Rhodium Pyrazolate Complexes as Potential CVD Precursors

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Supplementary Material

CVD Studies: Experimental Details

Complexes **1**-**5** were assessed for use as potential MOCVD precursors. Initial investigations of their volatility and thermal stability were carried out in sealed systems under N_2 both at 1 atm. and at reduced pressure (0.1 torr). None of the complexes were found to be volatile at atmospheric pressure. Complexes **2** and **4** both decomposed in the solid state at temperatures under 100 ^oC under 1 atmosphere of N_2 and they also showed no evidence of sublimation before decomposing under vacuum.

Complexes **1**, **4**, and **5** are all volatile under reduced pressures near their melting points. **1** sublimes at ca. 154 ^oC (0.1 torr), which is in the melting point range under 1 atmosphere of N_2. The melting of **1** (1 atm. N_2) is accompanied by a darkening of the liquid however its decomposition temperature could not be determined reliably by this method. **3** sublimes at ca. 100 ^oC under reduced pressure and melted at 103-105 ^oC under 1 atm. under N_2. A transition of the melt from bright yellow to black occurs at 182-184 ^oC and this was taken as the decomposition temperature. **5** has a slightly higher melting point than **3** (1 atm. N_2), but sublimes at the same temperature (ca. 100 ^oC). Analysis of the sublimate revealed that sublimation of **5** under reduced pressure results in loss of PMe_3 and formation of **3**

Films were deposited in a horizontal hot-wall CVD reactor comprising a tube furnace surrounding a quartz tube as the deposition chamber. All other parts of the apparatus were constructed of stainless steel and utilized ¼'' VCR fittings for interconnects. The sample path was kept warm with insulated heating tape covered with glass wool. High purity argon (99.999% Matheson) and ultra-high purity hydrogen (99.9999% Praxair) were used as the carrier gases regulated with a mass flow controller (range 1-50 sccm) and a rotary-vane vacuum pump (< 0.05 torr) was used to provide reduced pressure. 400 nm SiO_2/Si(100) wafers were used as substrates. In a typical experiment a saturator was charged with 50-100 mg of a complex under a nitrogen atmosphere.

The reactor was then pumped down under vacuum and purged with argon/hydrogen several times before a final evacuation. The carrier gas was then allowed to flow through the system (5-10 sccm) while the hot zone of the reactor system was gradually heated. Once thermal equilibrium was achieved at the desired temperature, the precursor was heated to initiate evaporation. The time taken for film growth was typically 30-120 min. before the precursor flow was stopped and the reactor allowed to cool to room temperature.

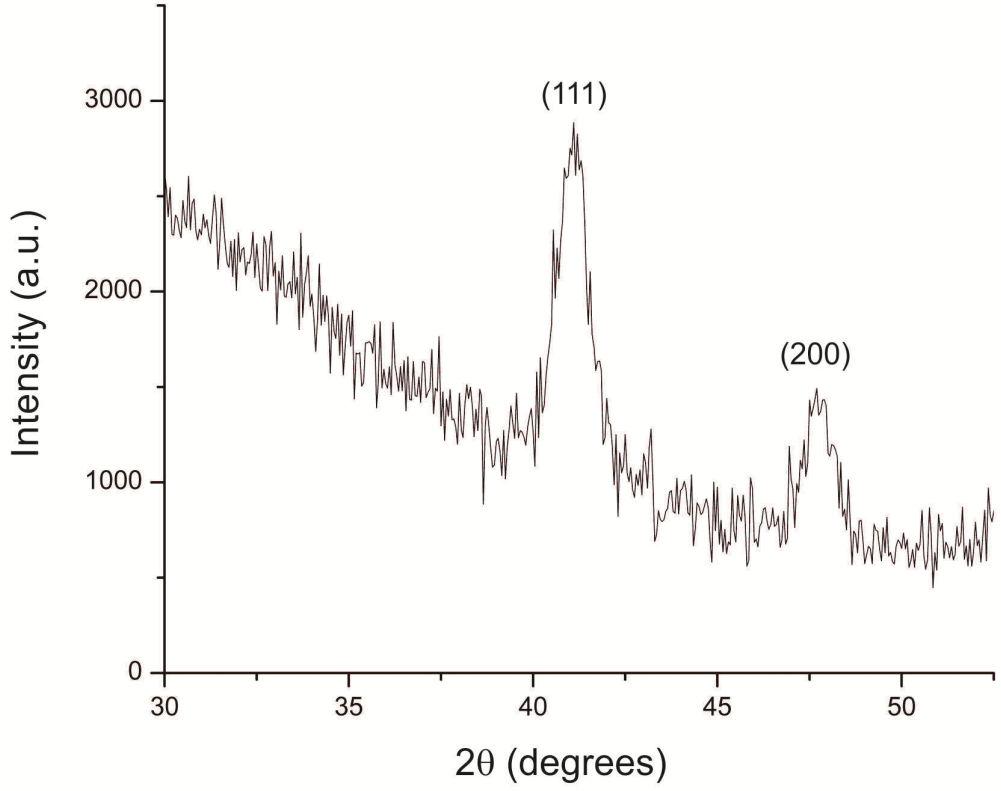
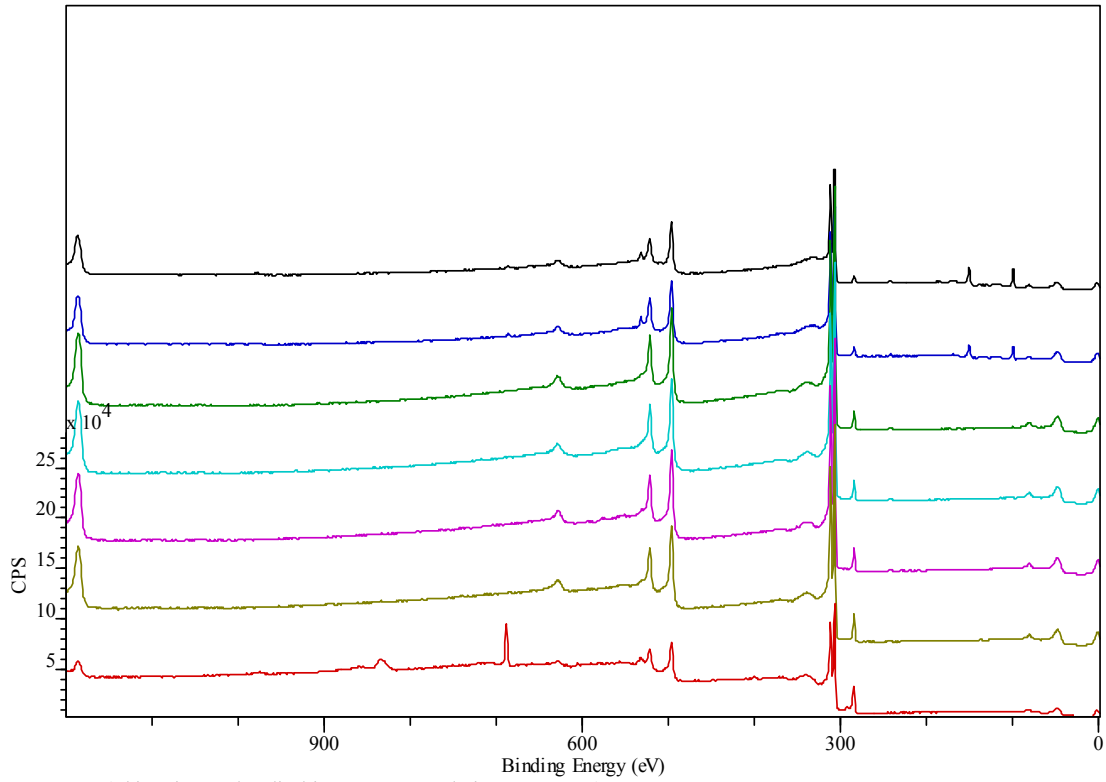


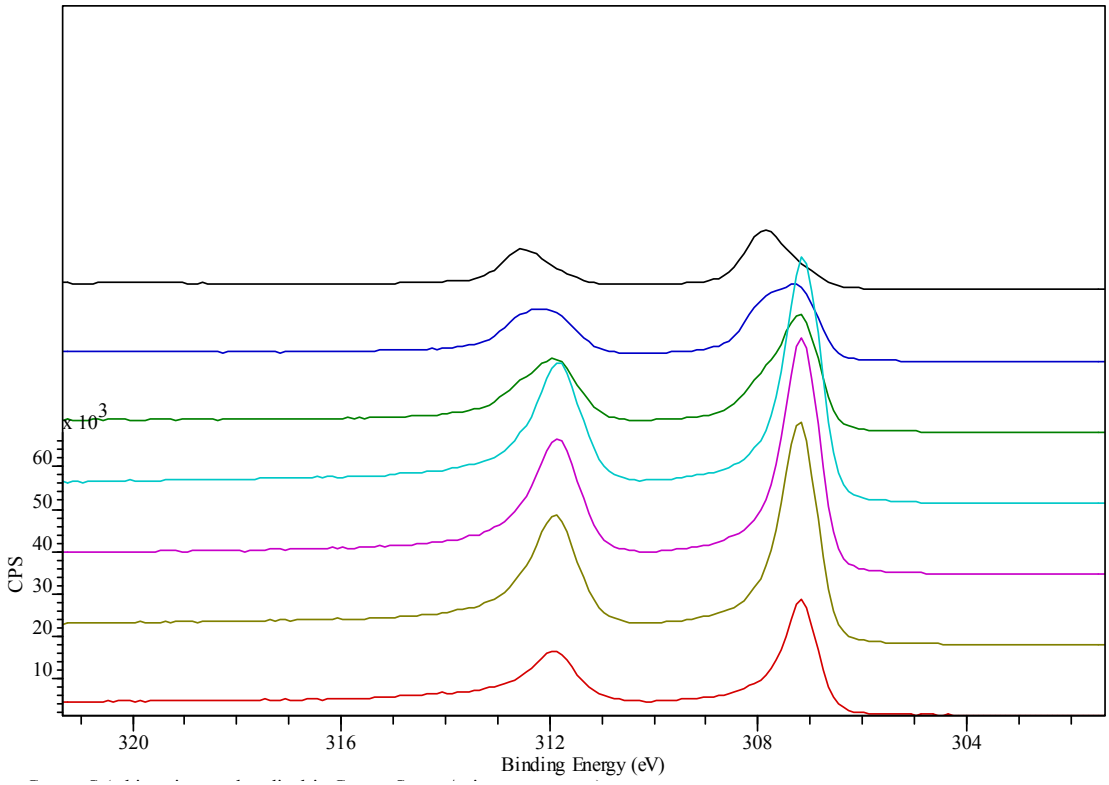
Figure S1. Low angle XRD of film grown from **1** using Ar carrier gas (flow rate 5 sccm, pressure 0.3 torr), deposition temperature of 500 °C for 60 minutes.

XPS spectroscopy of $[Rh(\eta^2\text{-}C_2H_4)_2(\mu\text{-}3,5\text{-}(CF_3)_2\text{-}Pz)]_2$ (**1**) using hydrogen carrier gas

