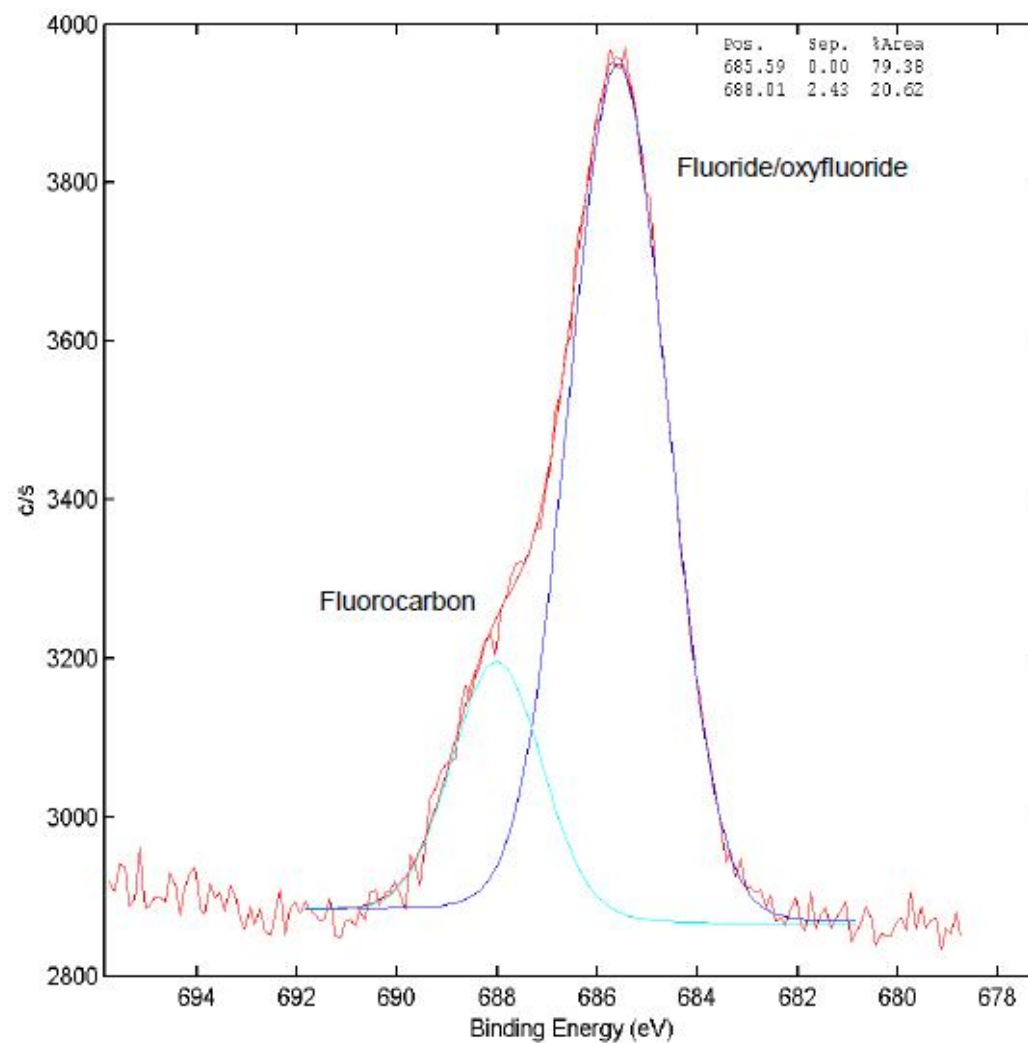
## High Resolution Analysis of CSI-06

Figure 10: High resolution and chemical state assignments



## High Resolution Analysis of CSI-06

**Figure 11: 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

<b>Instrument</b>	PHI Quantum 2000
<b>X-ray source</b>	Monochromated Al-k <sub>α</sub> 1486.6eV
<b>Acceptance Angle</b>	±23°
<b>Take-off angle</b>	45°
<b>Analysis area</b>	1400μm x 300μm
<b>Charge Correction</b>	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.