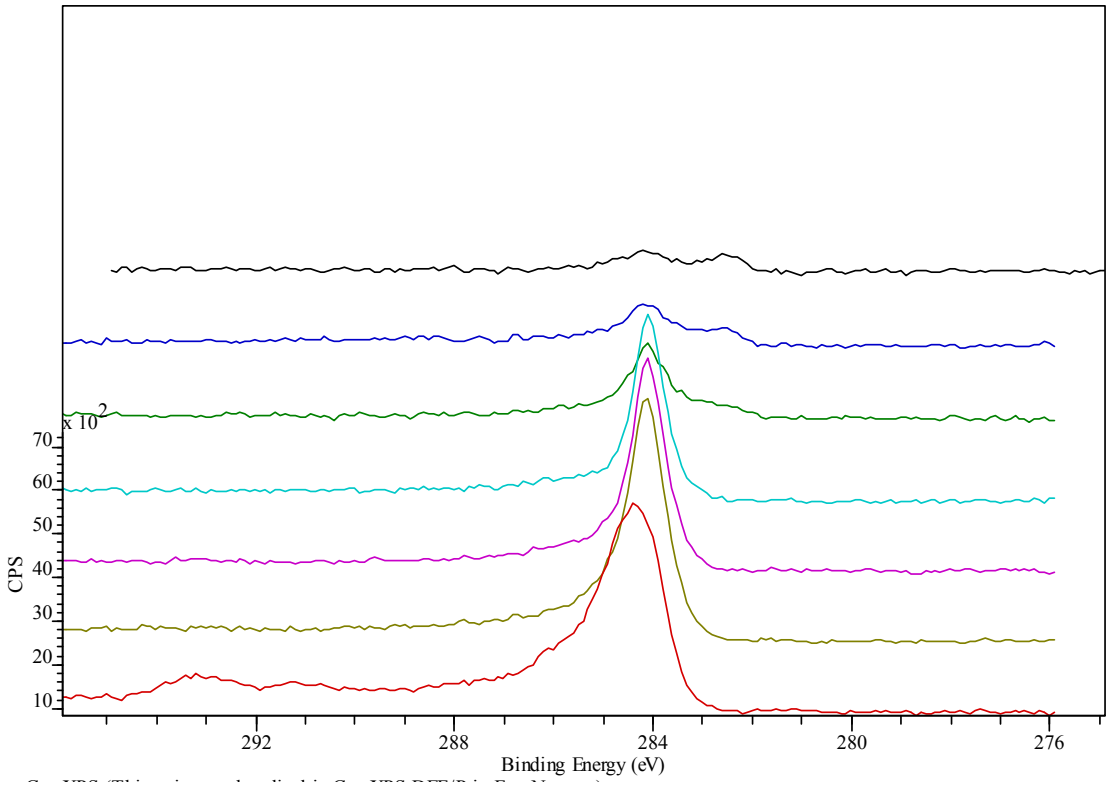
surveys of (1) from 0-300 seconds



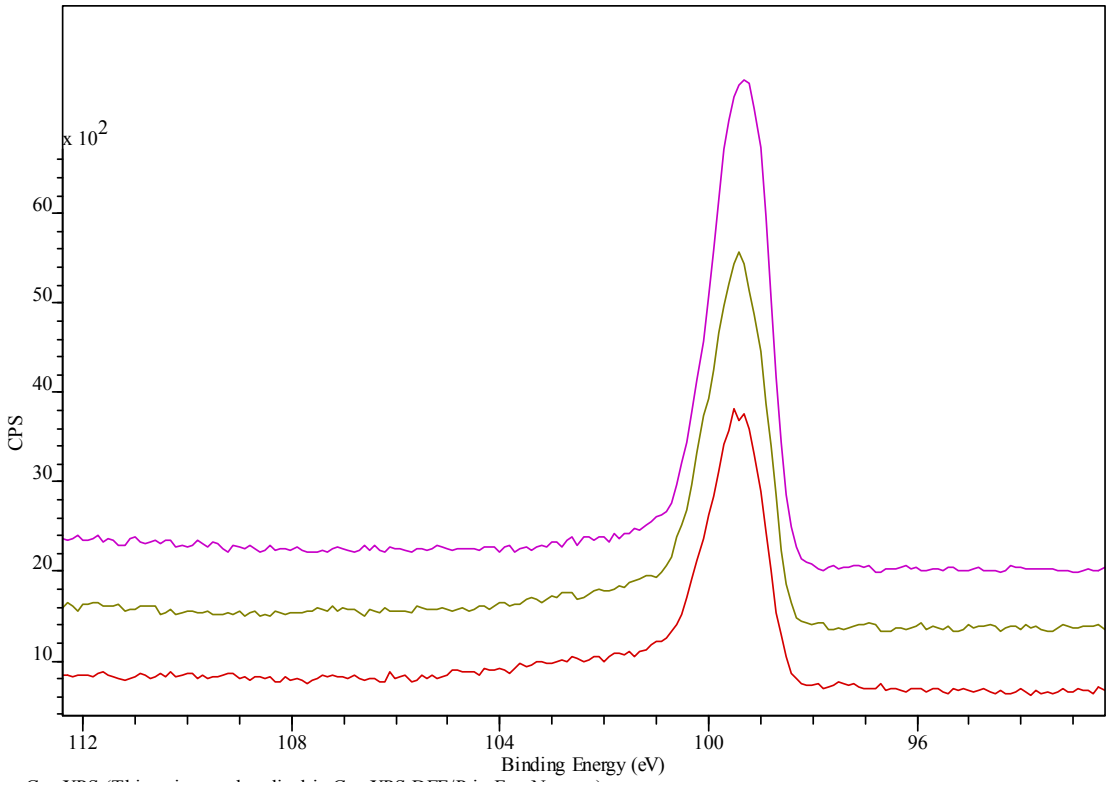
Rh 3d of (1) from 0-300 seconds



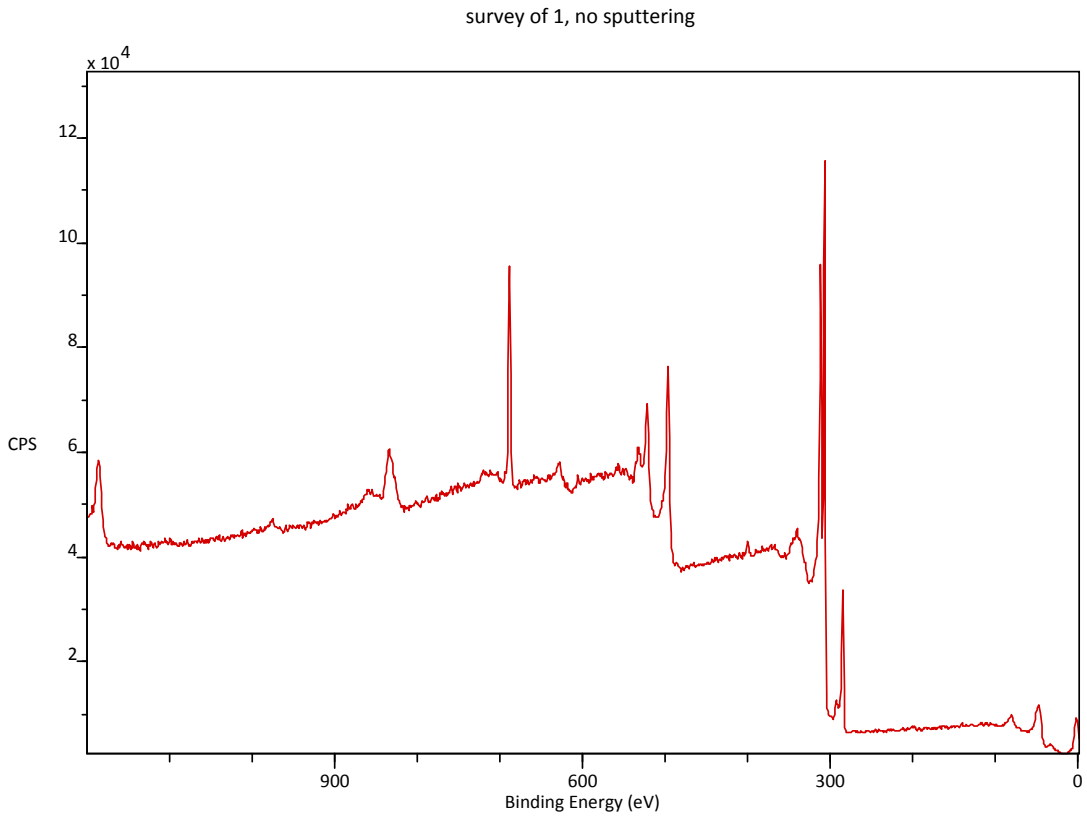
C 1s of (1) from 0-300 seconds

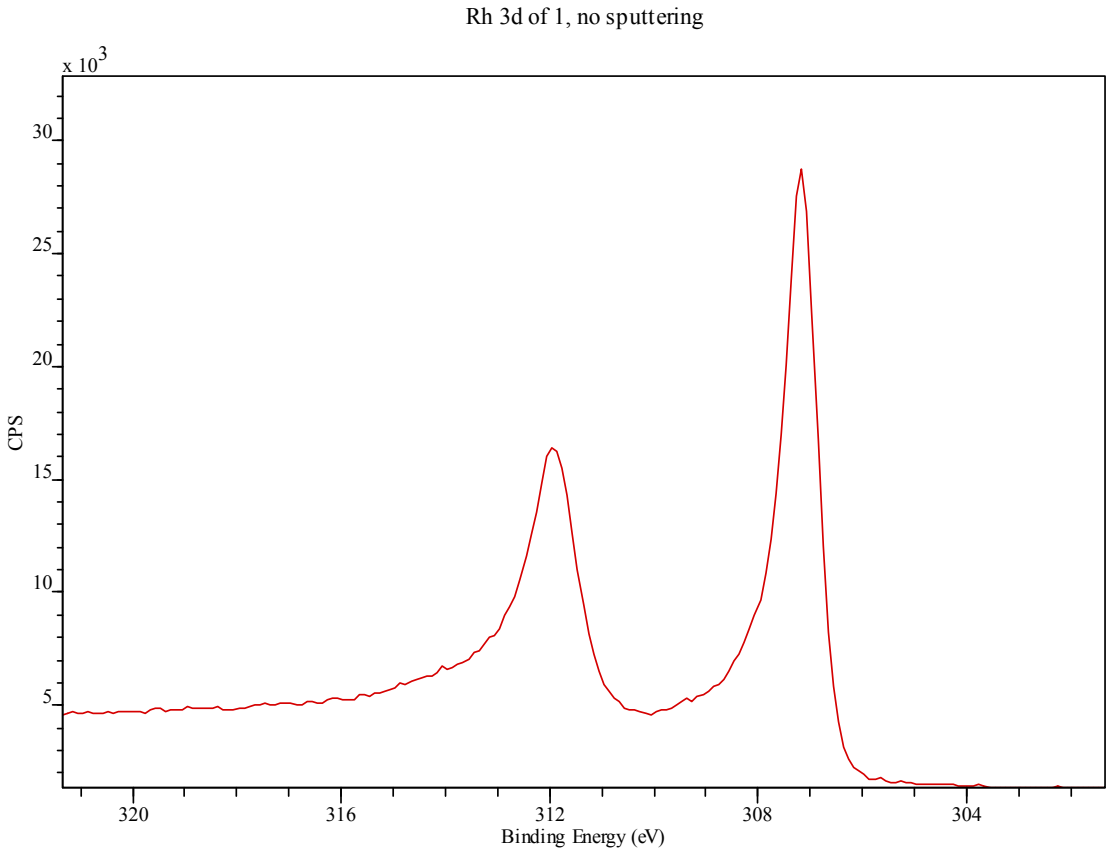


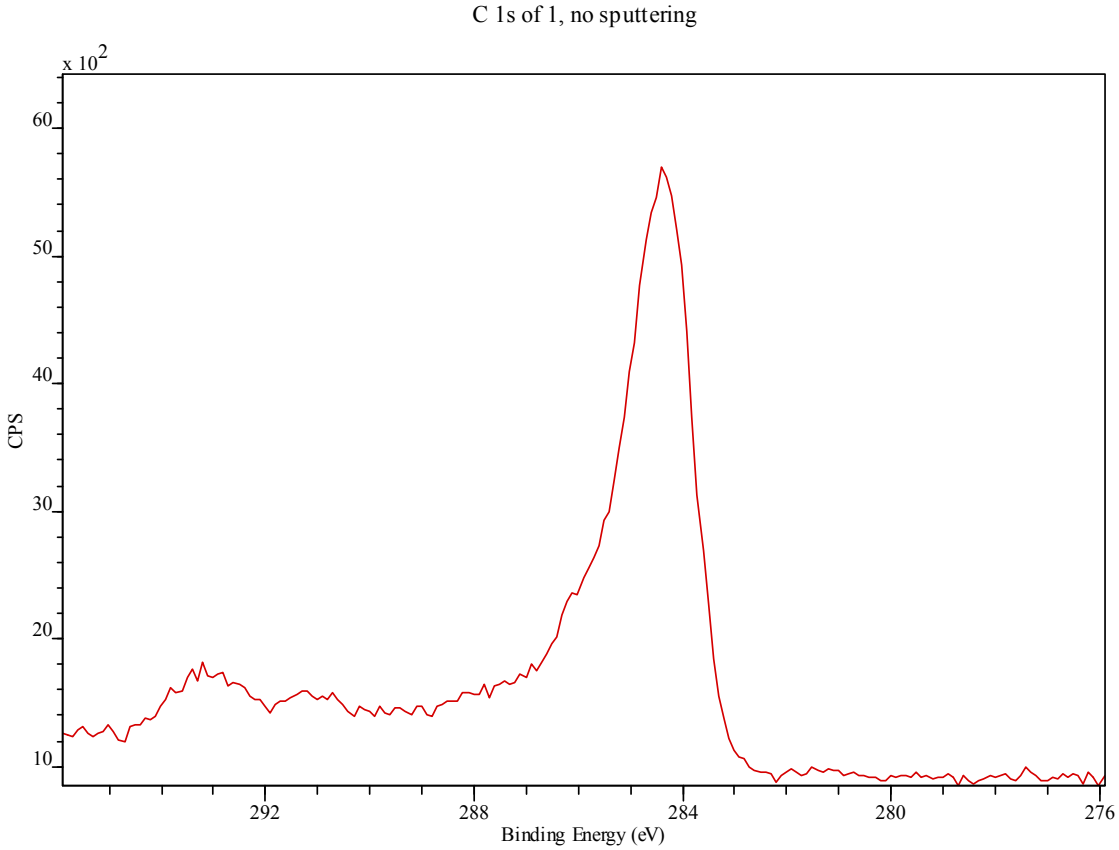
Si 2p of (1) from 210-300 seconds

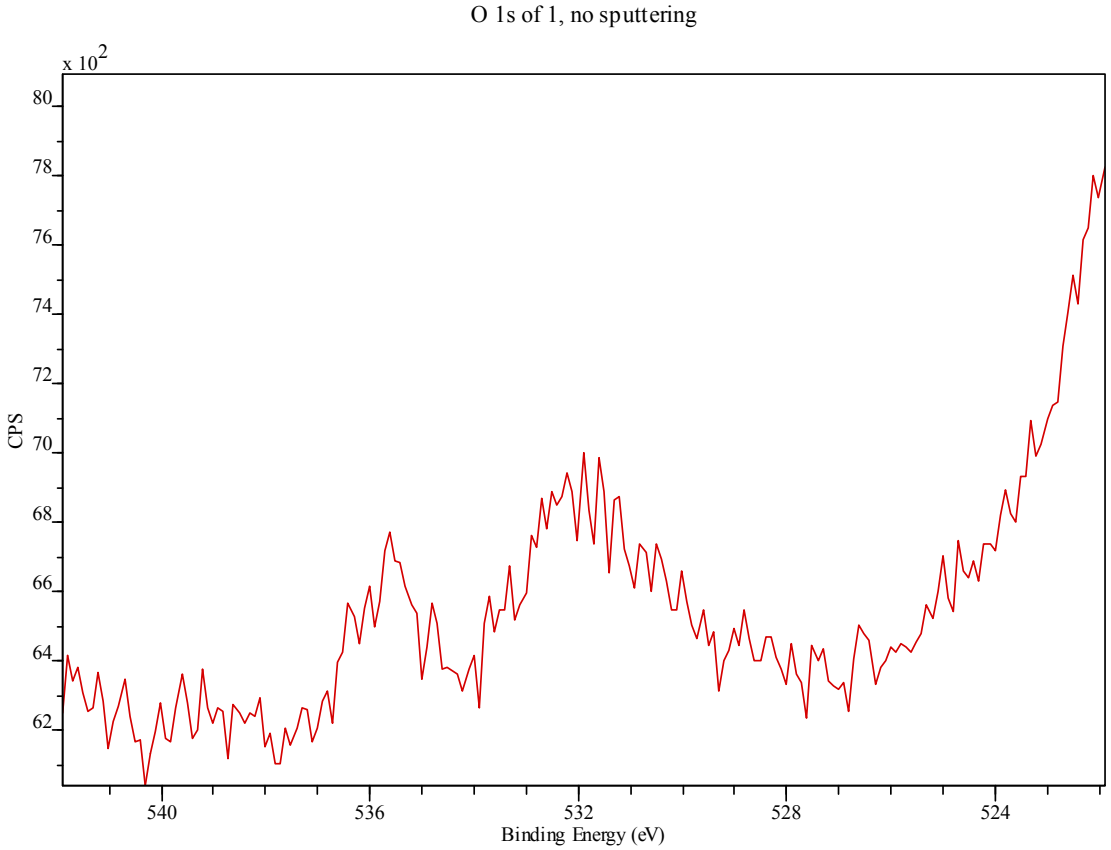


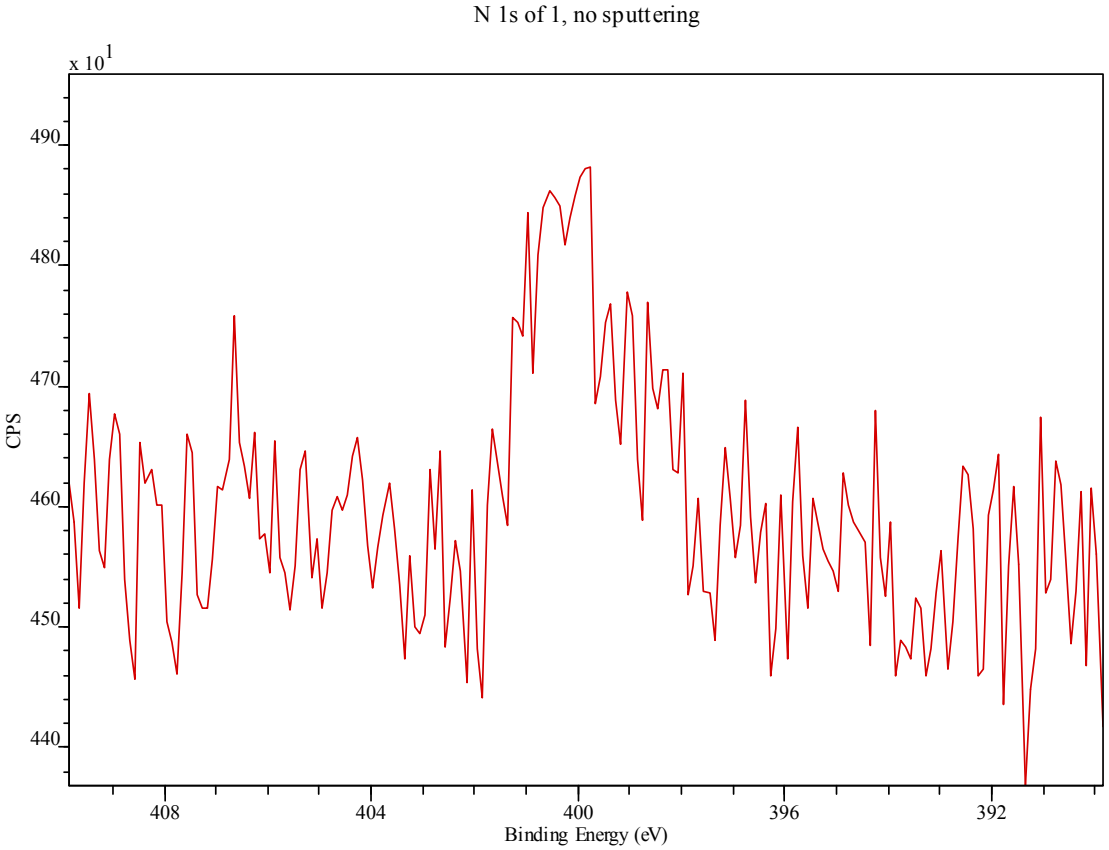
0 seconds of sputtering:

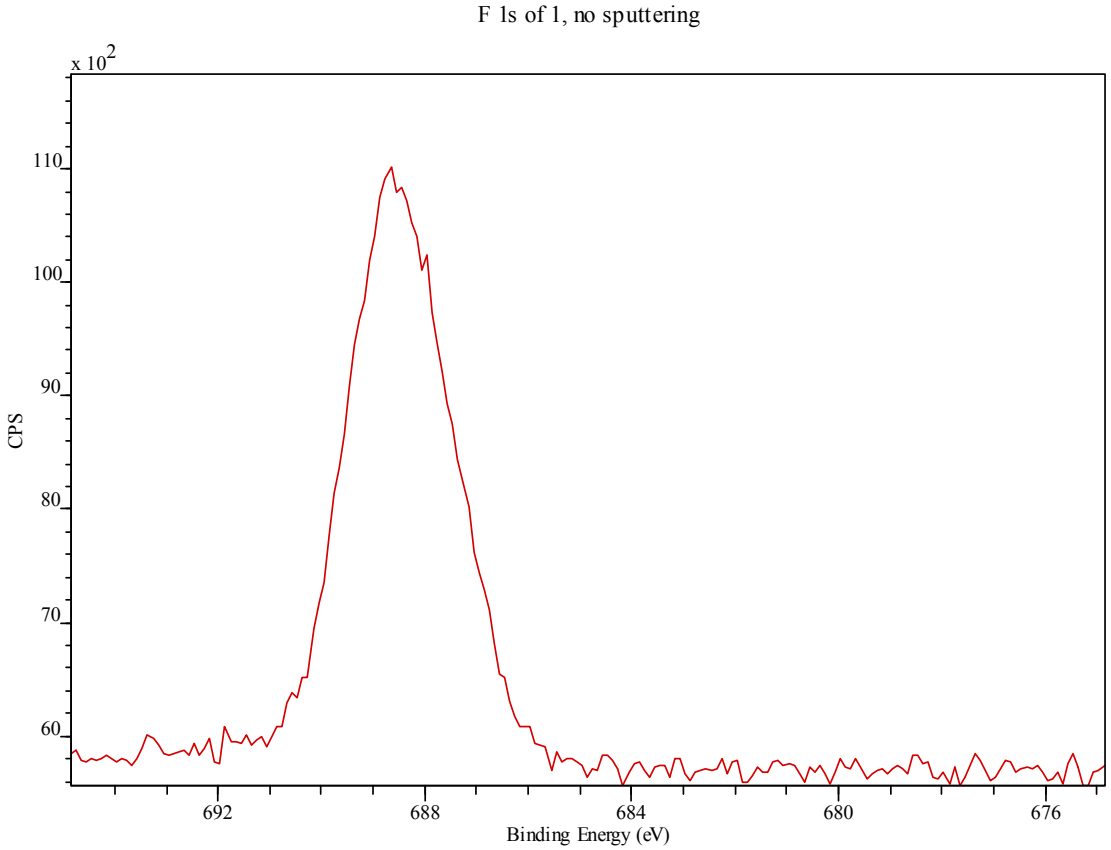



Rh 3d of 1, no sputtering
x 10^3
30
25
20
15
10
5
CPS
320
316
312
308
304
Binding Energy (eV)

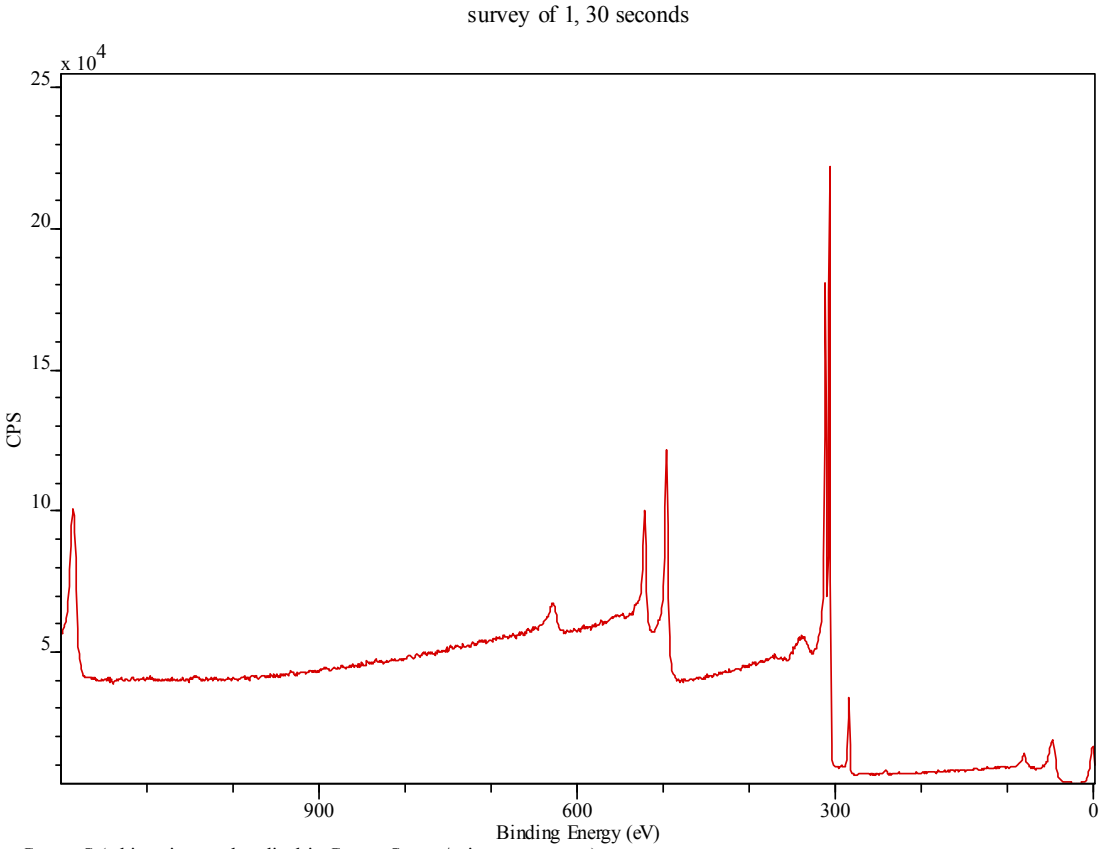

C 1s of 1, no sputtering
x 10^2
60
50
40
30
20
10
CPS
292
288
284
280
276
Binding Energy (eV)

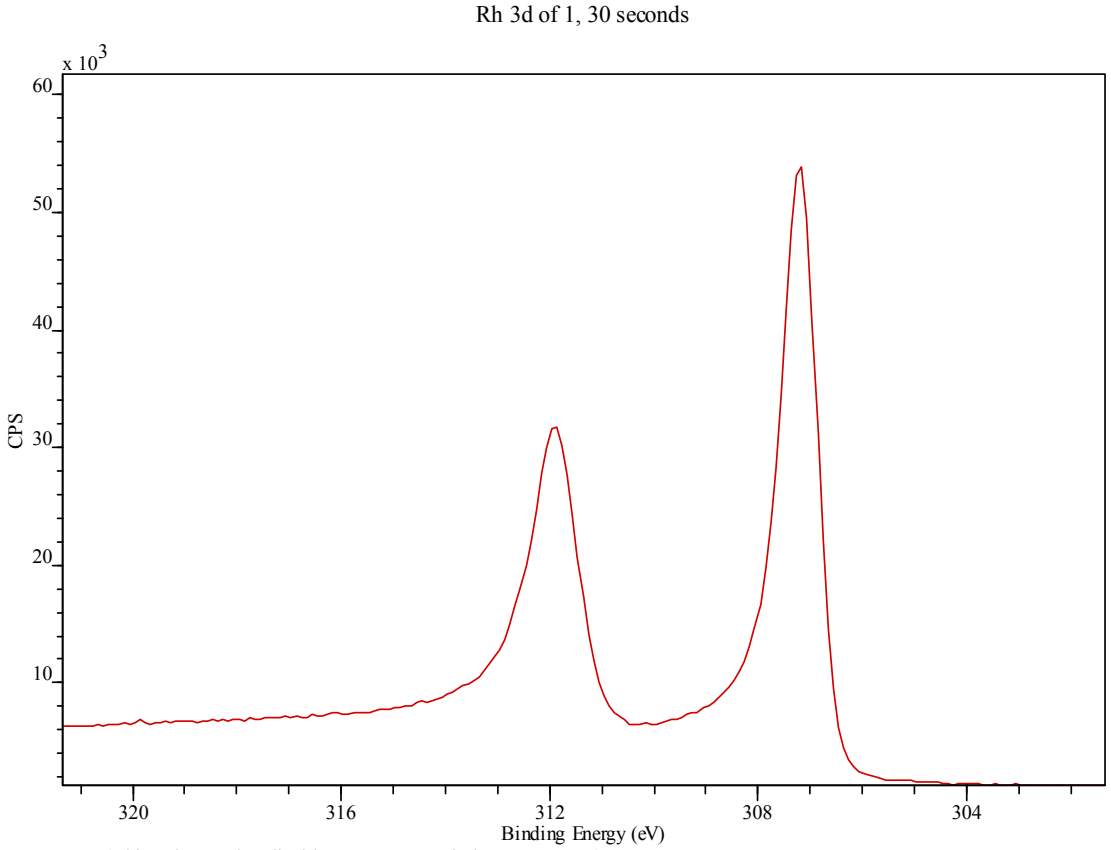

O 1s of 1, no sputtering
x 10^2
80
78
76
74
72
70
68
66
64
62
CPS
540
536
532
528
524
Binding Energy (eV)

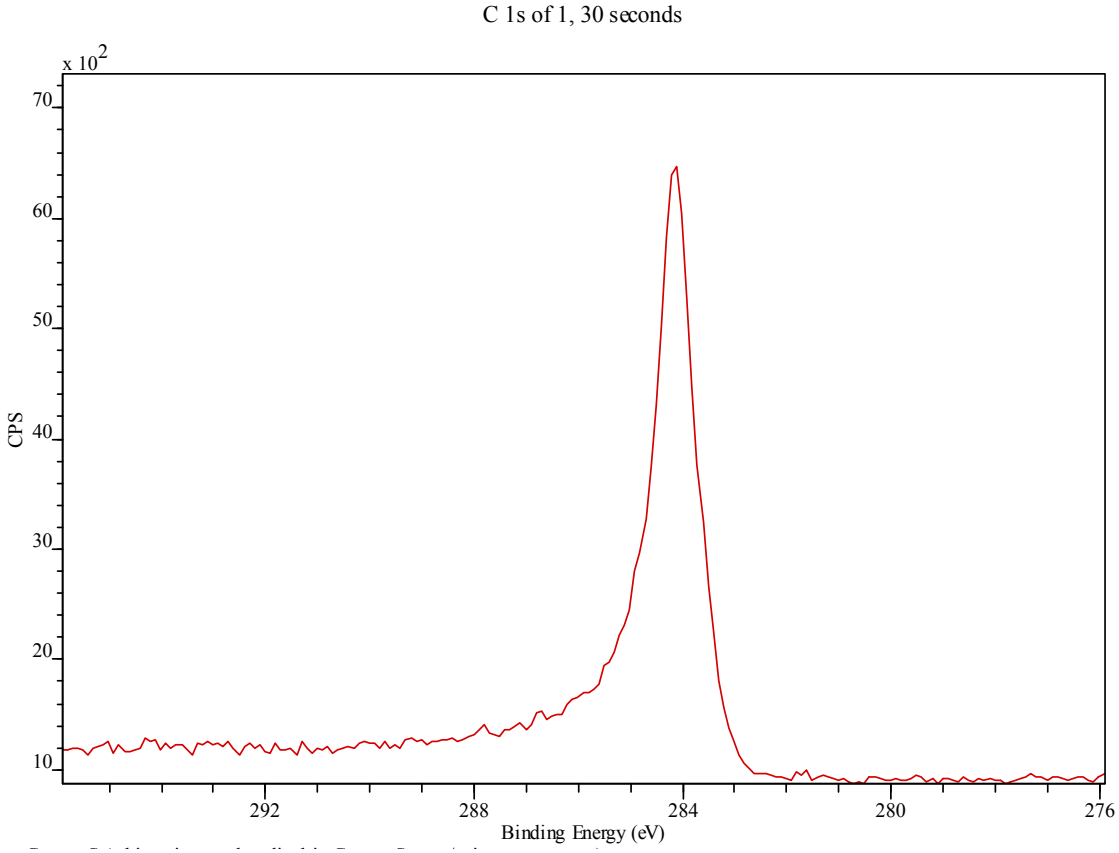

N 1s of 1, no sputtering
x 10^1
490
480
470
460
450
440
CPS
408
404
400
396
392
Binding Energy (eV)



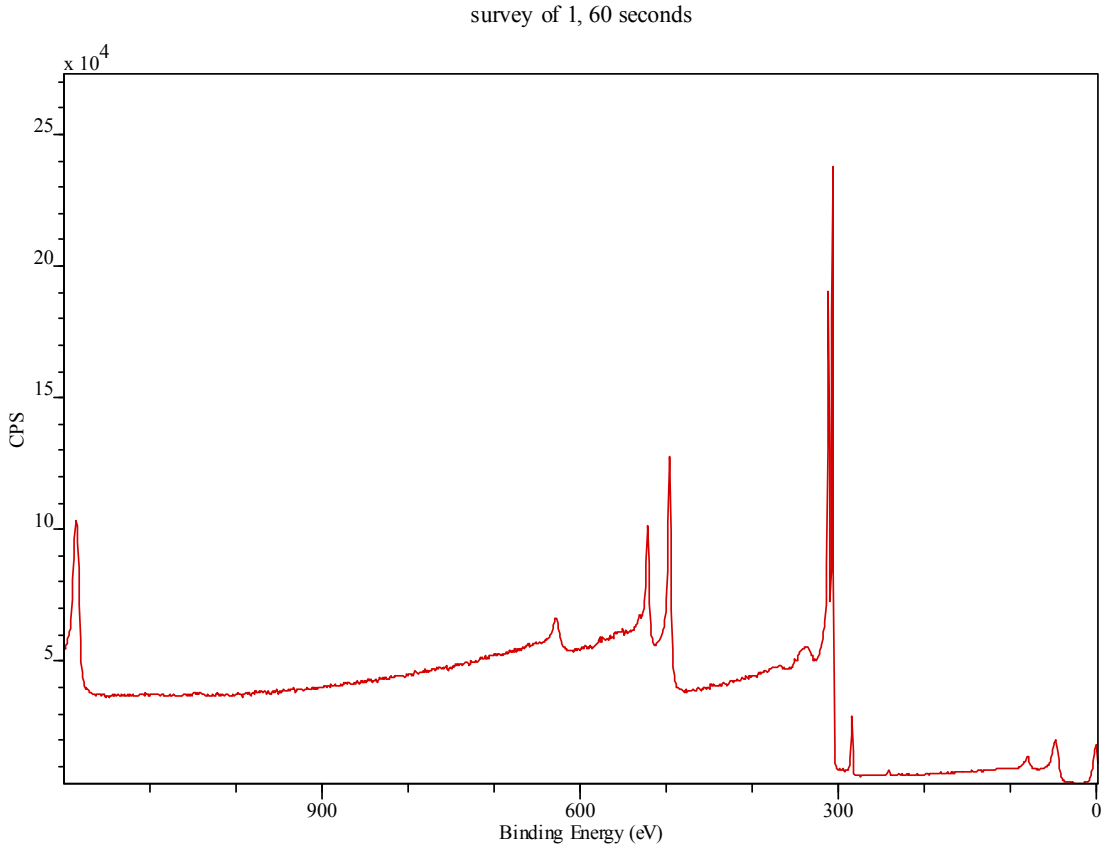
30 seconds of sputtering:

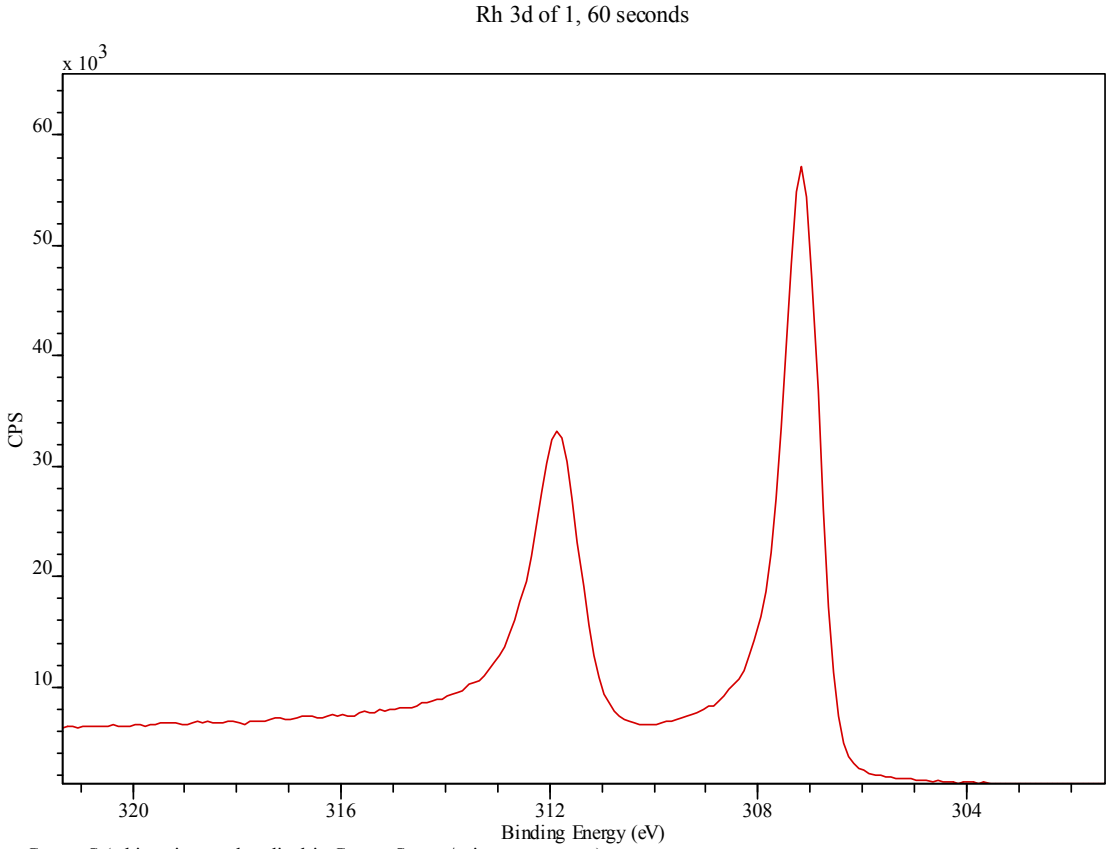

survey of 1, 30 seconds
x 10^4
25
20
15
10
5
CPS
900
600
300
0
Binding Energy (eV)

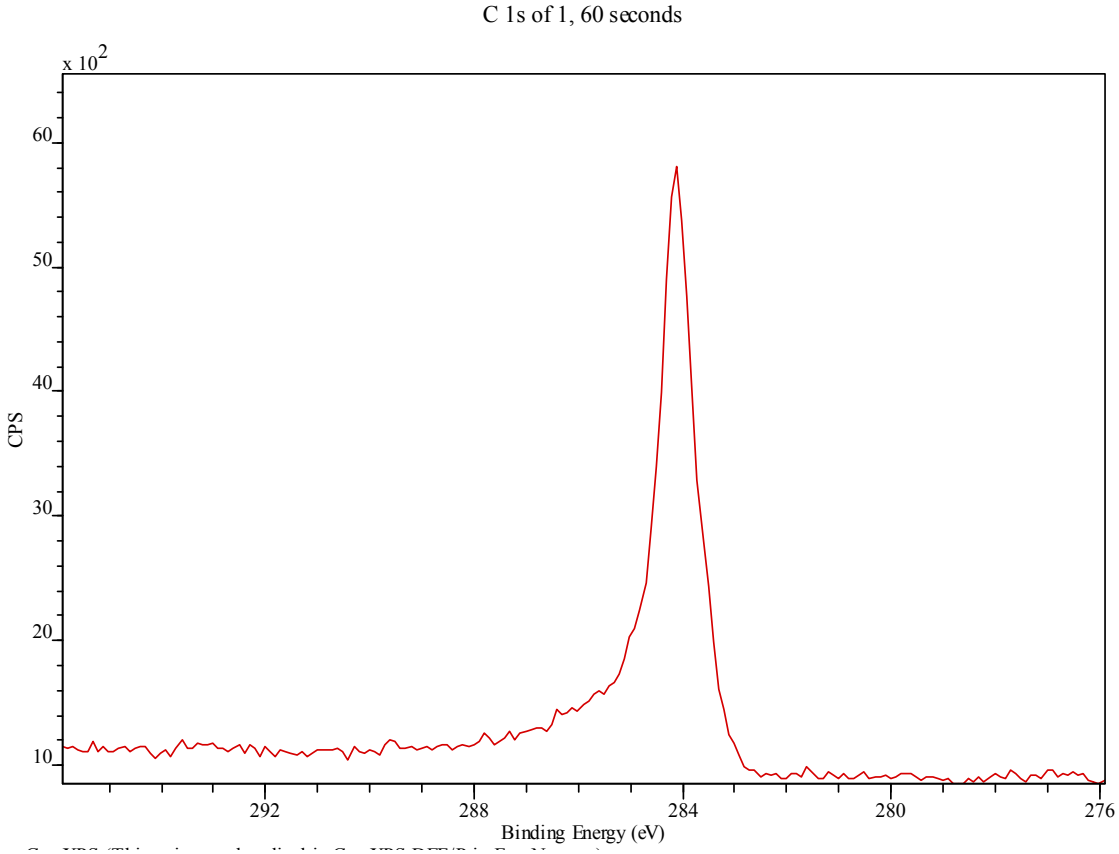

Rh 3d of 1, 30 seconds
x 10^3
60
50
40
30
20
10
CPS
320
316
312
308
304
Binding Energy (eV)



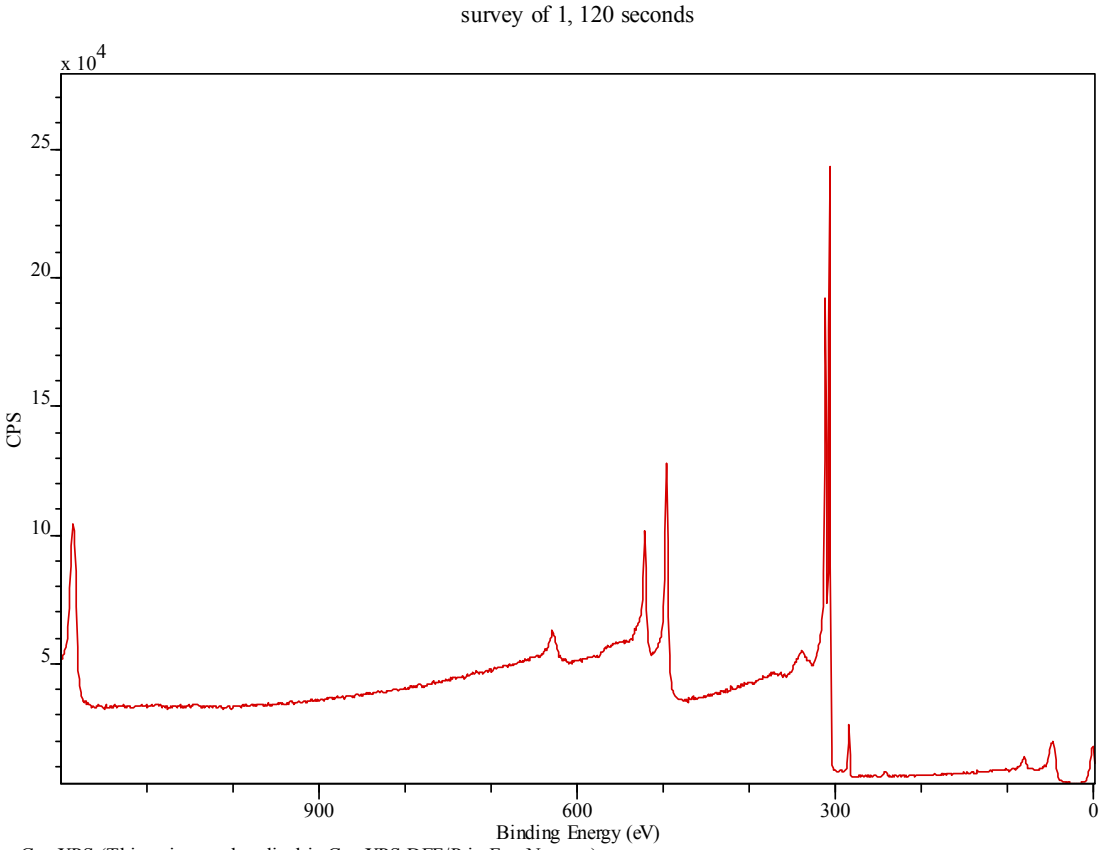
60 seconds of sputtering:

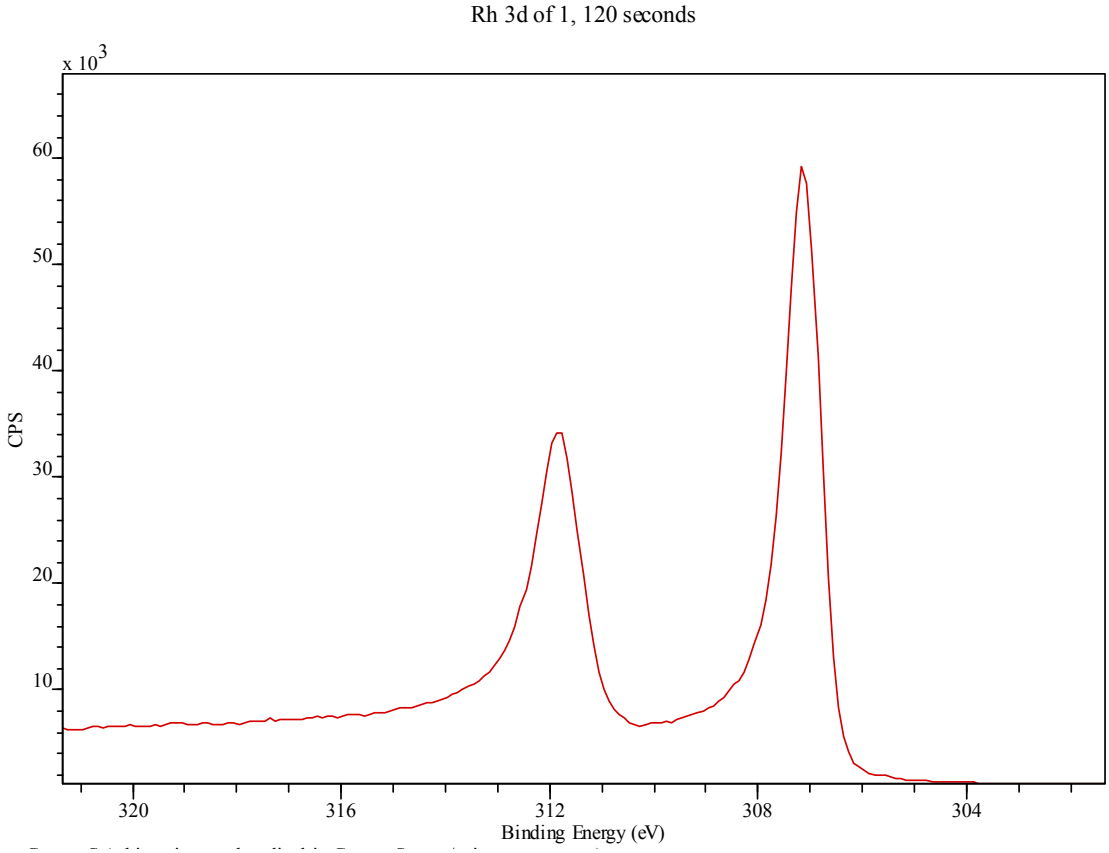


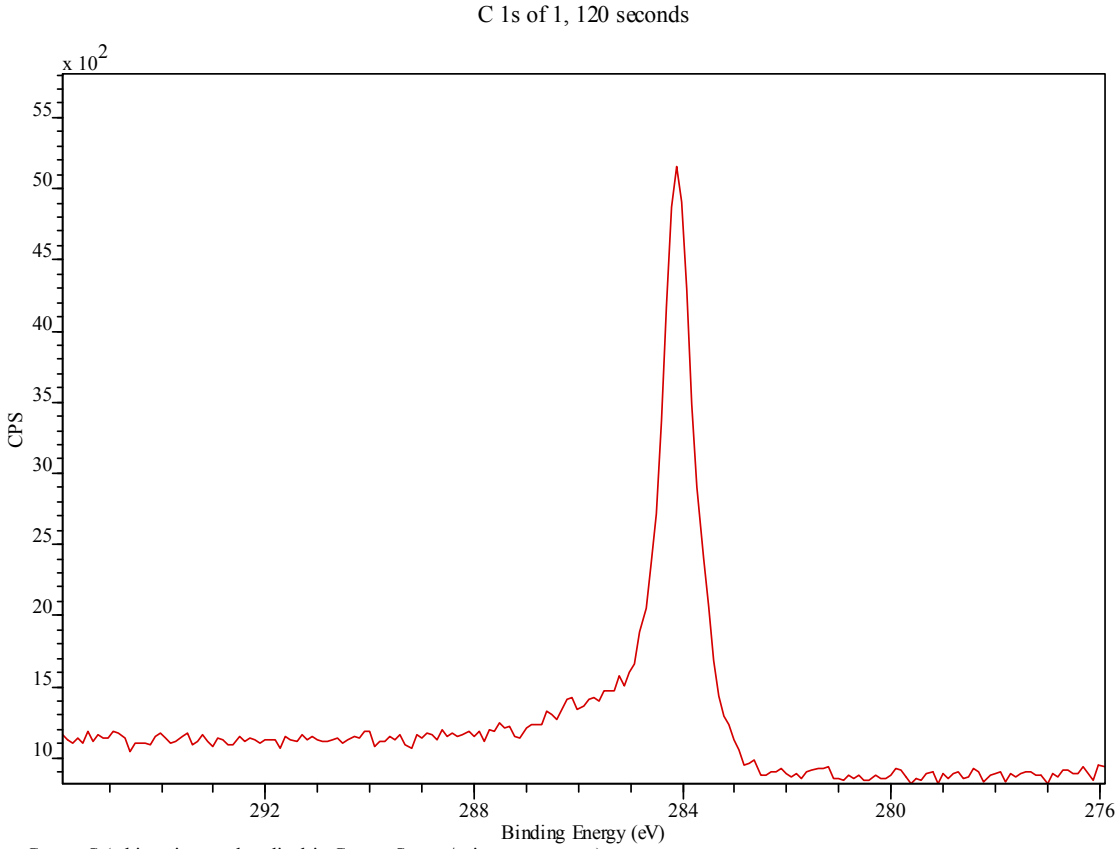

Rh 3d of 1, 60 seconds
x 10^3
60
50
40
30
20
10
CPS
320
316
312
308
304
Binding Energy (eV)



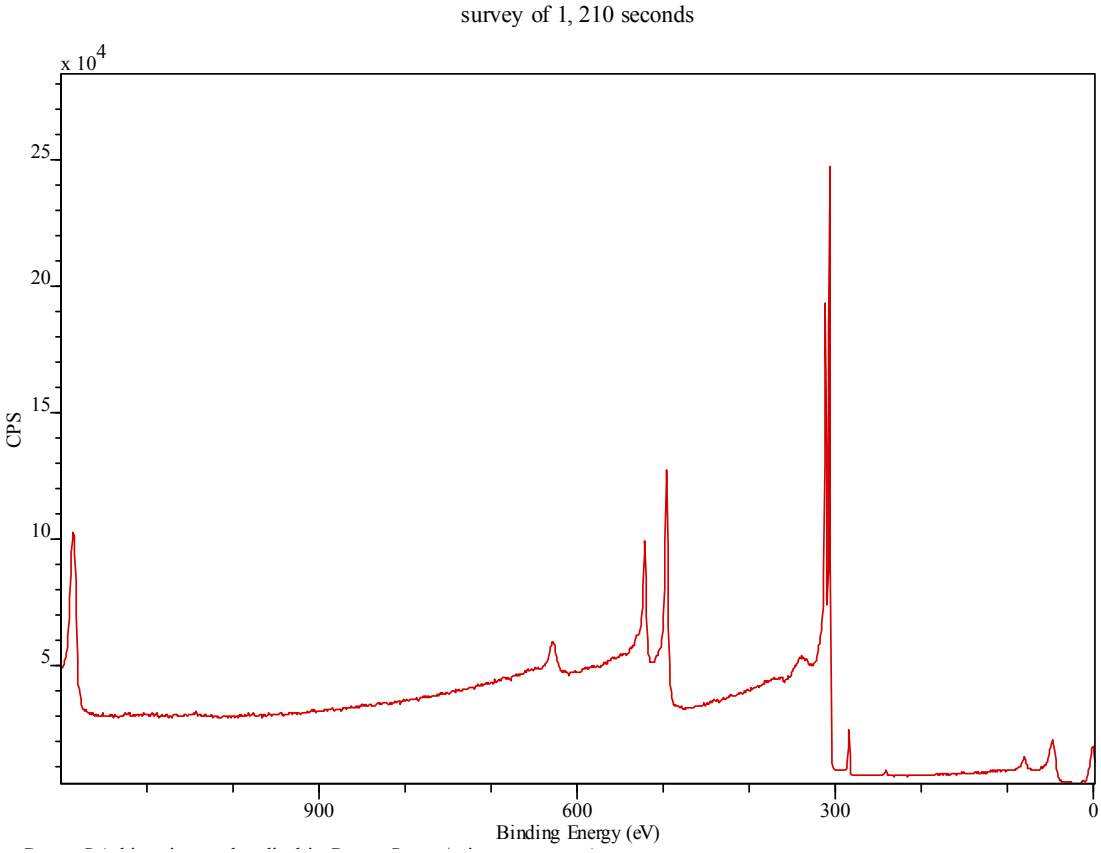
120 seconds of sputtering:

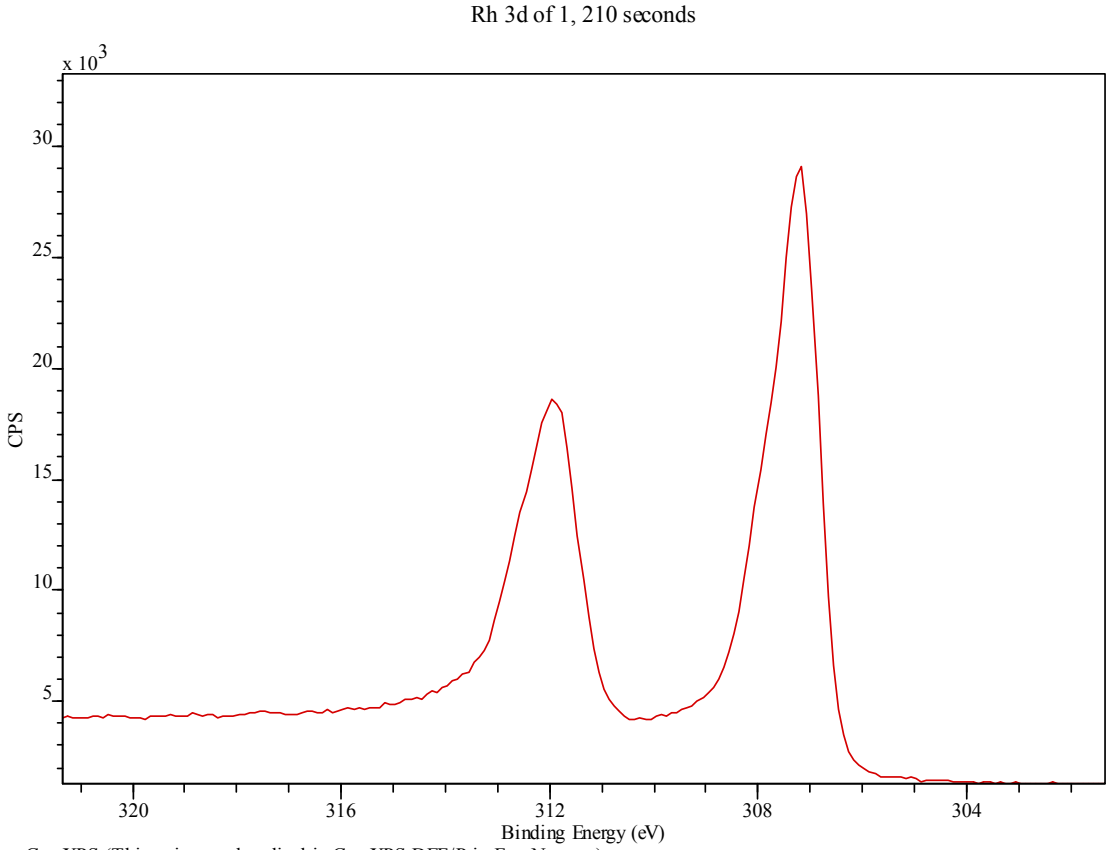

survey of 1, 120 seconds
x 10^4
25
20
15
10
5
CPS
900
600
300
0
Binding Energy (eV)

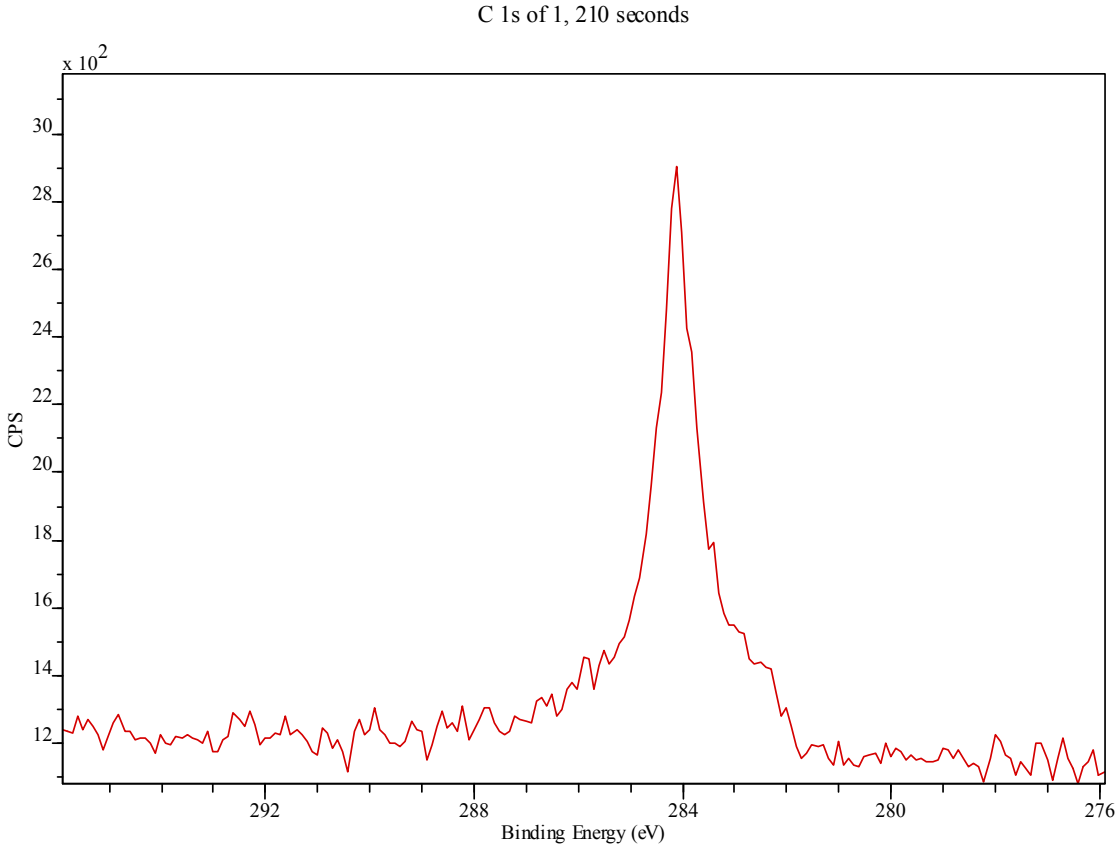

Rh 3d of 1, 120 seconds
x 10^3
60
50
40
30
20
10
CPS
320
316
312
308
304
Binding Energy (eV)

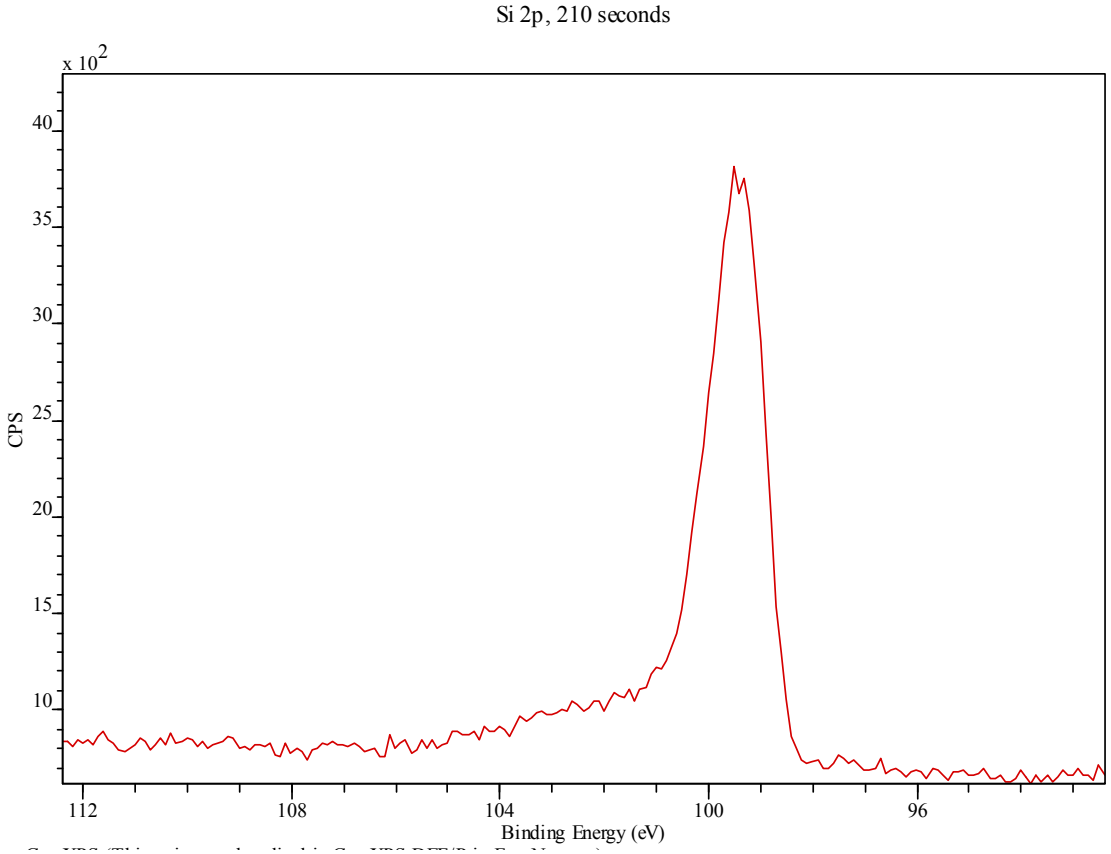


210 seconds of sputtering:

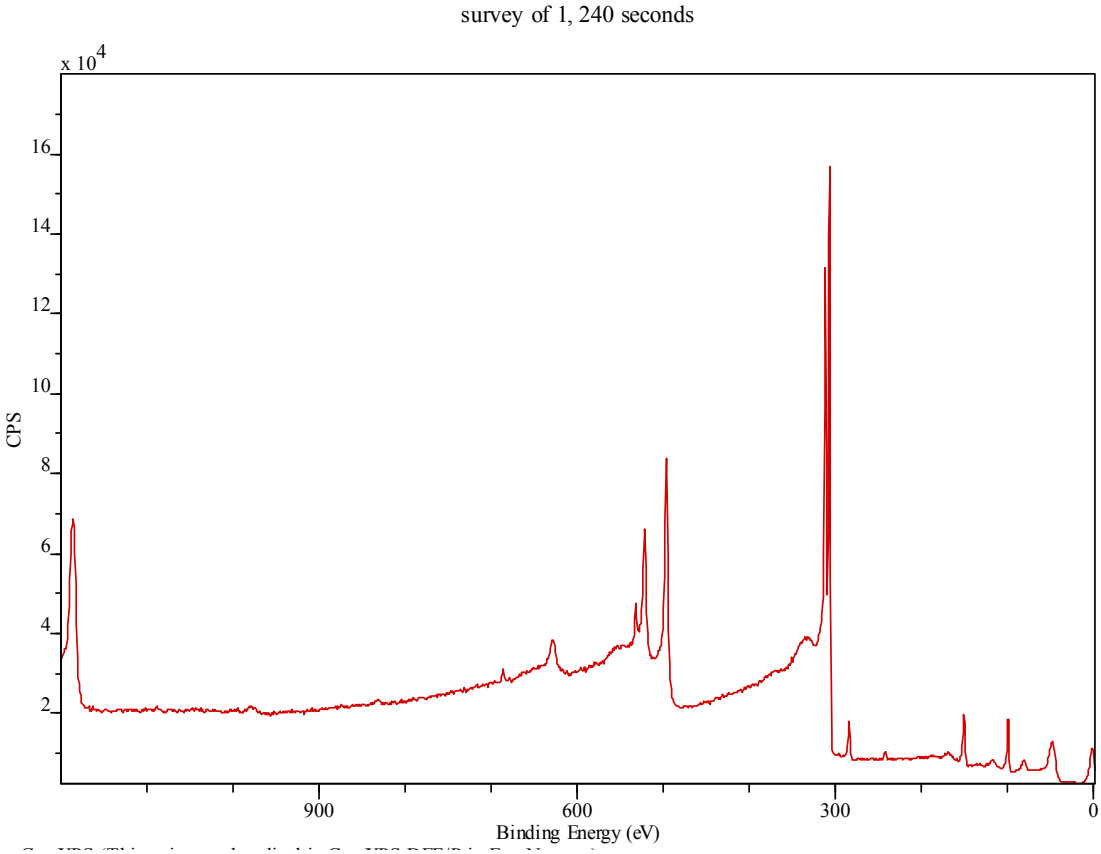

survey of 1, 210 seconds
x 10^4
25
20
15
10
5
CPS
900
600
300
0
Binding Energy (eV)

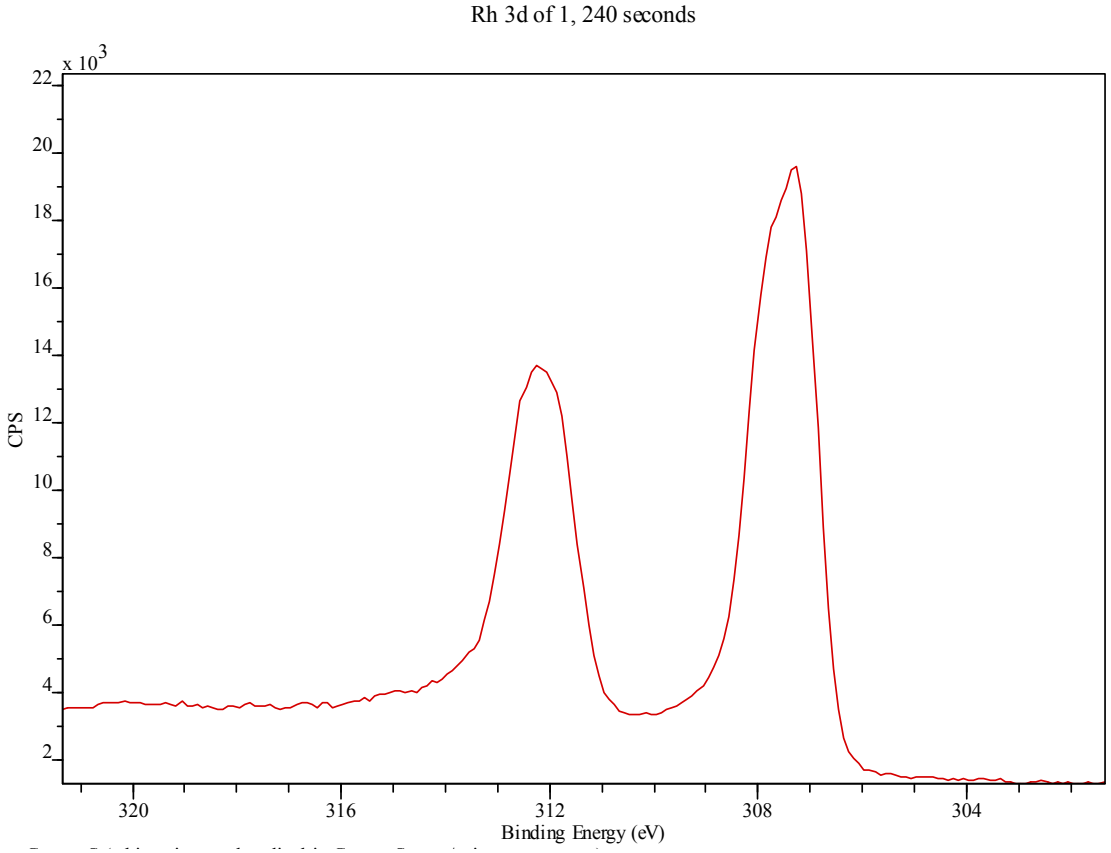

Rh 3d of 1, 210 seconds
x 10^3
30
25
20
15
10
5
CPS
320
316
312
308
304
Binding Energy (eV)

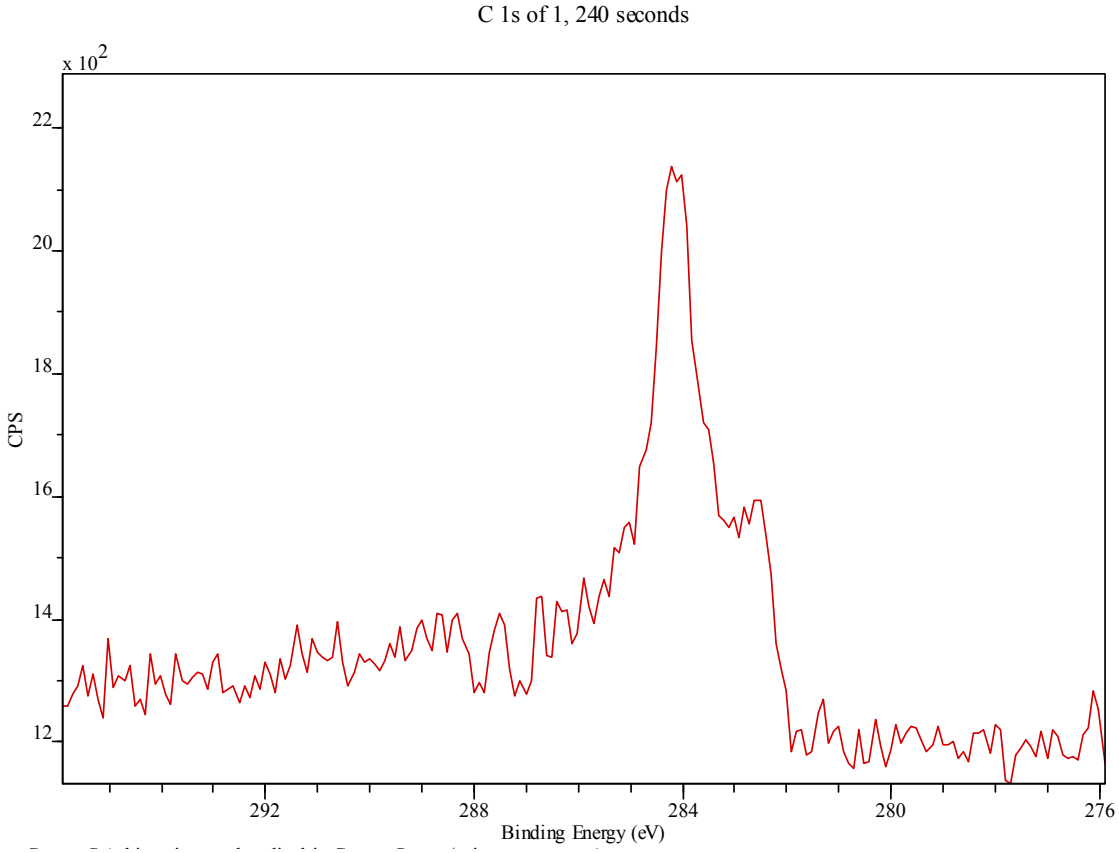


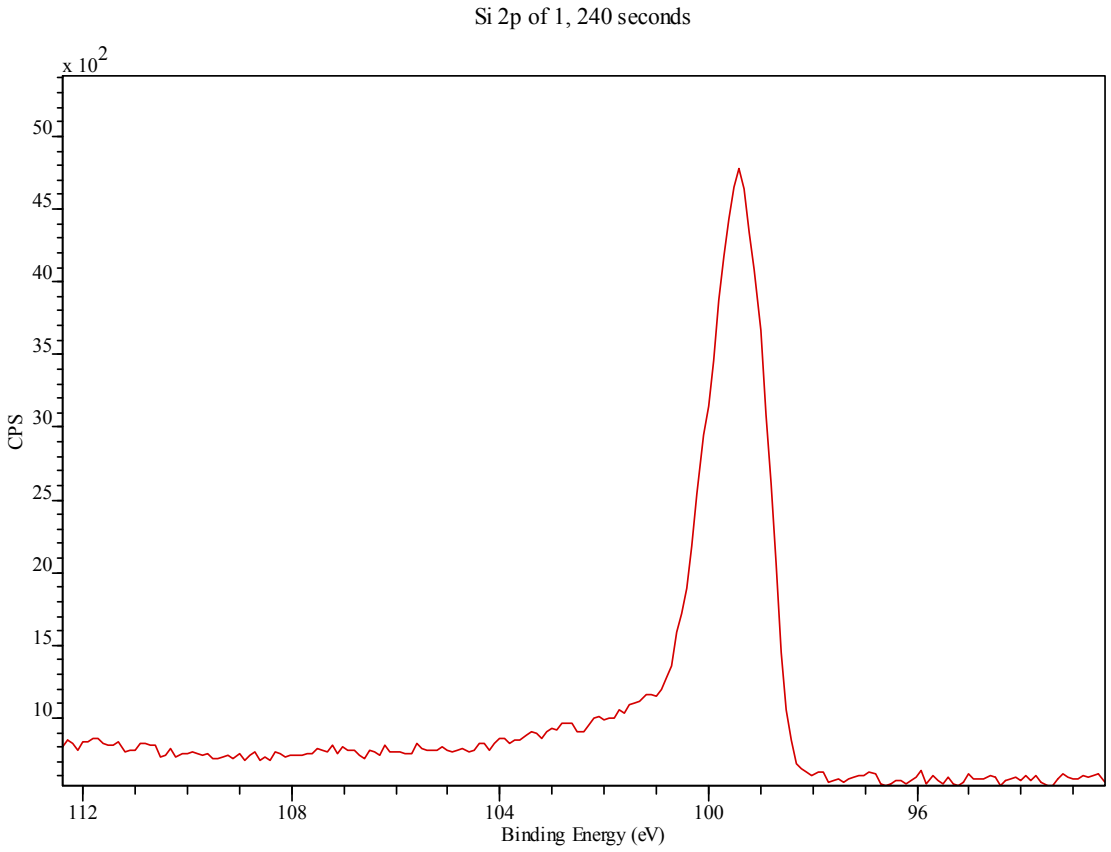


240 seconds of sputtering:

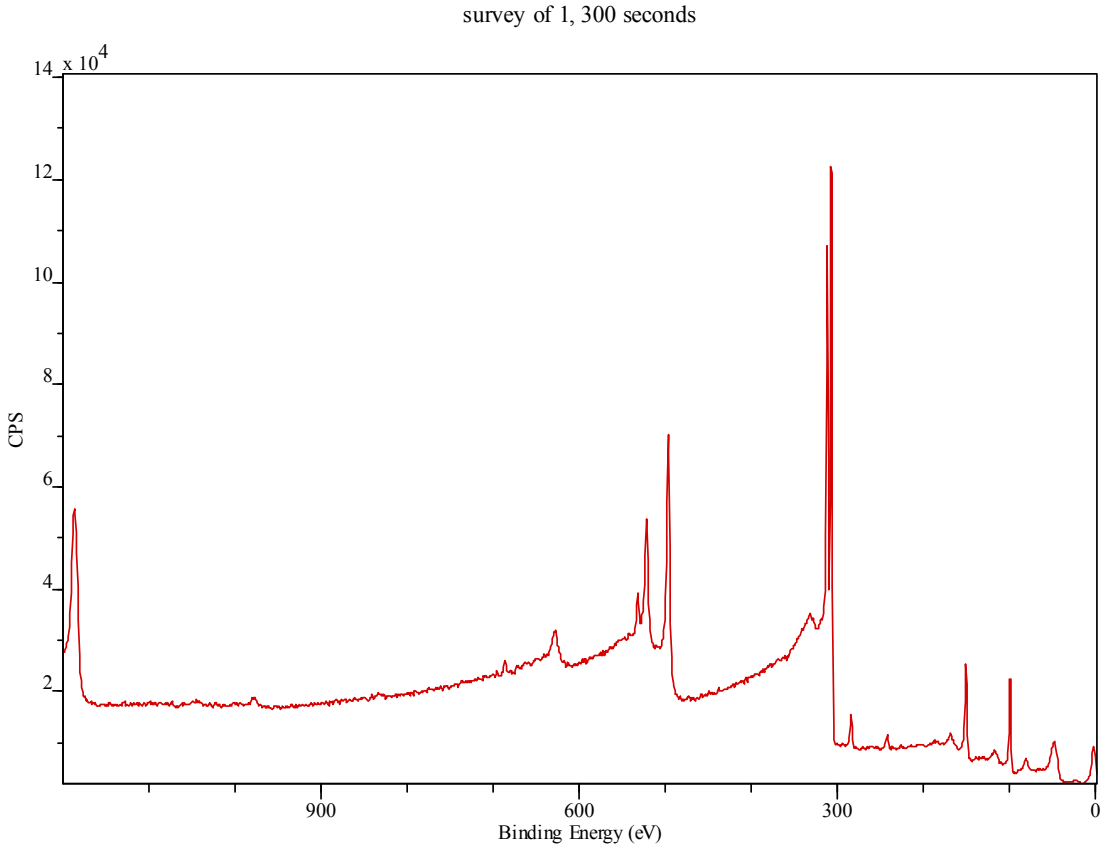

survey of 1, 240 seconds
x 10^4
16
14
12
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

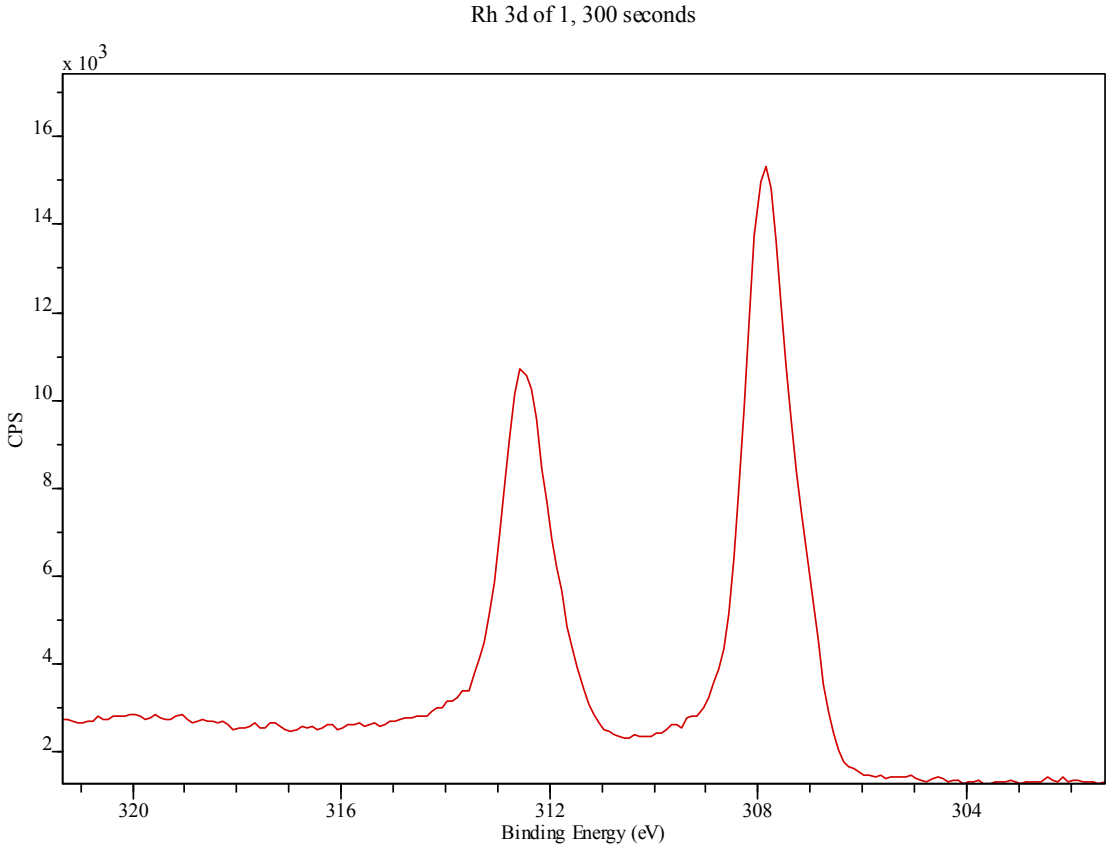

Rh 3d of 1, 240 seconds
x 10^3
22
20
18
16
14
12
10
8
6
4
2
CPS
320
316
312
308
304
Binding Energy (eV)

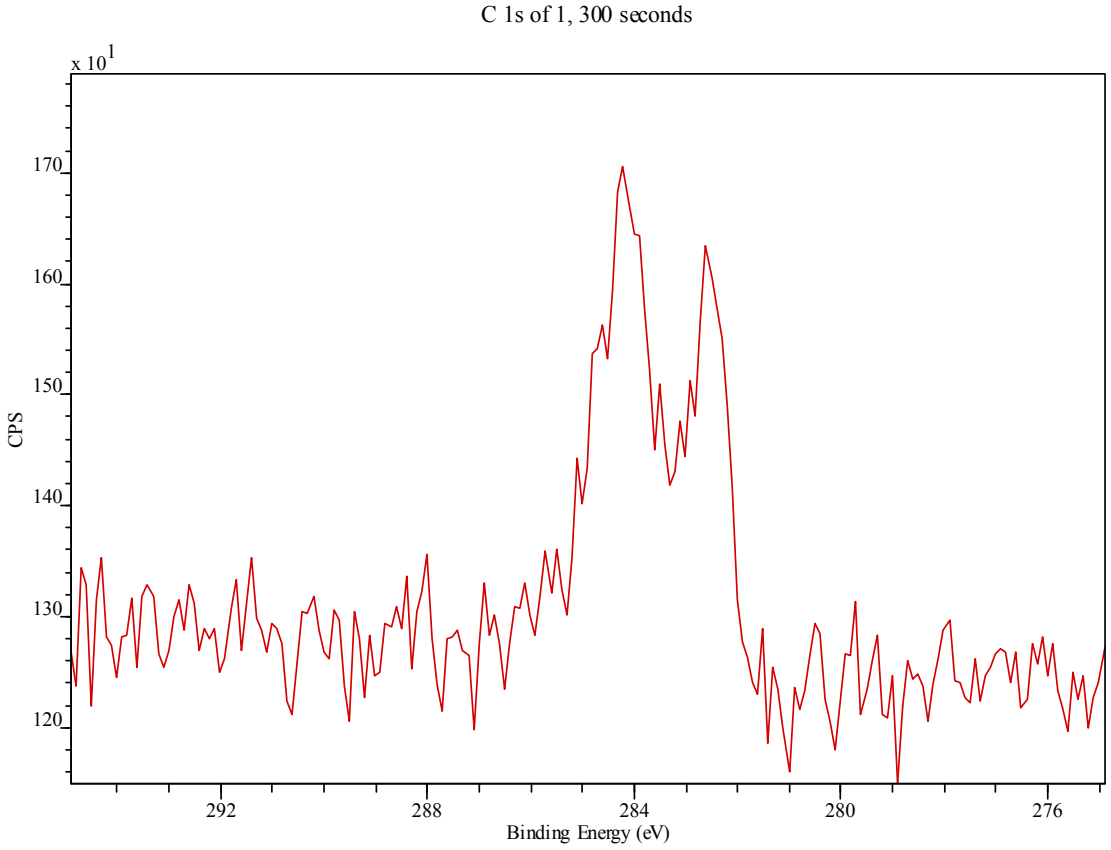

C 1s of 1, 240 seconds
x 10^2
22
20
18
16
14
12
CPS
292
288
284
280
276
Binding Energy (eV)

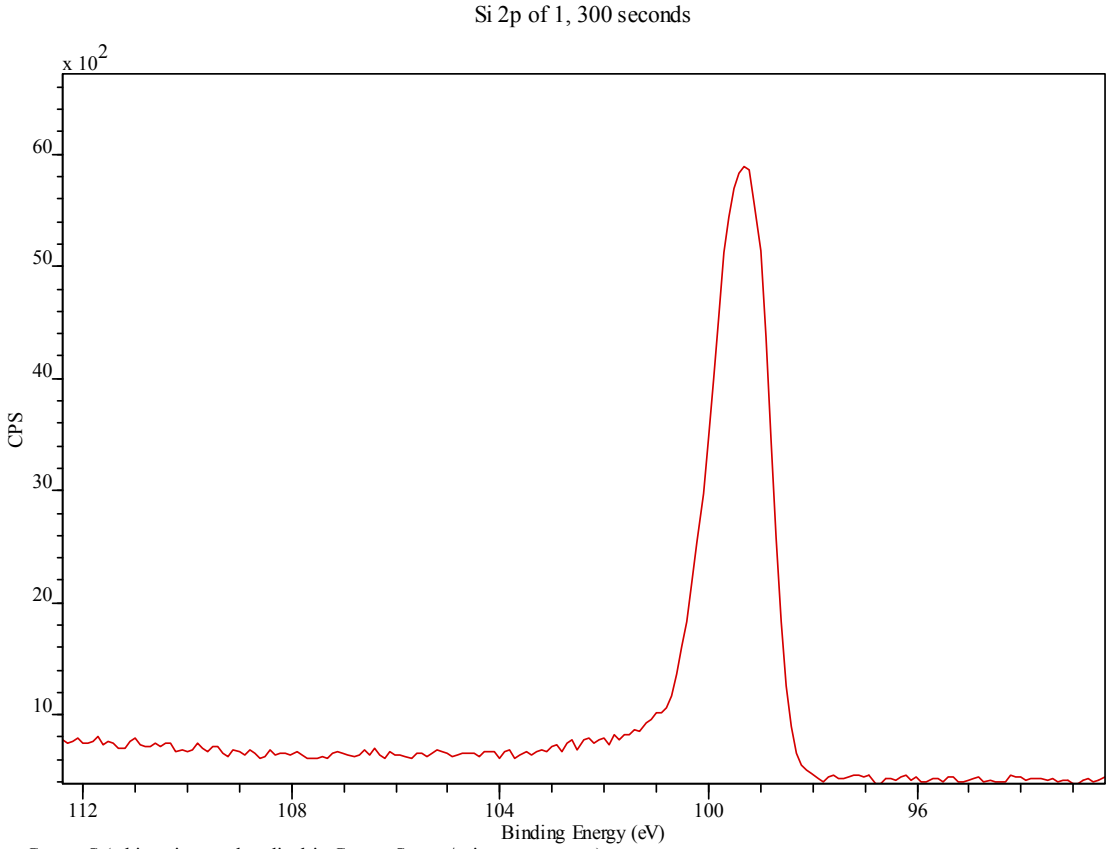


300 seconds of sputtering:


survey of 1, 300 seconds
x 10^4
14
12
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

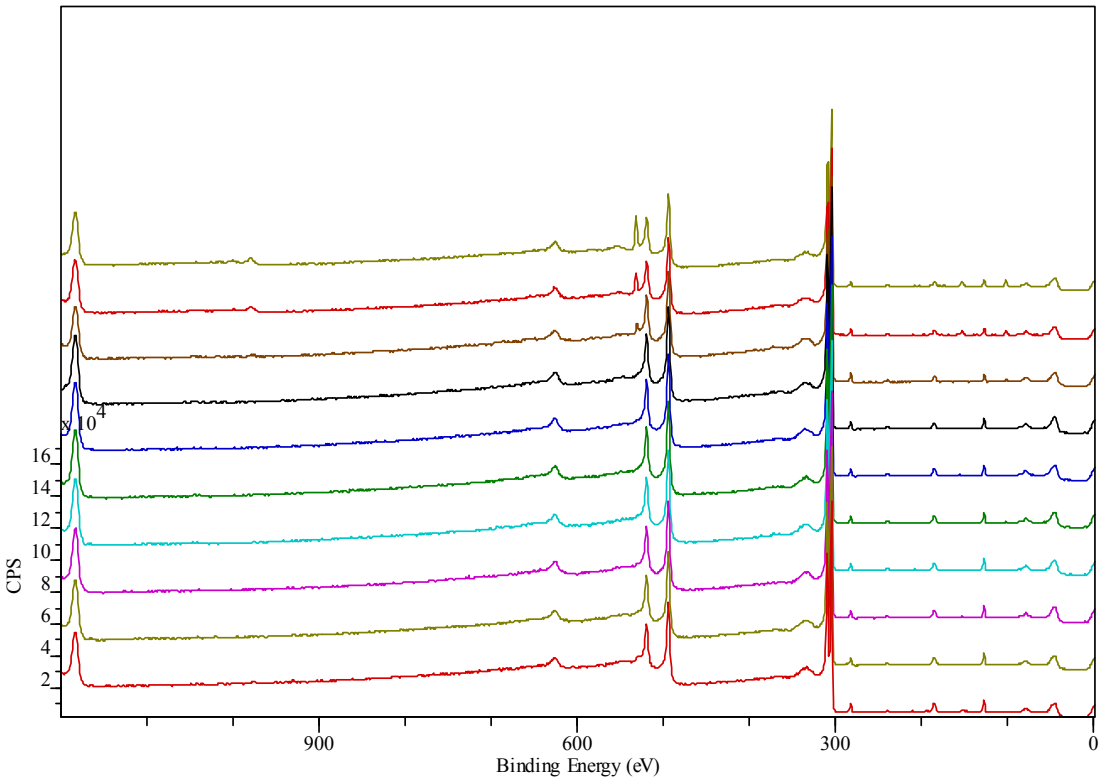

Rh 3d of 1, 300 seconds
x 10^3
16
14
12
10
8
6
4
2
CPS
320
316
312
308
304
Binding Energy (eV)


C 1s of 1, 300 seconds
x 10^1
170
160
150
140
130
120
CPS
292
288
284
280
276
Binding Energy (eV)

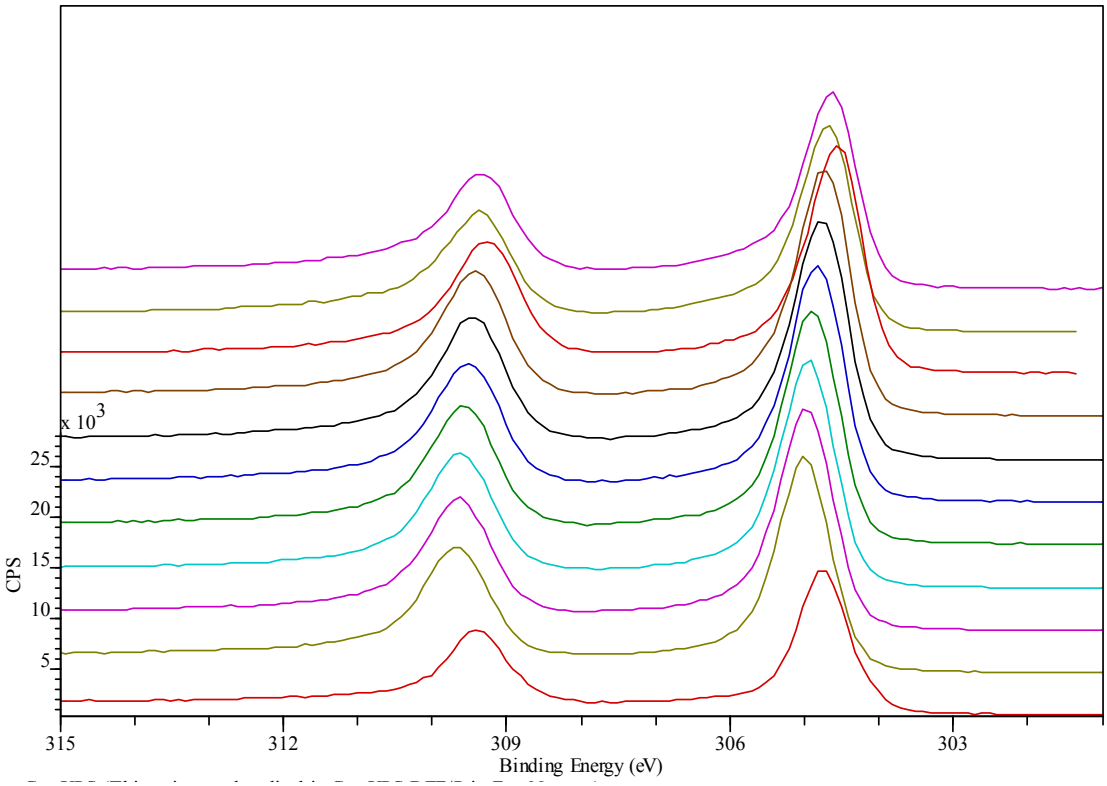

Si 2p of 1, 300 seconds
x 10^2
60
50
40
30
20
10
CPS
112
108
104
100
96
Binding Energy (eV)

XPS spectroscopy of [Rh(3,5-$(CF_3)_2$-Pz)$(PMe_3)_3$] (**3**) using hydrogen carrier gas

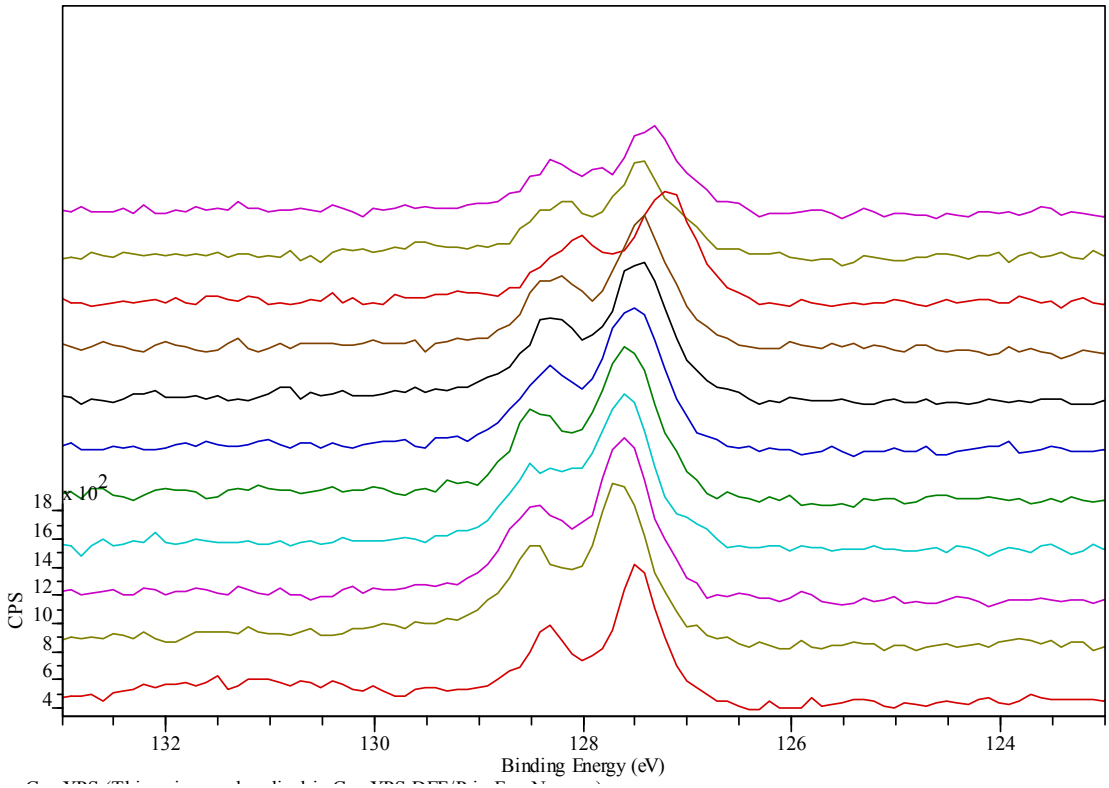
surveys of (3) from 0-360 seconds



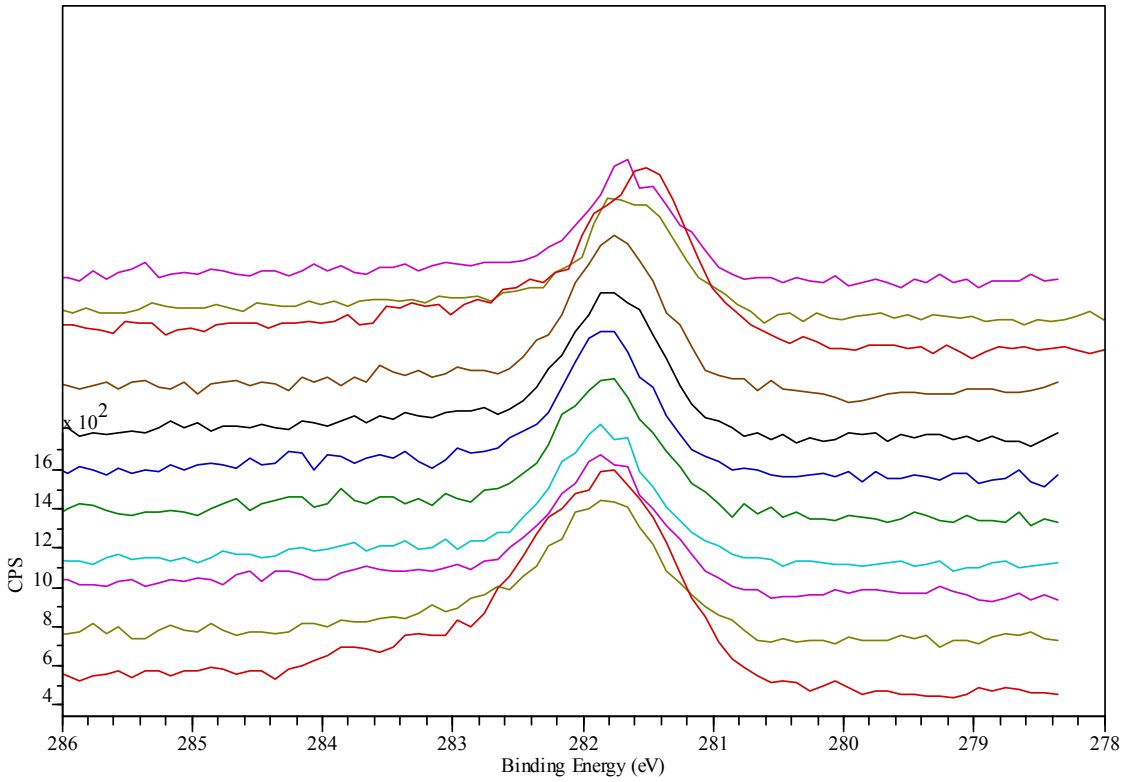
Rh 3d of (3) from 0-360 seconds of sputtering

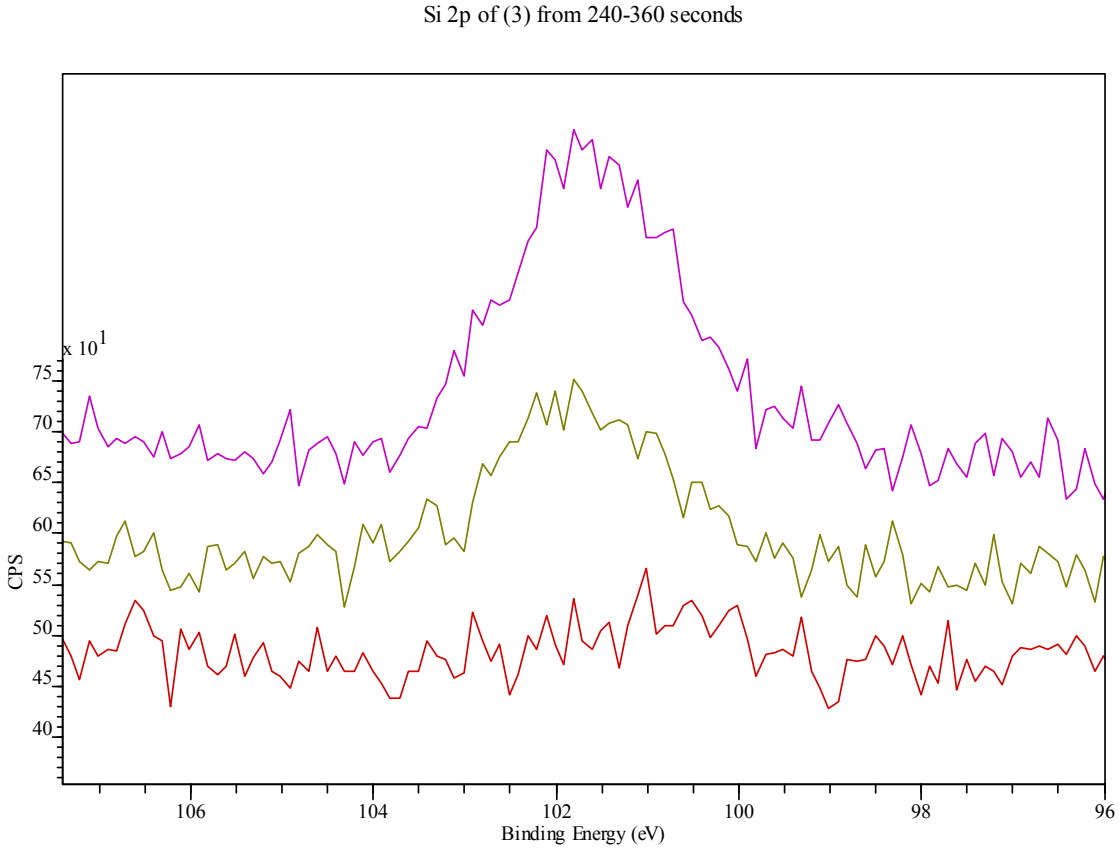


P 2p of (3) from 0-360 seconds

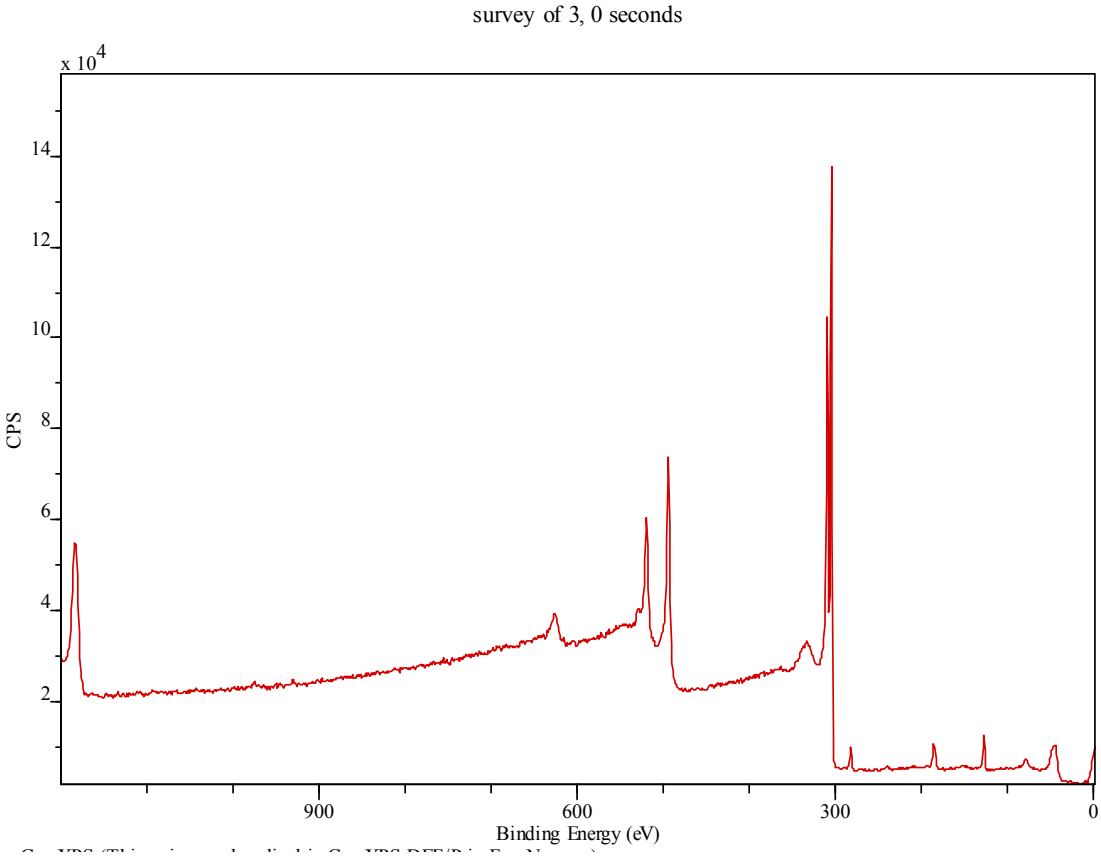


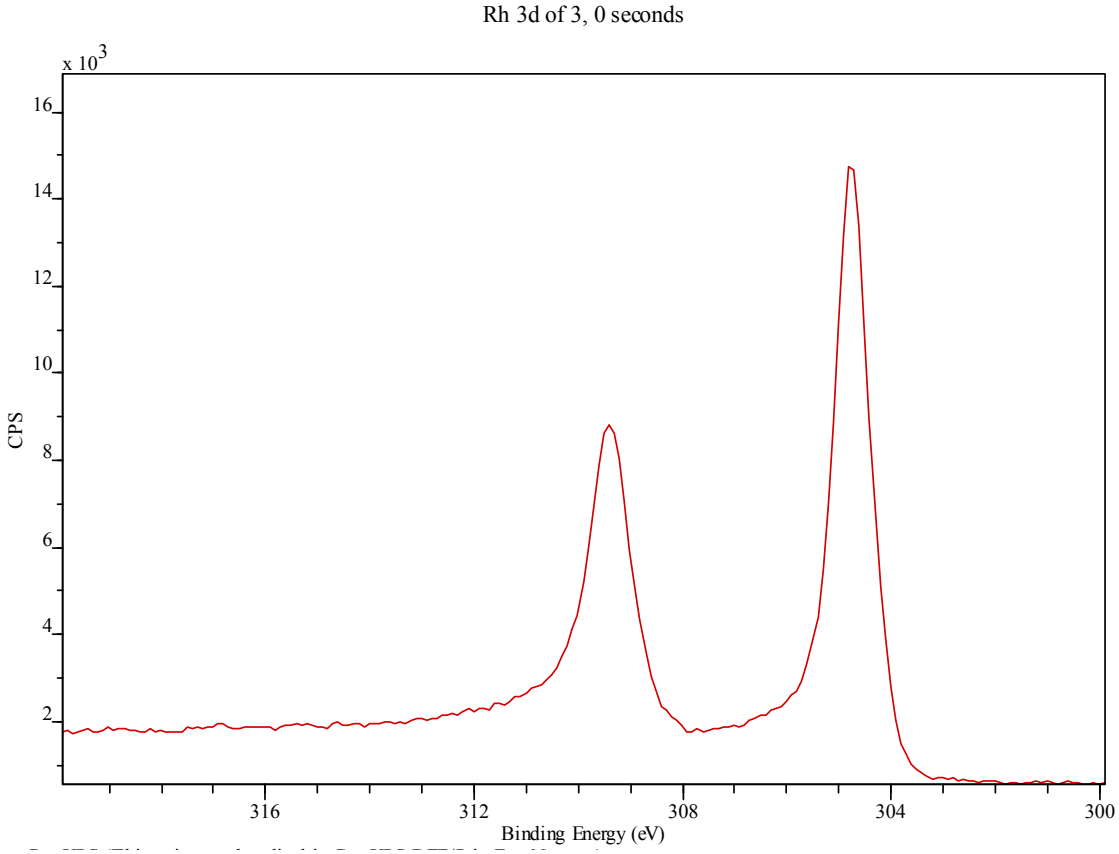
C 1s of (3) from 0-360 seconds

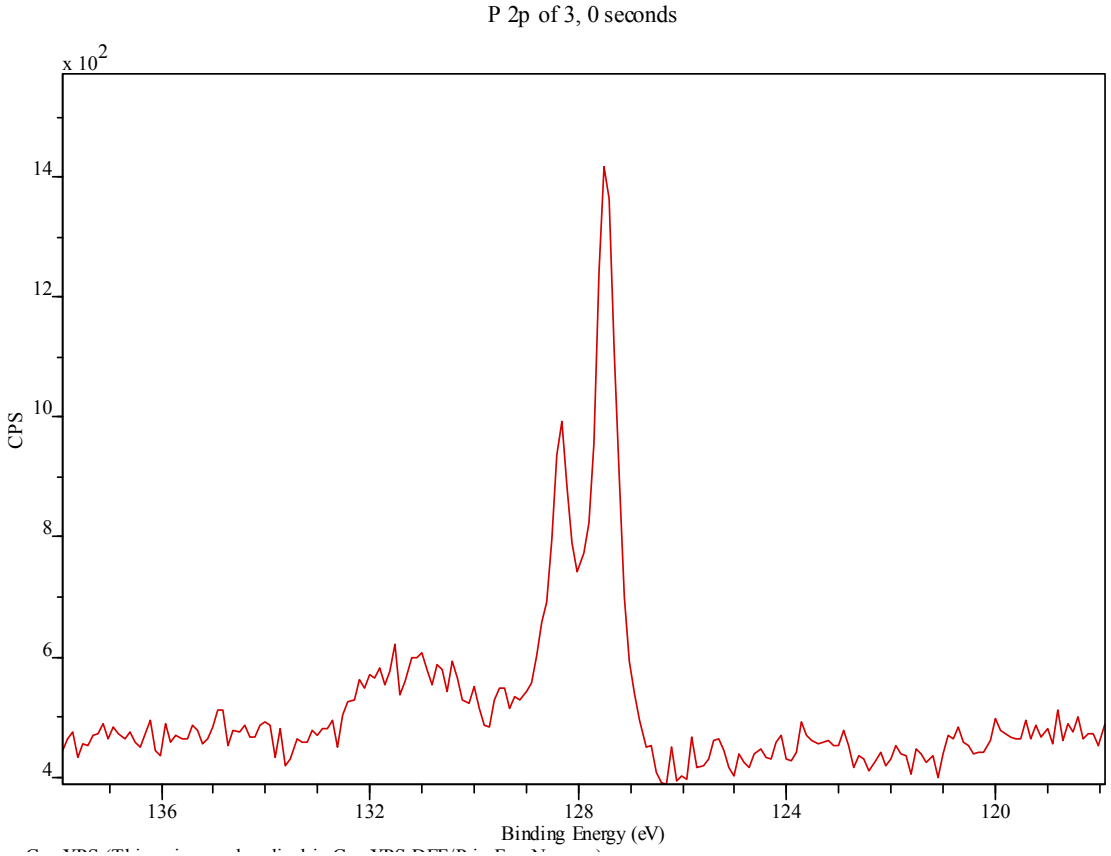


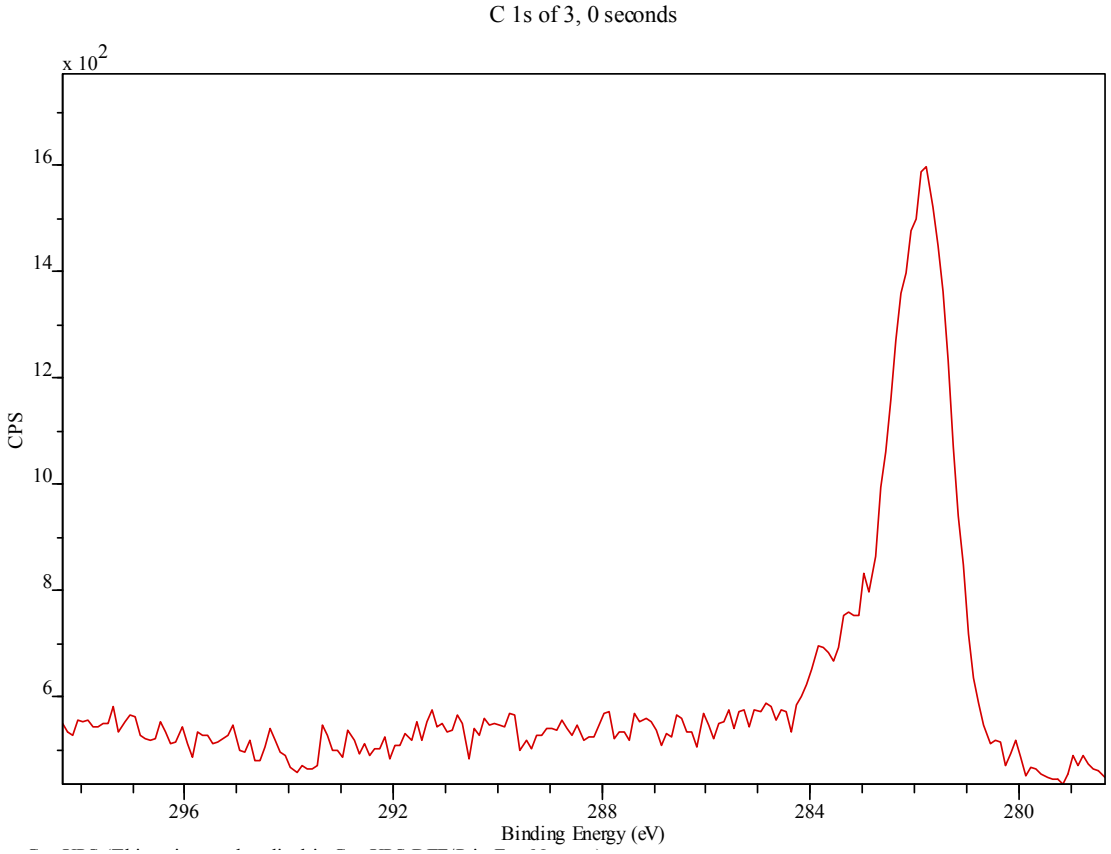


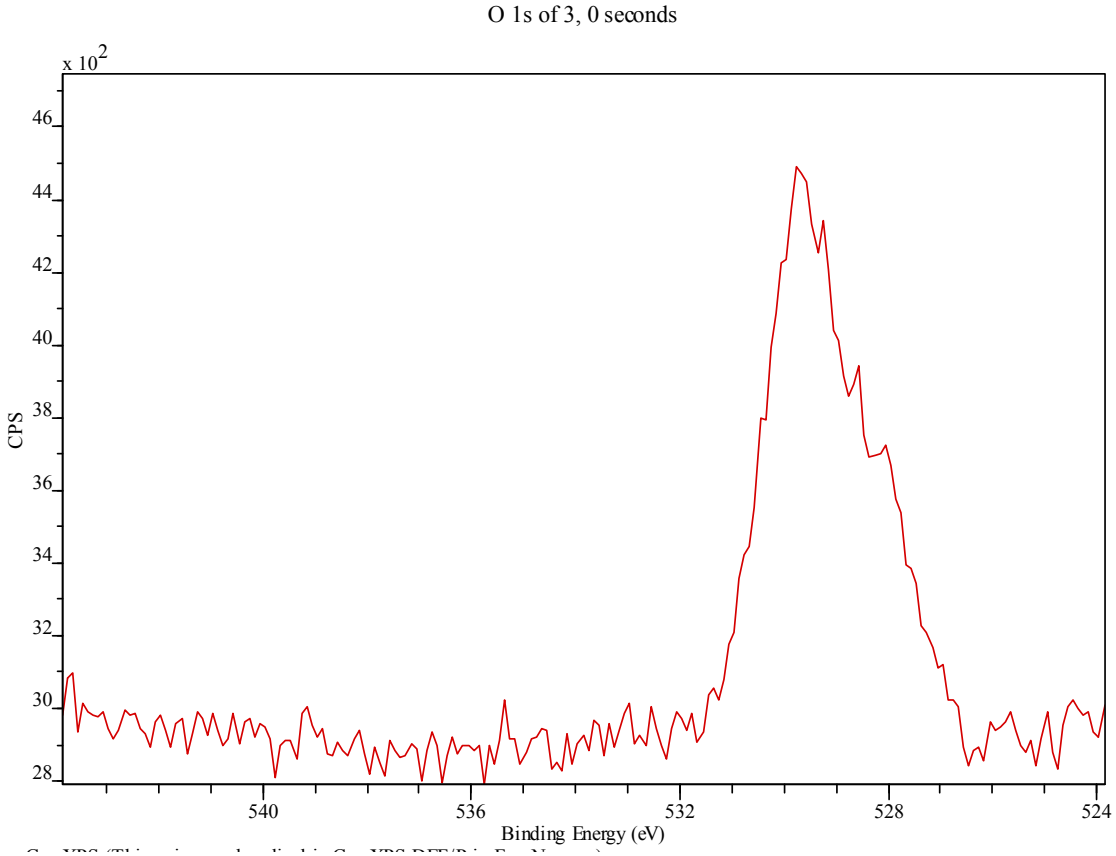
0 seconds of sputtering:

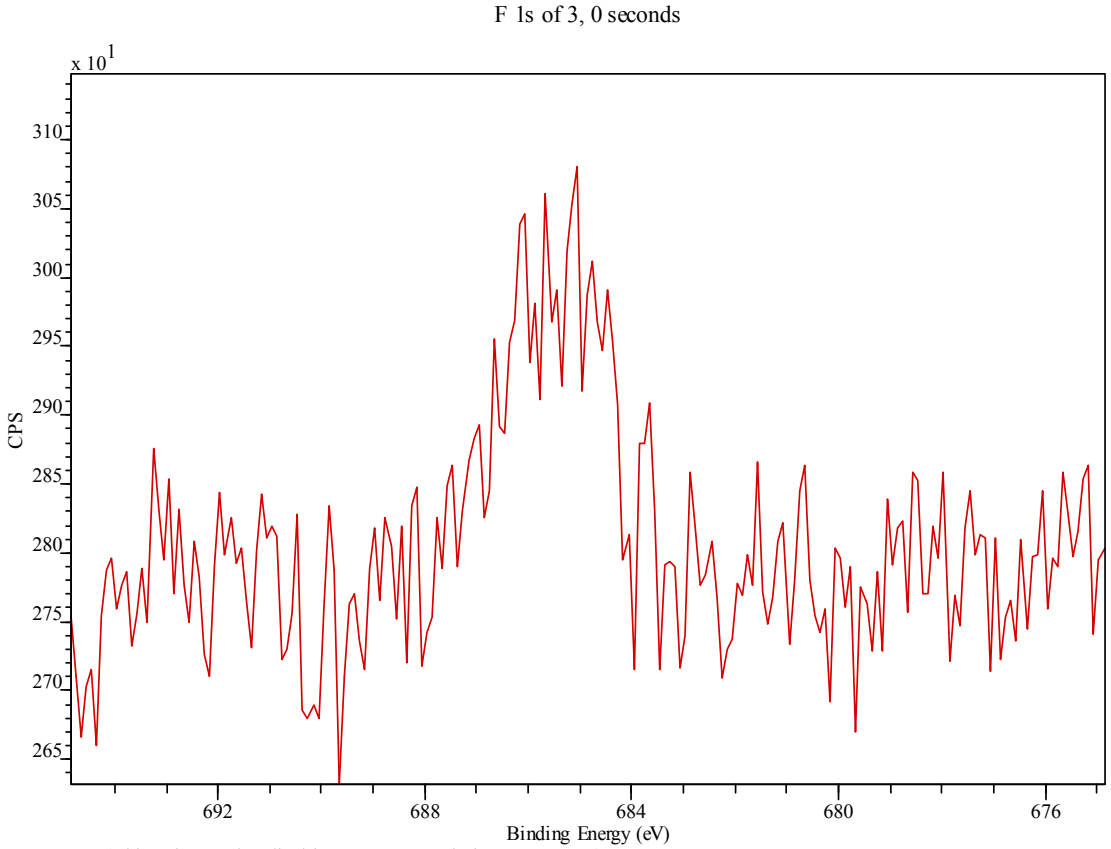

survey of 3, 0 seconds
x 10^4
14
12
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)


Rh 3d of 3, 0 seconds
x 10^3
16
14
12
10
8
6
4
2
CPS
316
312
308
304
300
Binding Energy (eV)

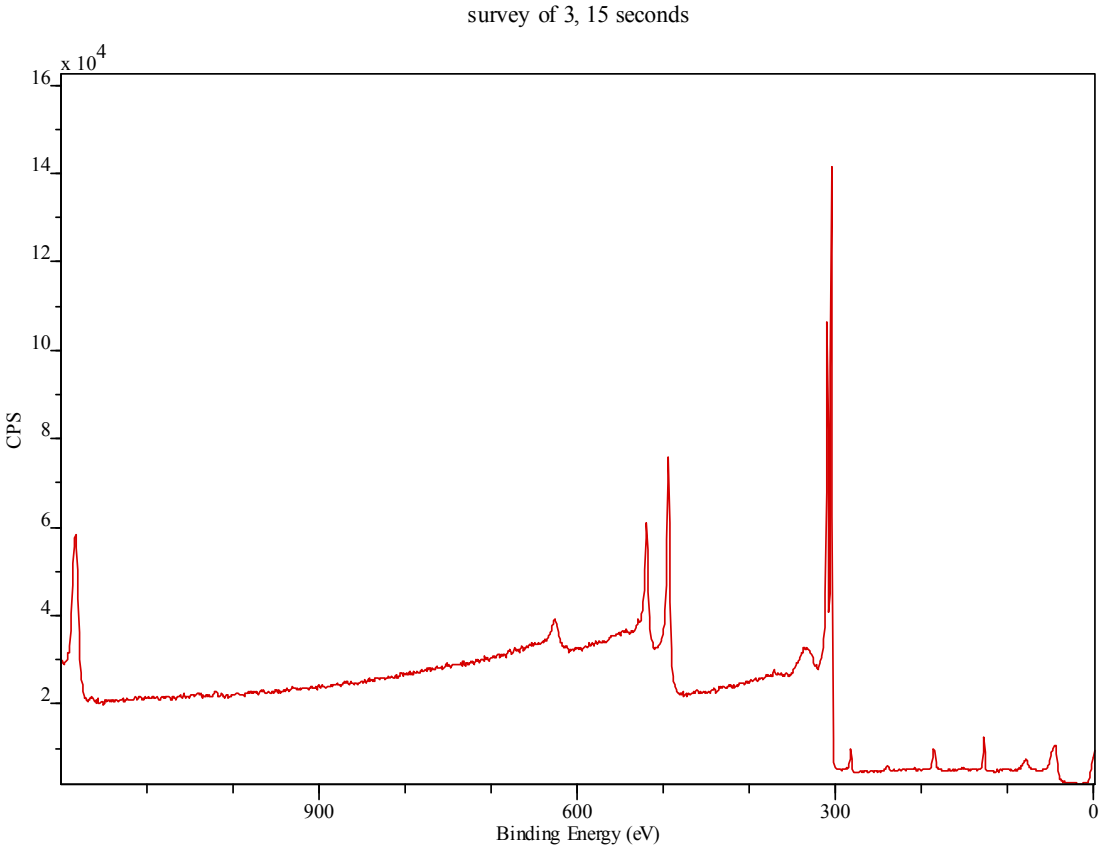

P 2p of 3, 0 seconds
x 10^2
14
12
10
8
6
4
CPS
136
132
128
124
120
Binding Energy (eV)

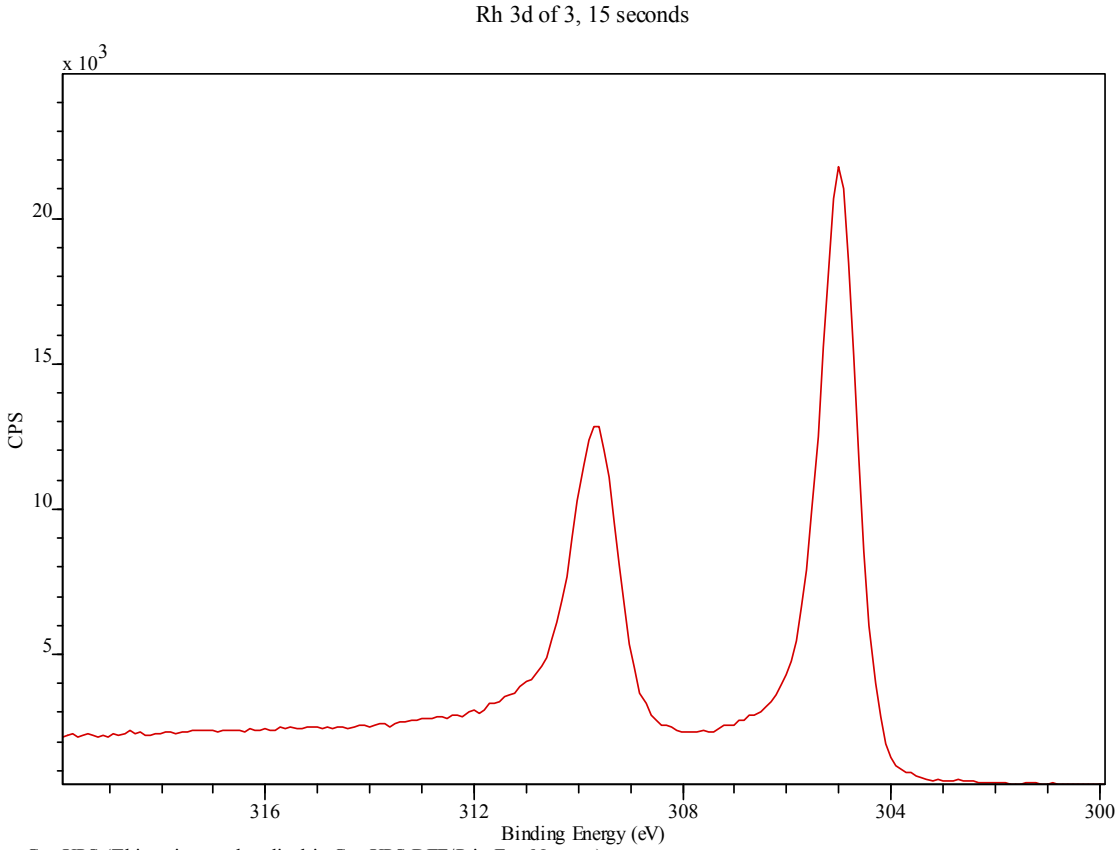

C 1s of 3, 0 seconds
x 10^2
16
14
12
10
8
6
CPS
296
292
288
284
280
Binding Energy (eV)

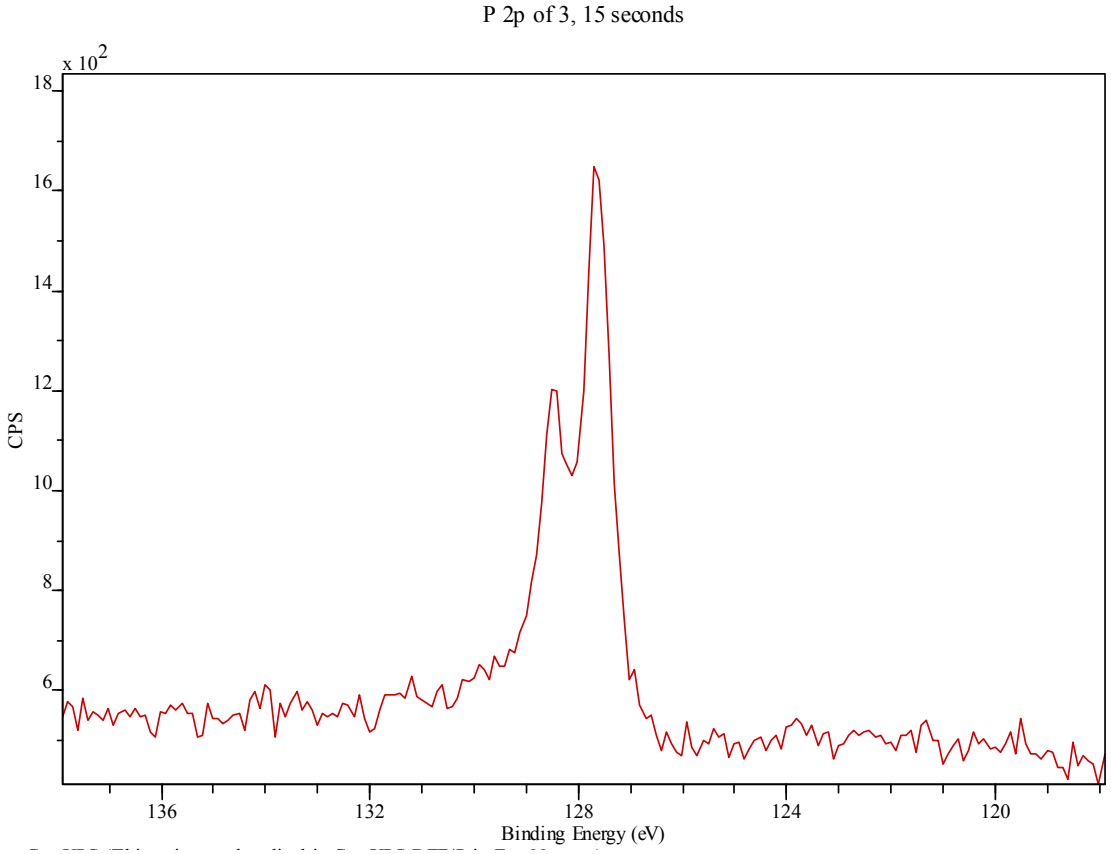

O 1s of 3, 0 seconds
x 10^2
46
44
42
40
38
36
34
32
30
28
CPS
540
536
532
528
524
Binding Energy (eV)

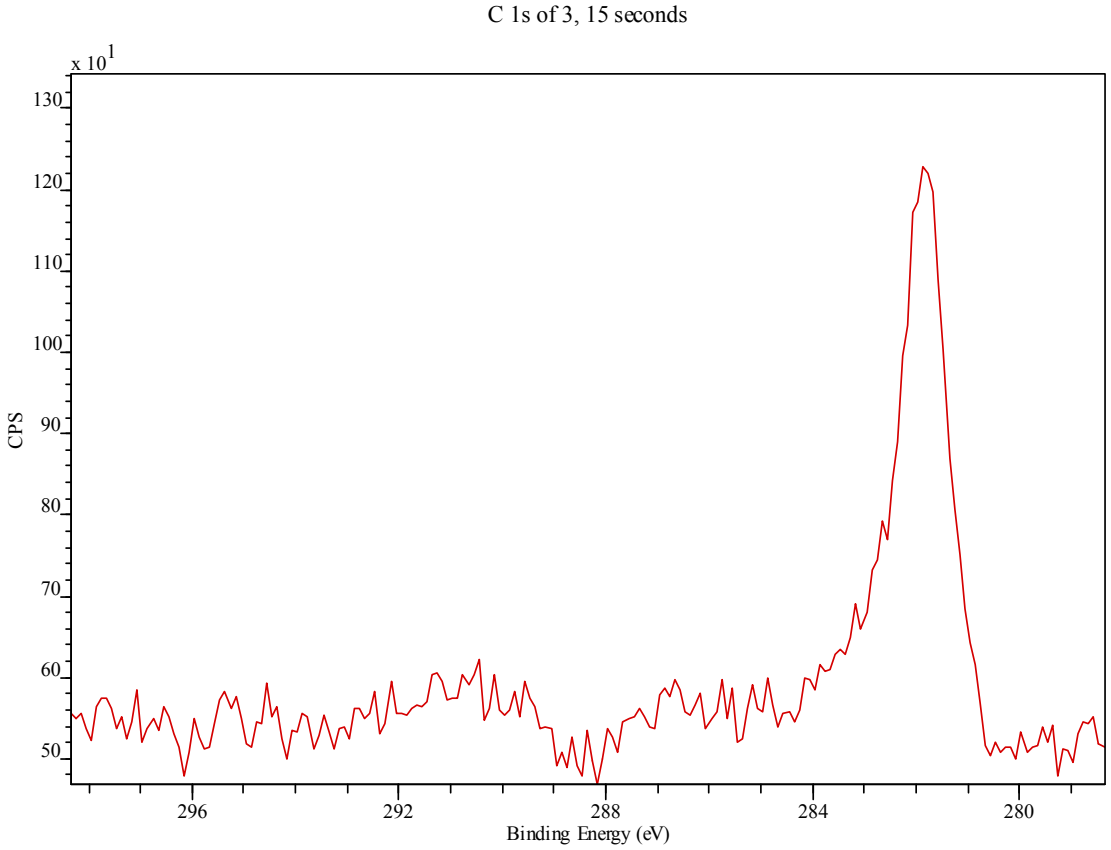


15 seconds of sputtering:

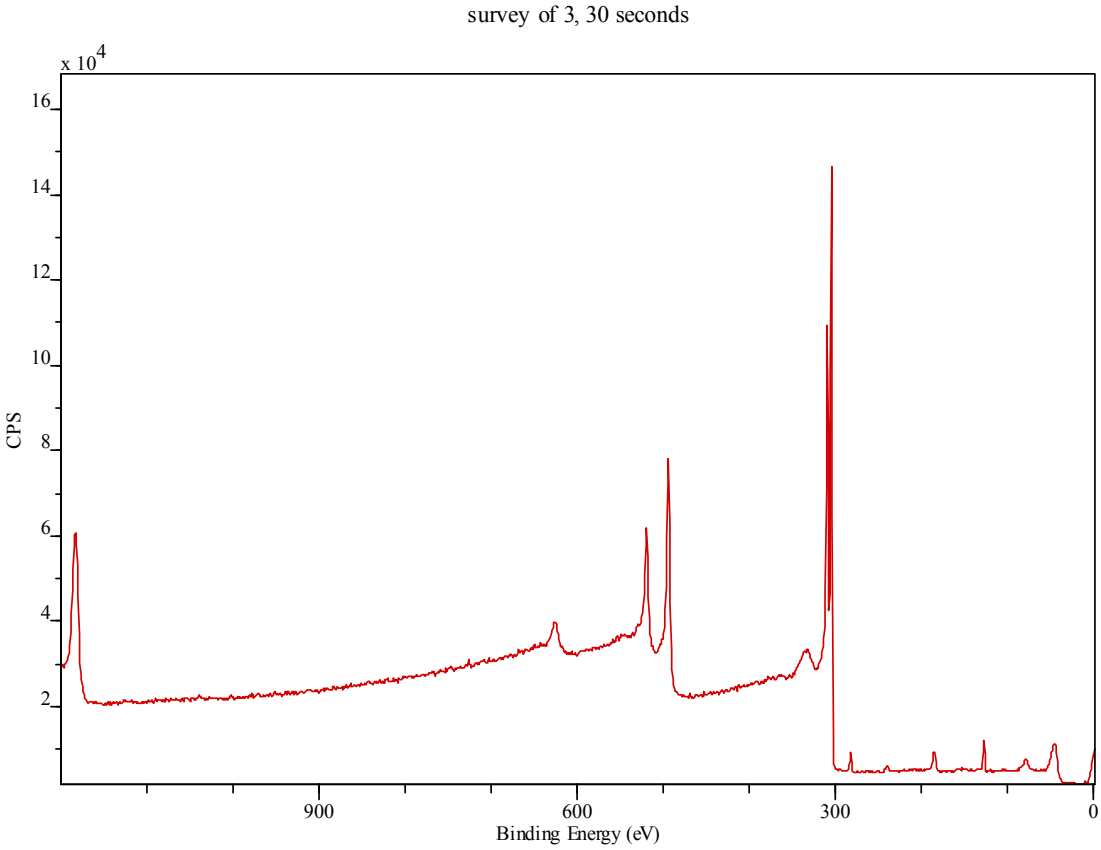


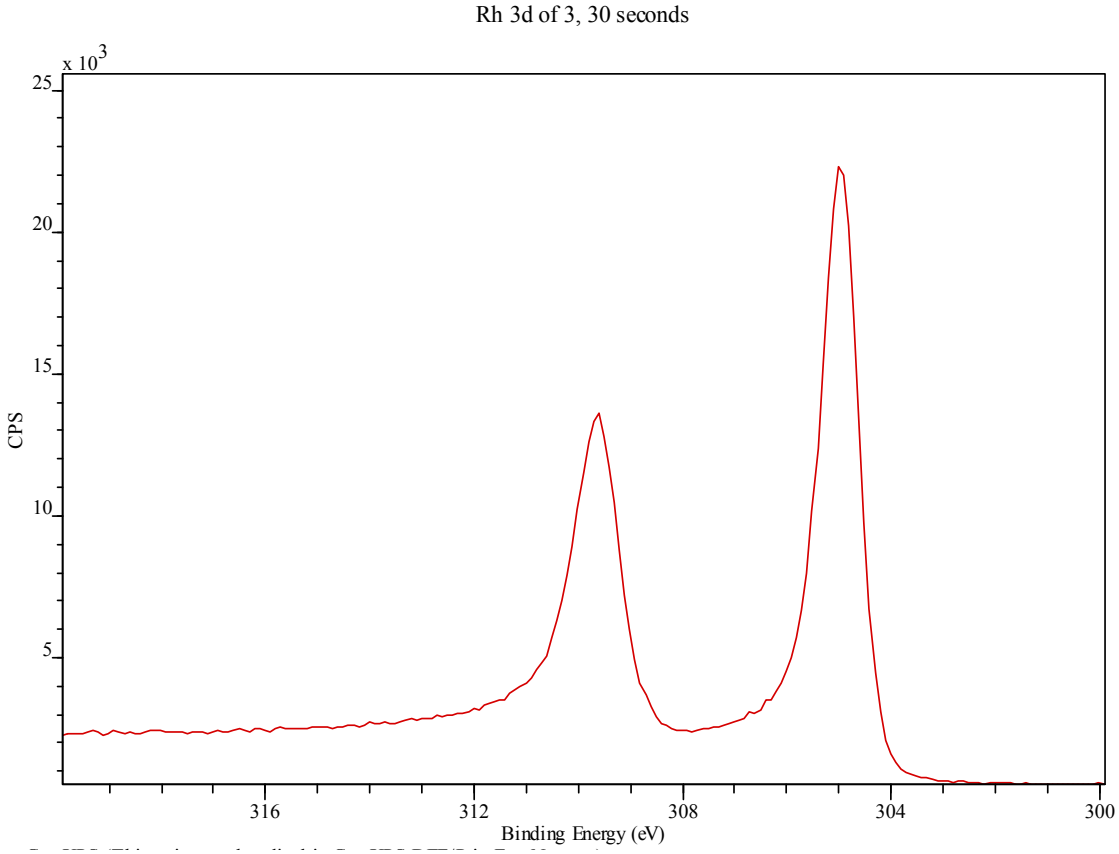

Rh 3d of 3, 15 seconds
x 10^3
20
15
10
5
CPS
316
312
308
304
300
Binding Energy (eV)

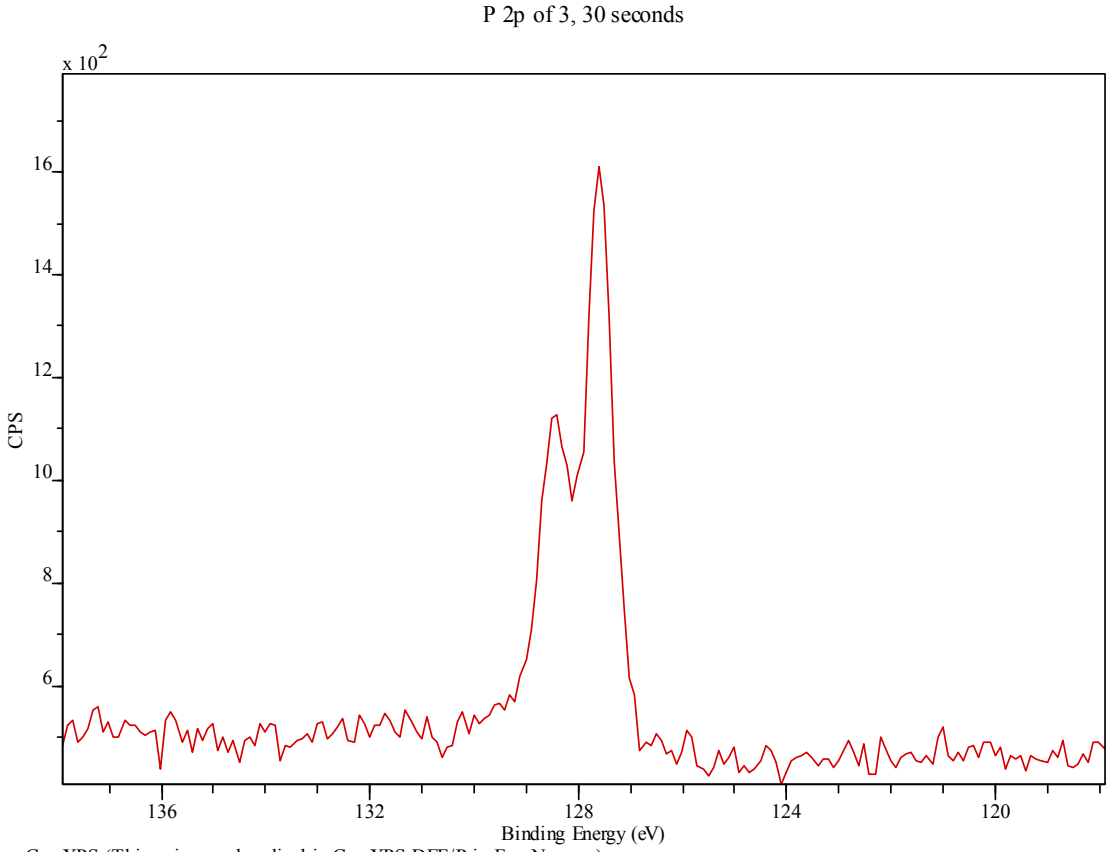

P 2p of 3, 15 seconds
x 10^2
18
16
14
12
10
8
6
CPS
136
132
128
124
120
Binding Energy (eV)

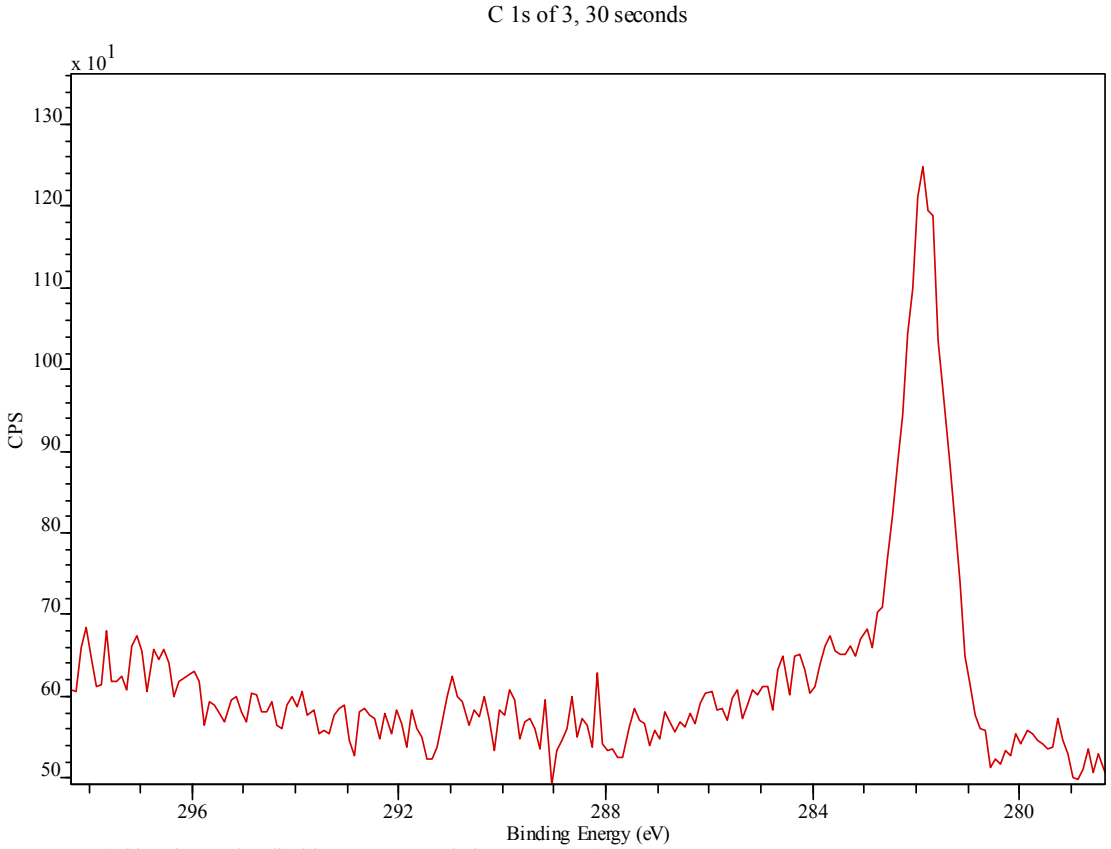


30 seconds of sputtering:

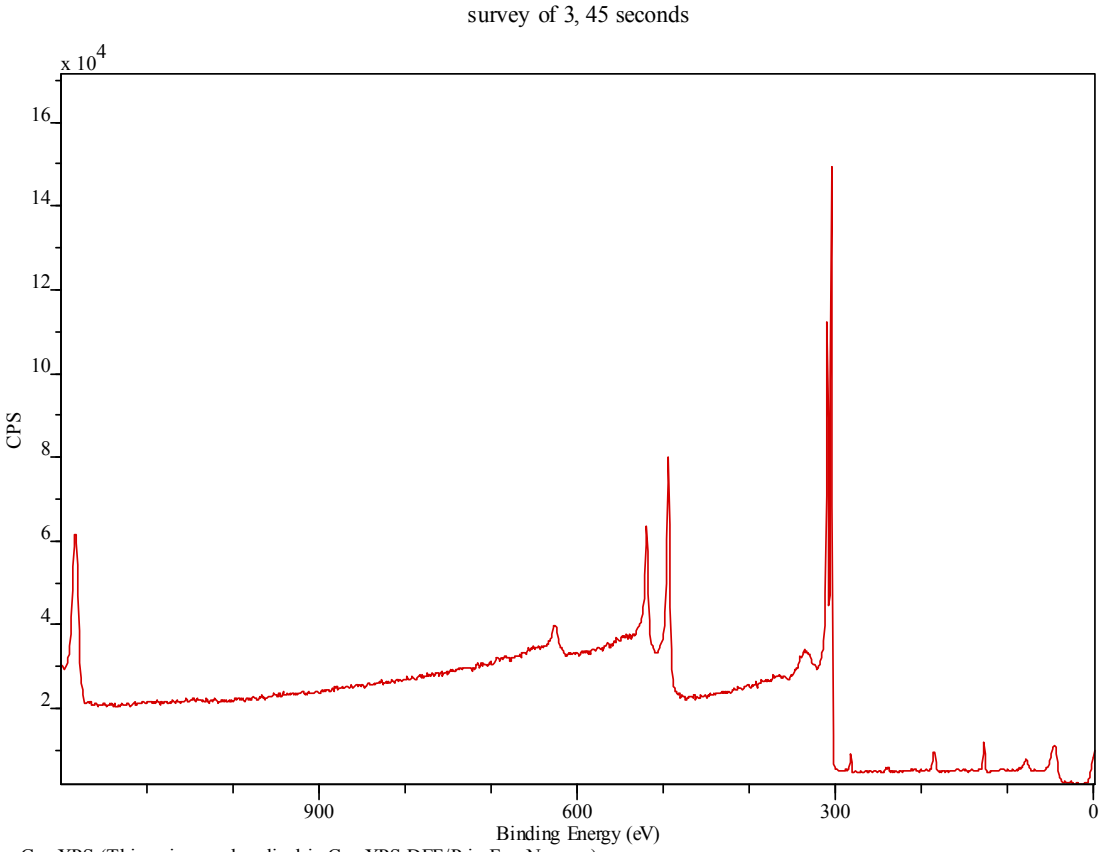

survey of 3, 30 seconds
x 10^4
16
14
12
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

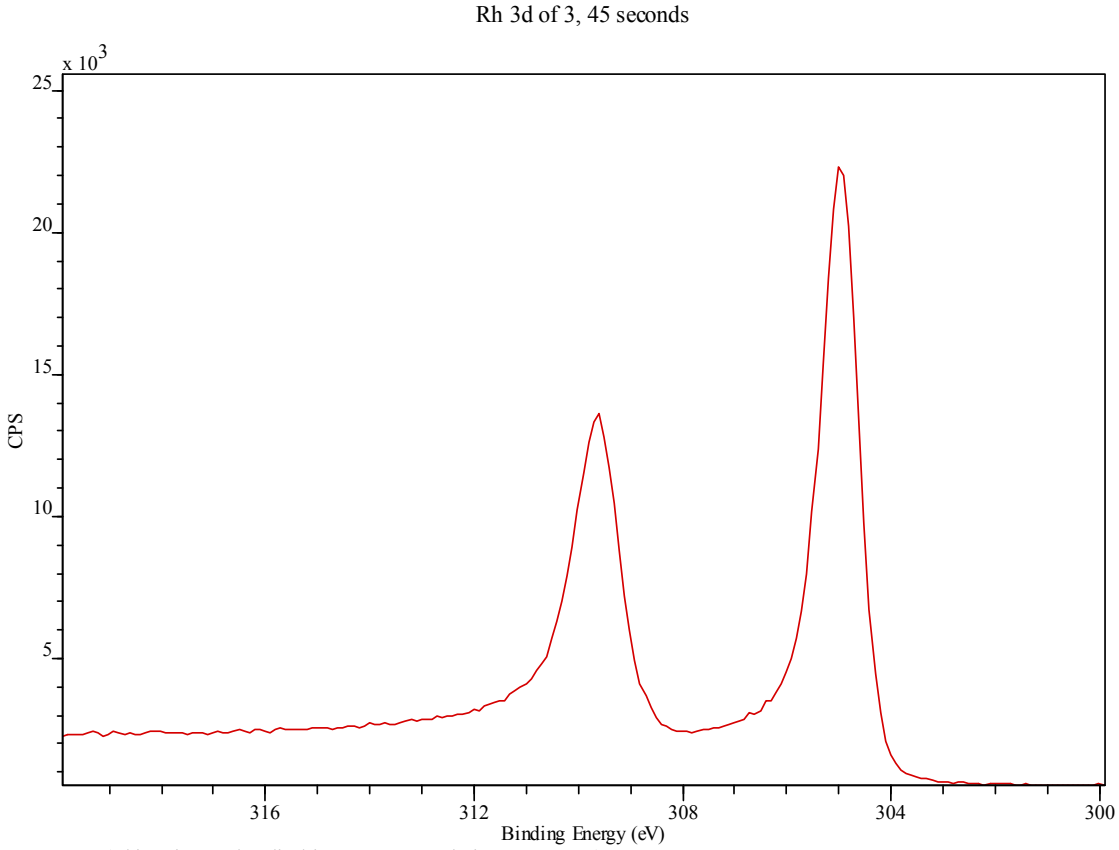

Rh 3d of 3, 30 seconds
x 10^3
25
20
15
10
5
CPS
316
312
308
304
300
Binding Energy (eV)

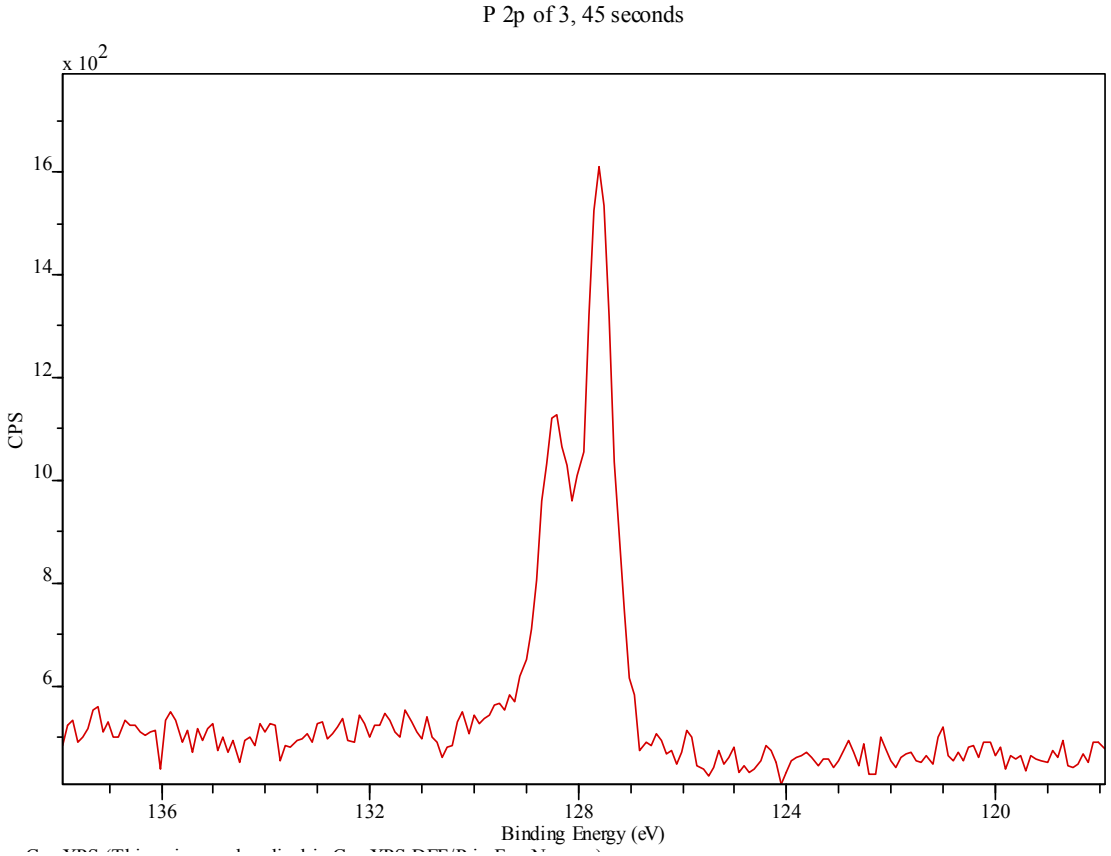

P 2p of 3, 30 seconds
x 10^2
16
14
12
10
8
6
CPS
136
132
128
124
120
Binding Energy (eV)

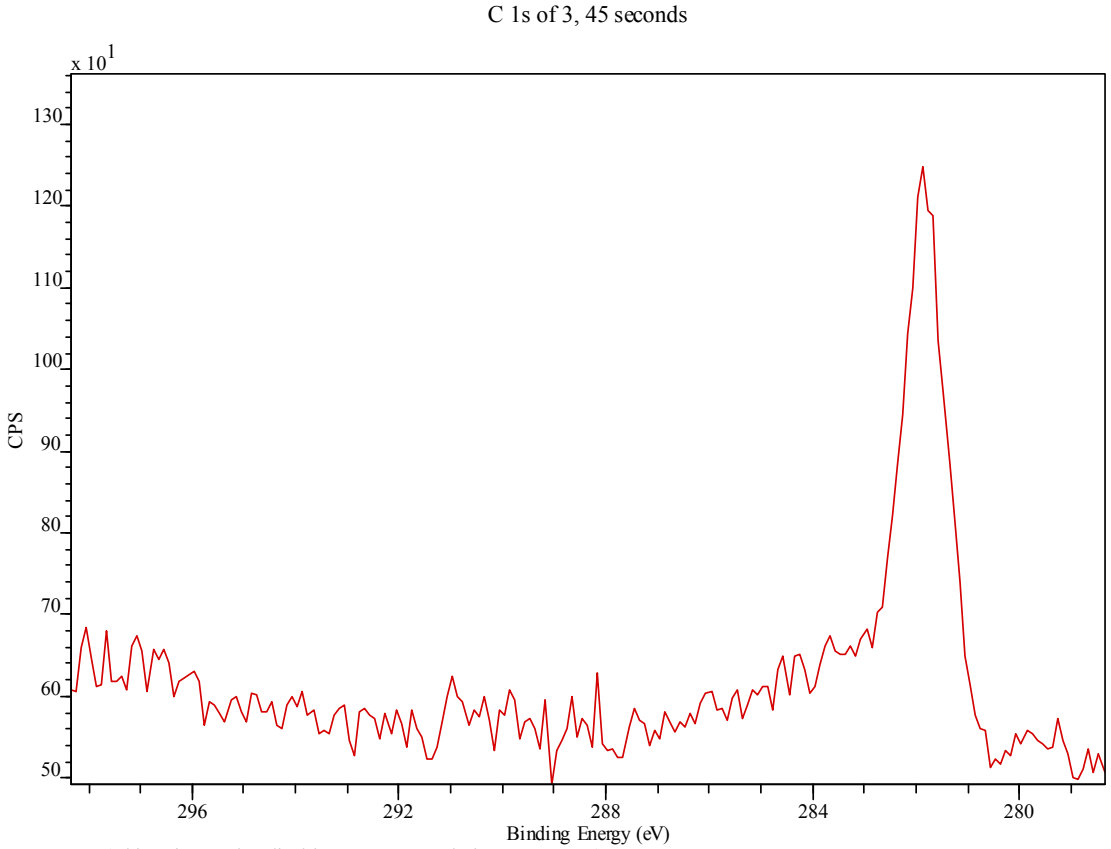


45 seconds of sputtering:

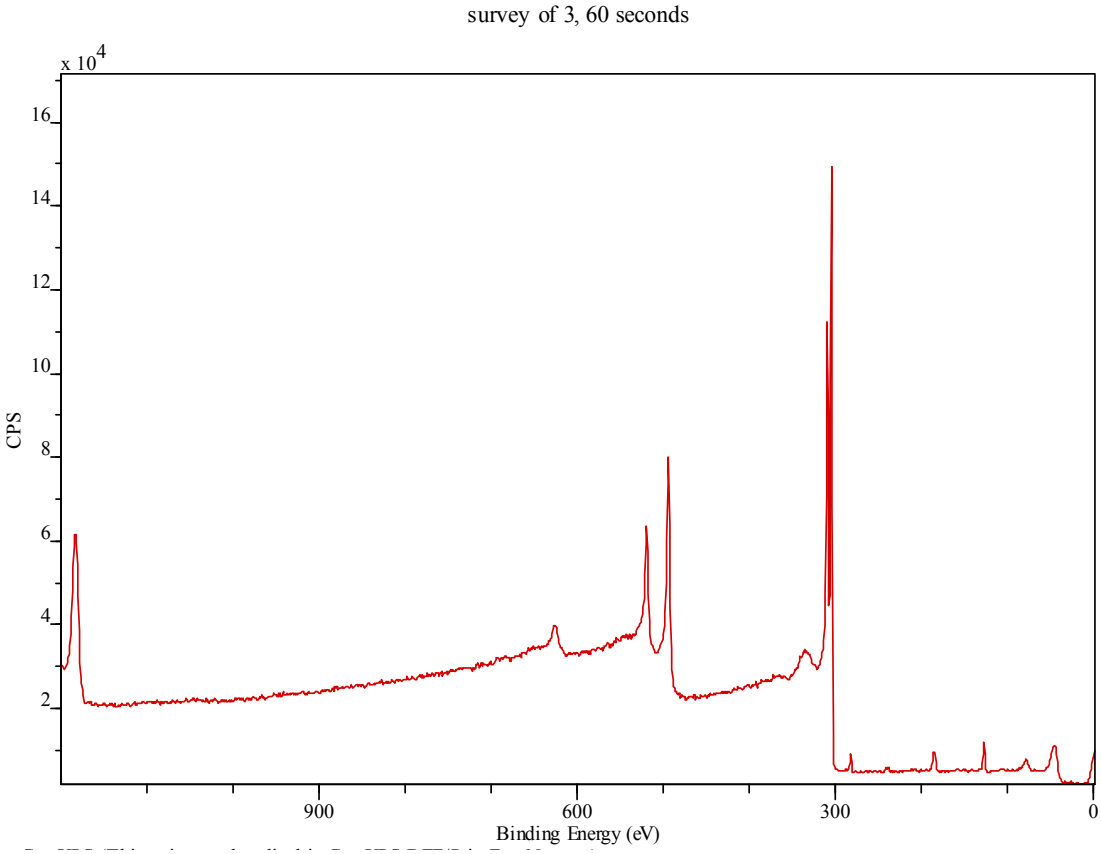

survey of 3, 45 seconds
x 10^4
16
14
12
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

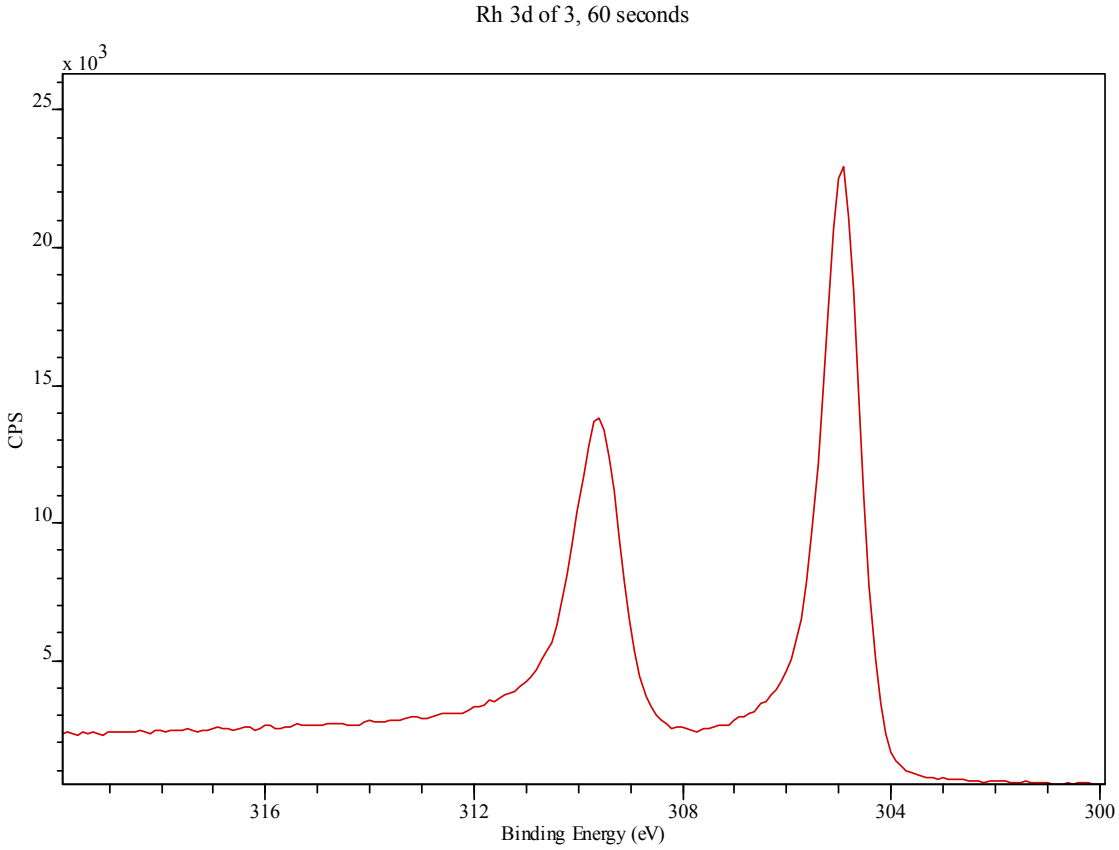

Rh 3d of 3, 45 seconds
x 10^3
25
20
15
10
5
CPS
316
312
308
304
300
Binding Energy (eV)

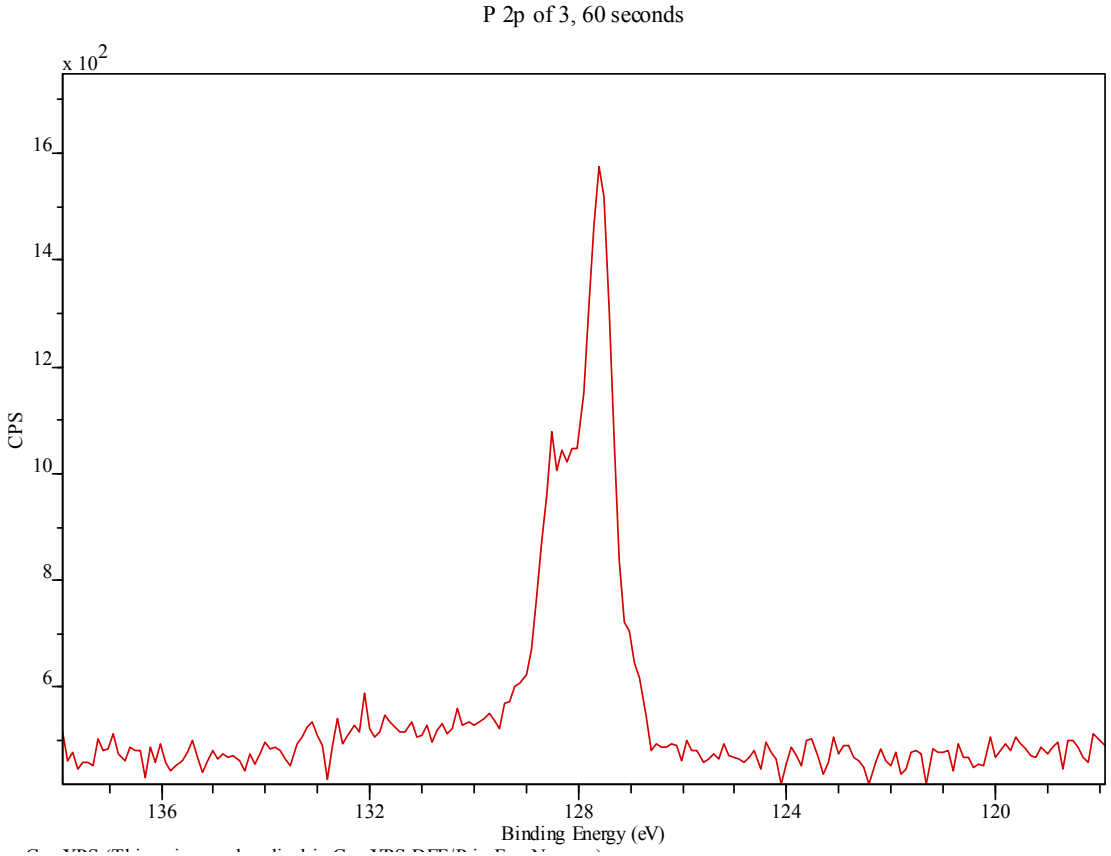

P 2p of 3, 45 seconds
x 10^2
16
14
12
10
8
6
CPS
136
132
128
124
120
Binding Energy (eV)

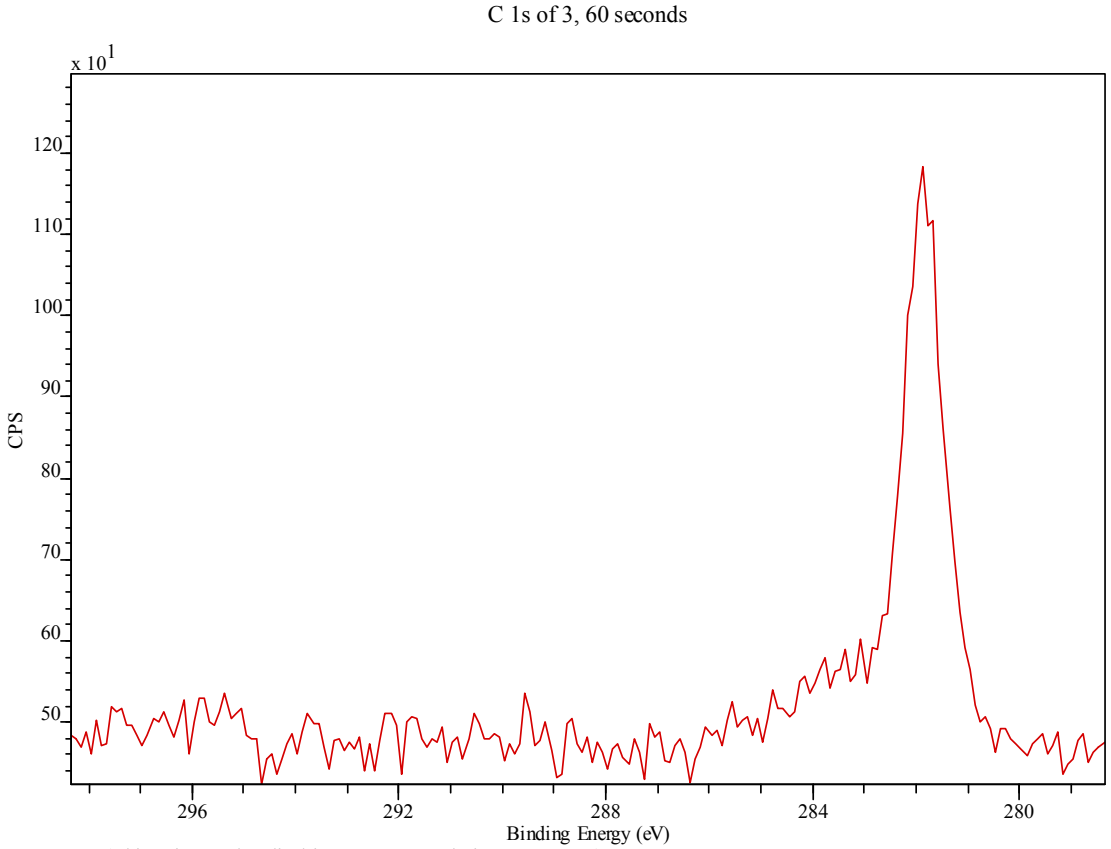


60 seconds of sputtering:

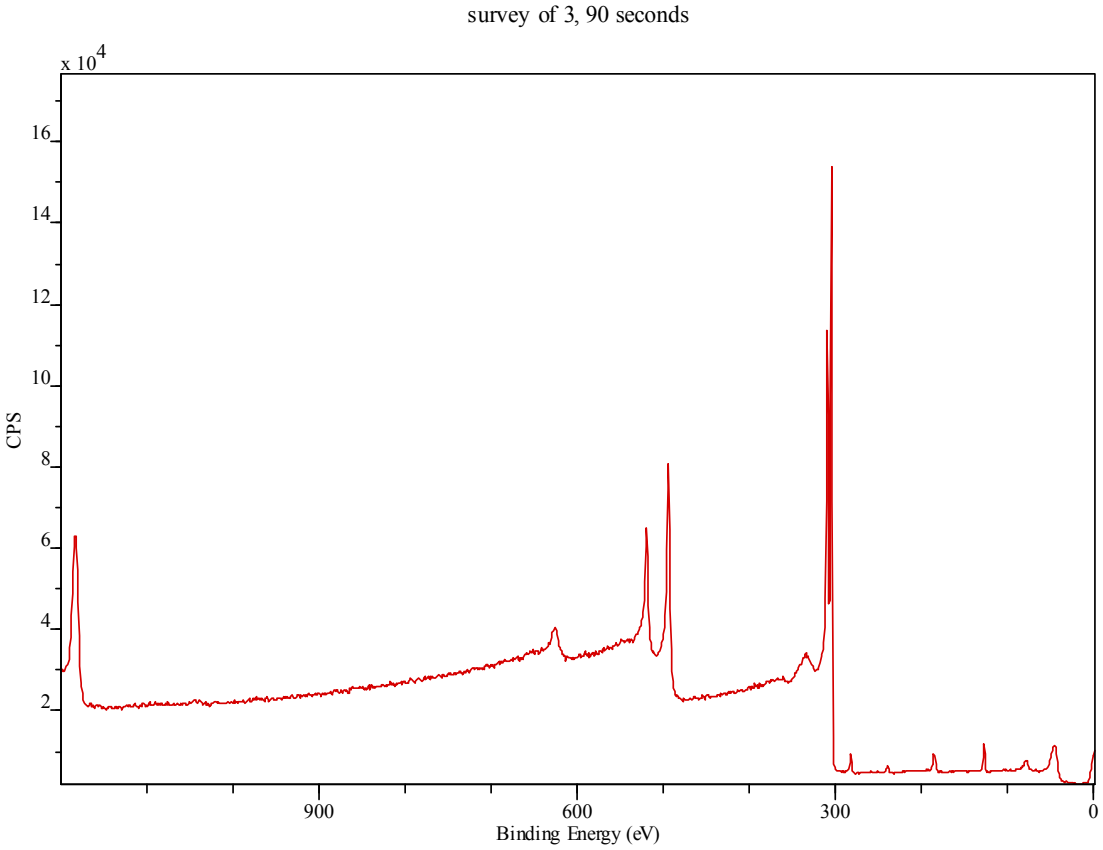

survey of 3, 60 seconds
x 10^4
16
14
12
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

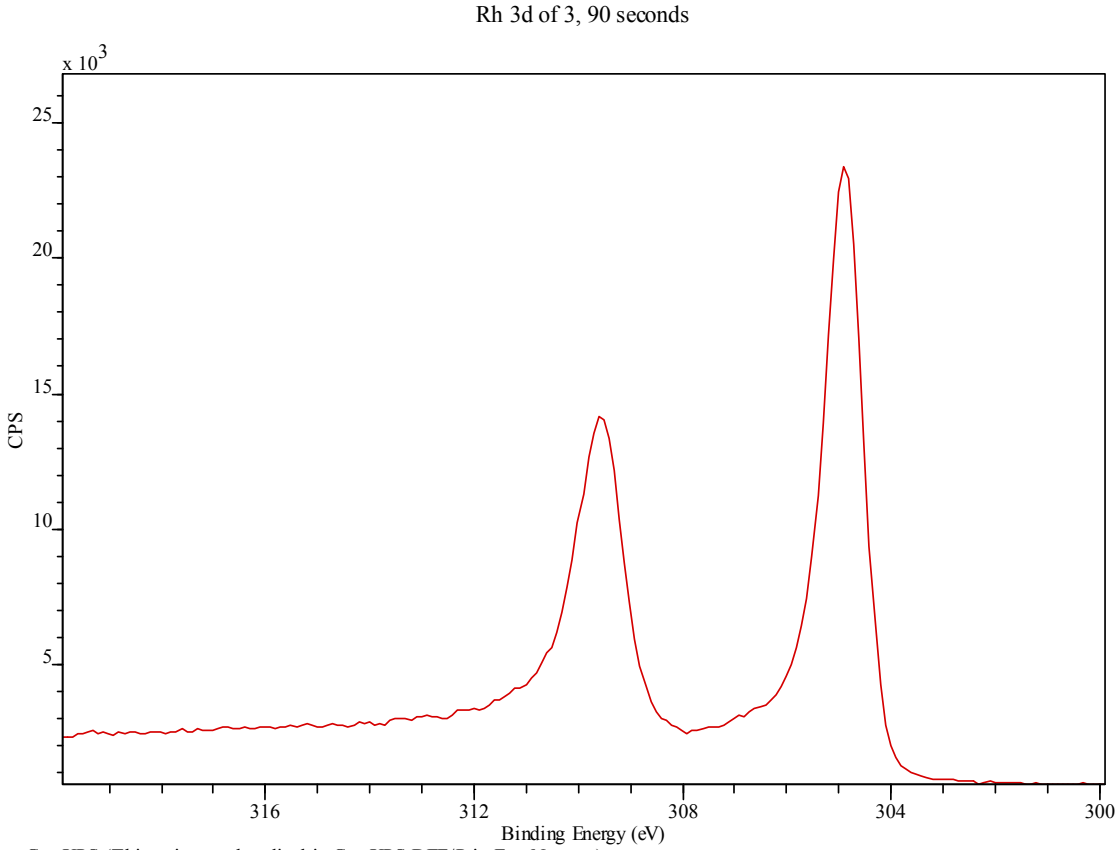

Rh 3d of 3, 60 seconds
x 10^3
25
20
15
10
5
CPS
316
312
308
304
300
Binding Energy (eV)

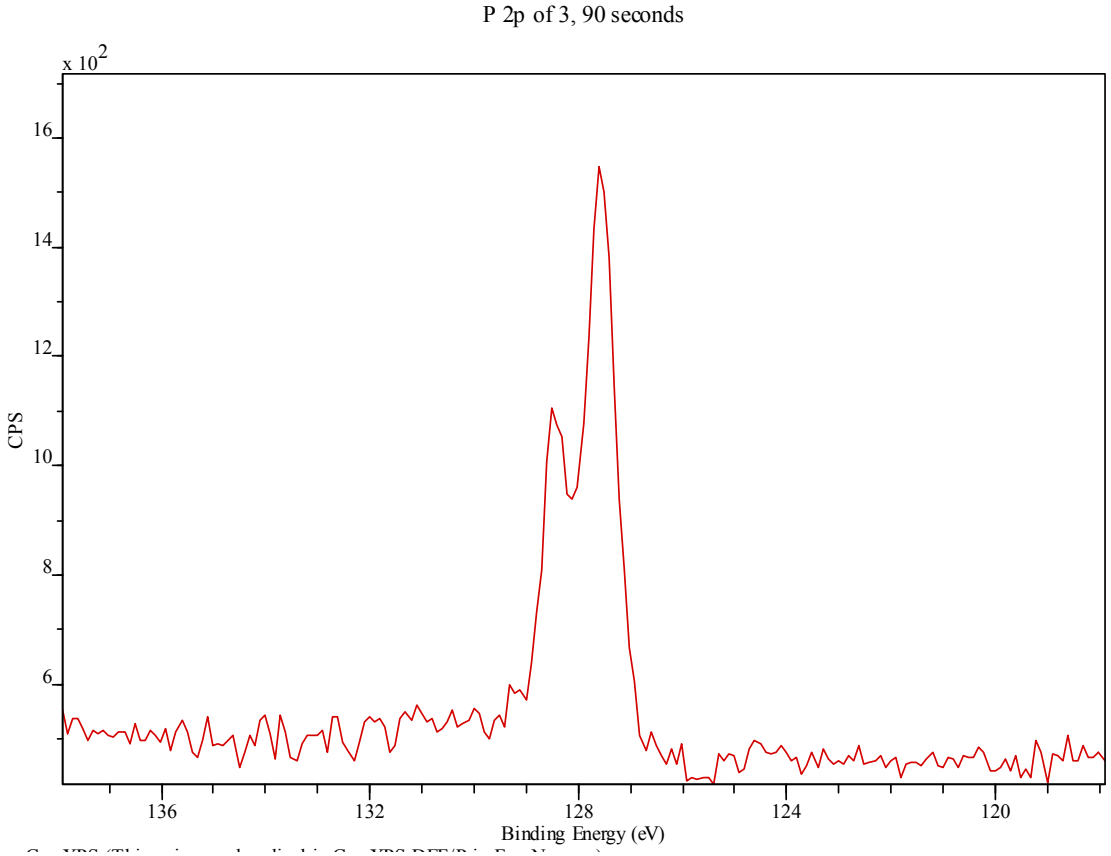

P 2p of 3, 60 seconds
x 10^2
16
14
12
10
8
6
CPS
136
132
128
124
120
Binding Energy (eV)

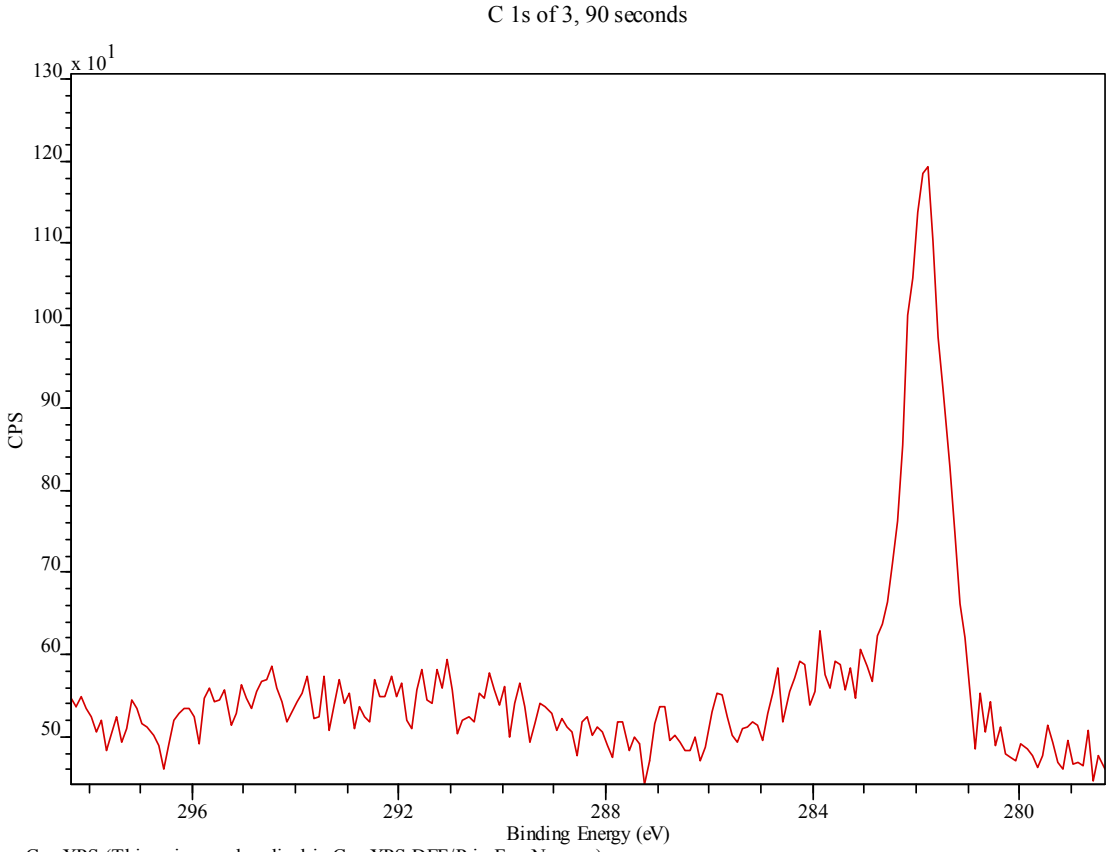


90 seconds of sputtering:

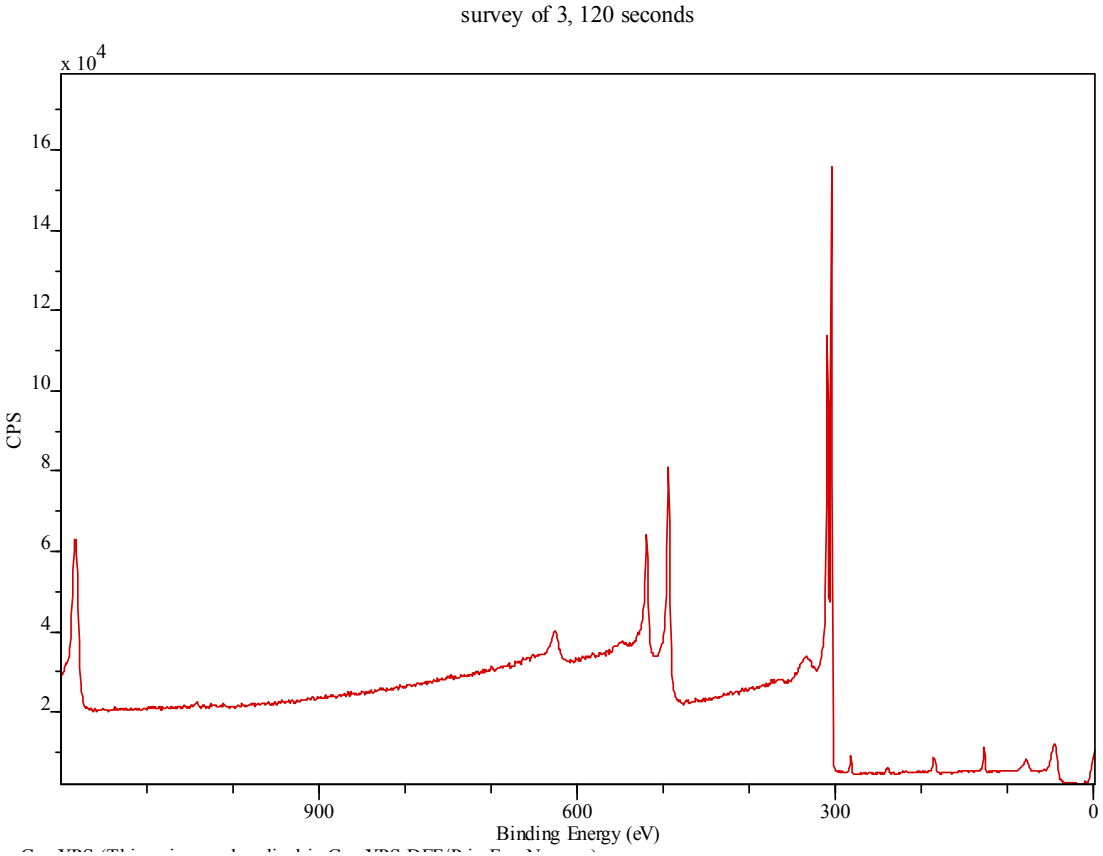


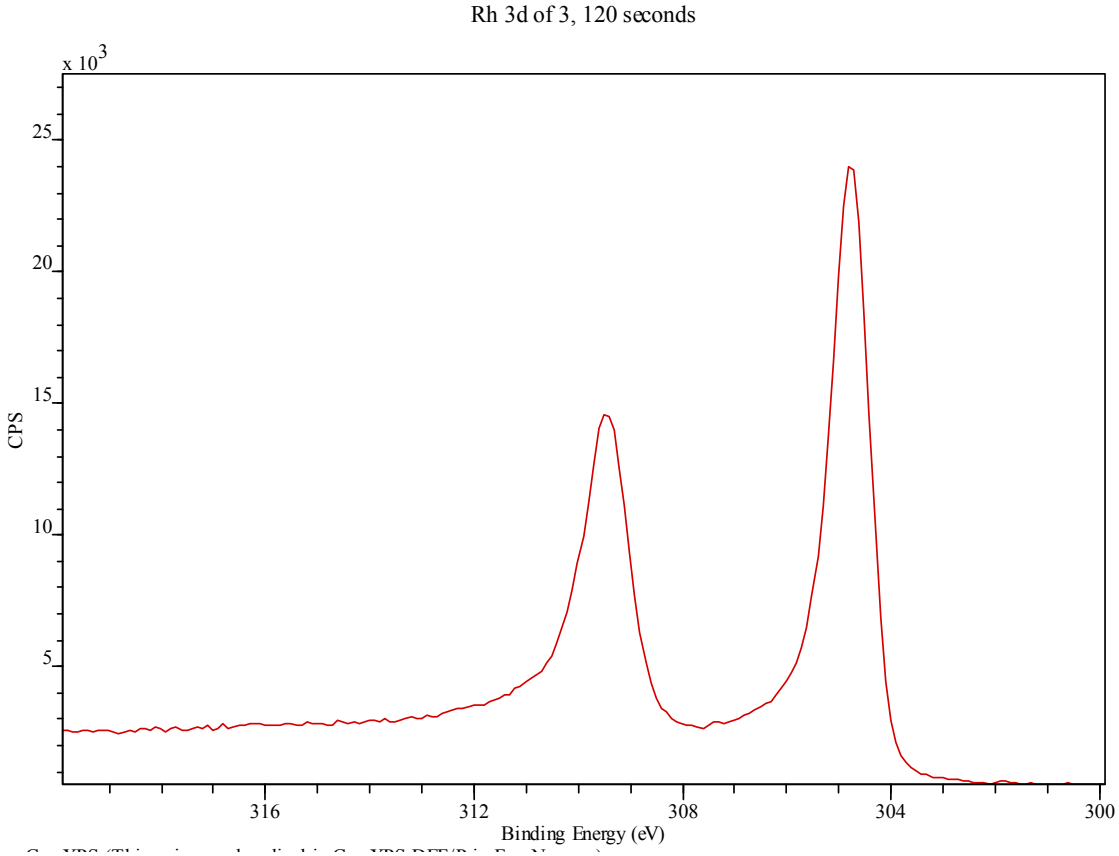

Rh 3d of 3, 90 seconds
x 10^3
25
20
15
10
5
CPS
316
312
308
304
300
Binding Energy (eV)

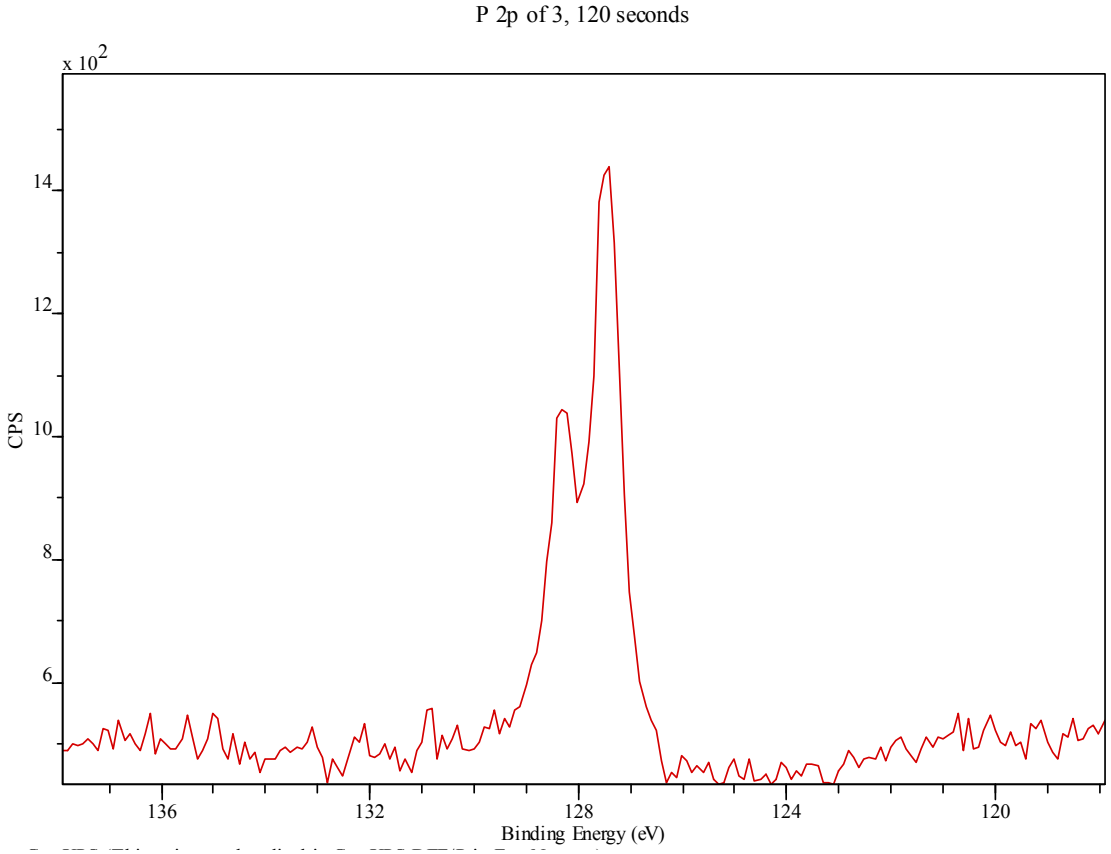

P 2p of 3, 90 seconds
x 10^2
16
14
12
10
8
6
CPS
136
132
128
124
120
Binding Energy (eV)

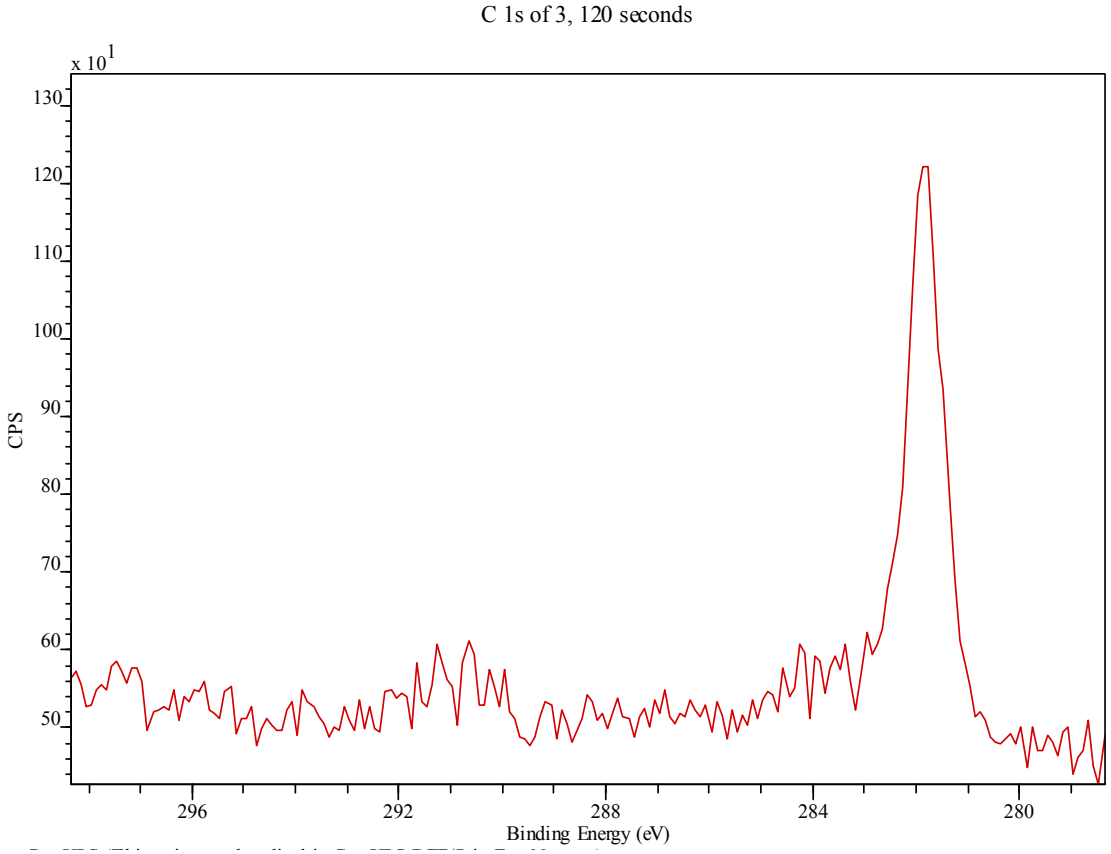


120 seconds of sputtering:

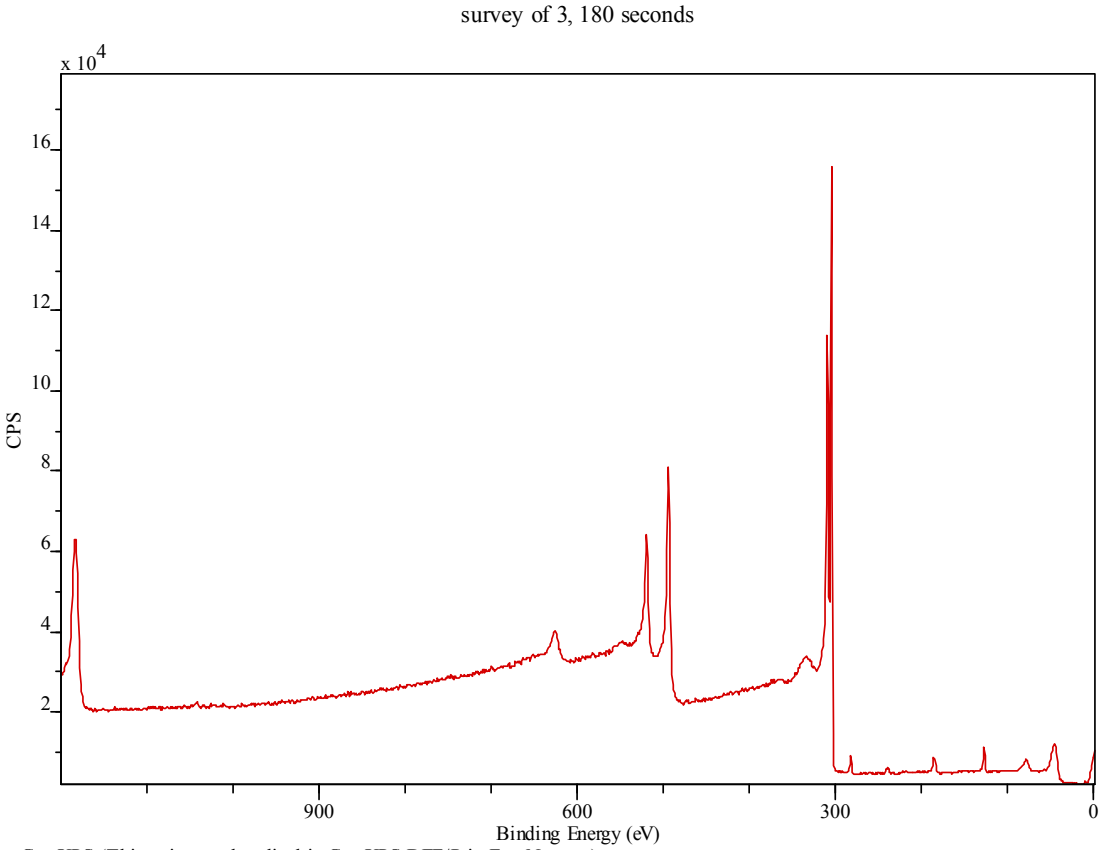

survey of 3, 120 seconds
x 10^4
16
14
12
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

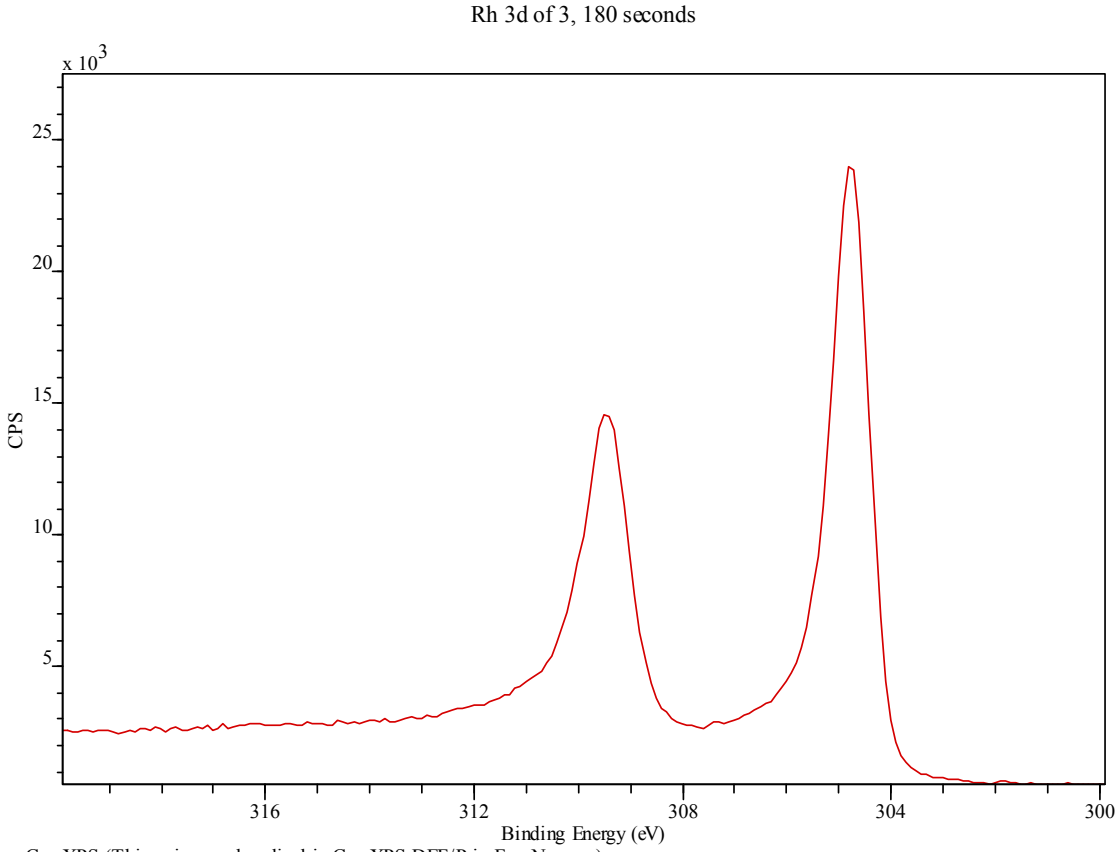

Rh 3d of 3, 120 seconds
x 10^3
25
20
15
10
5
CPS
316
312
308
304
300
Binding Energy (eV)

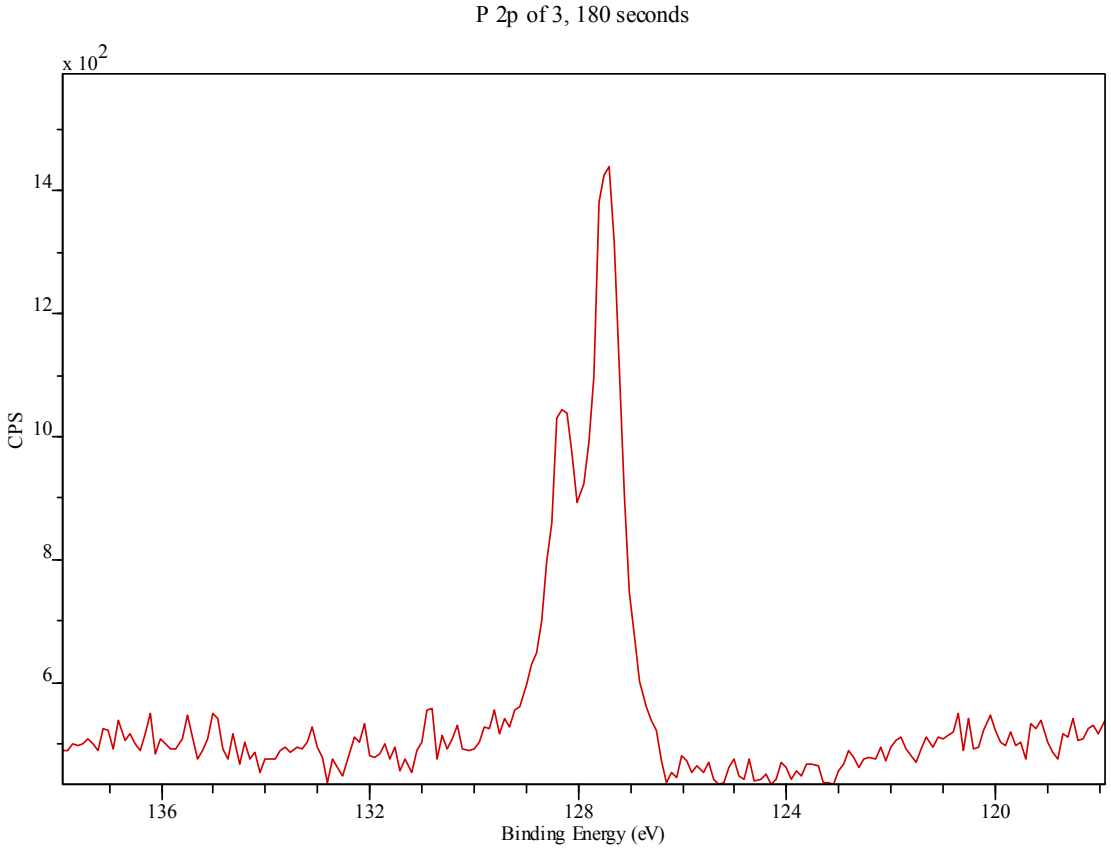

P 2p of 3, 120 seconds
x 10^2
14
12
10
8
6
CPS
136
132
128
124
120
Binding Energy (eV)

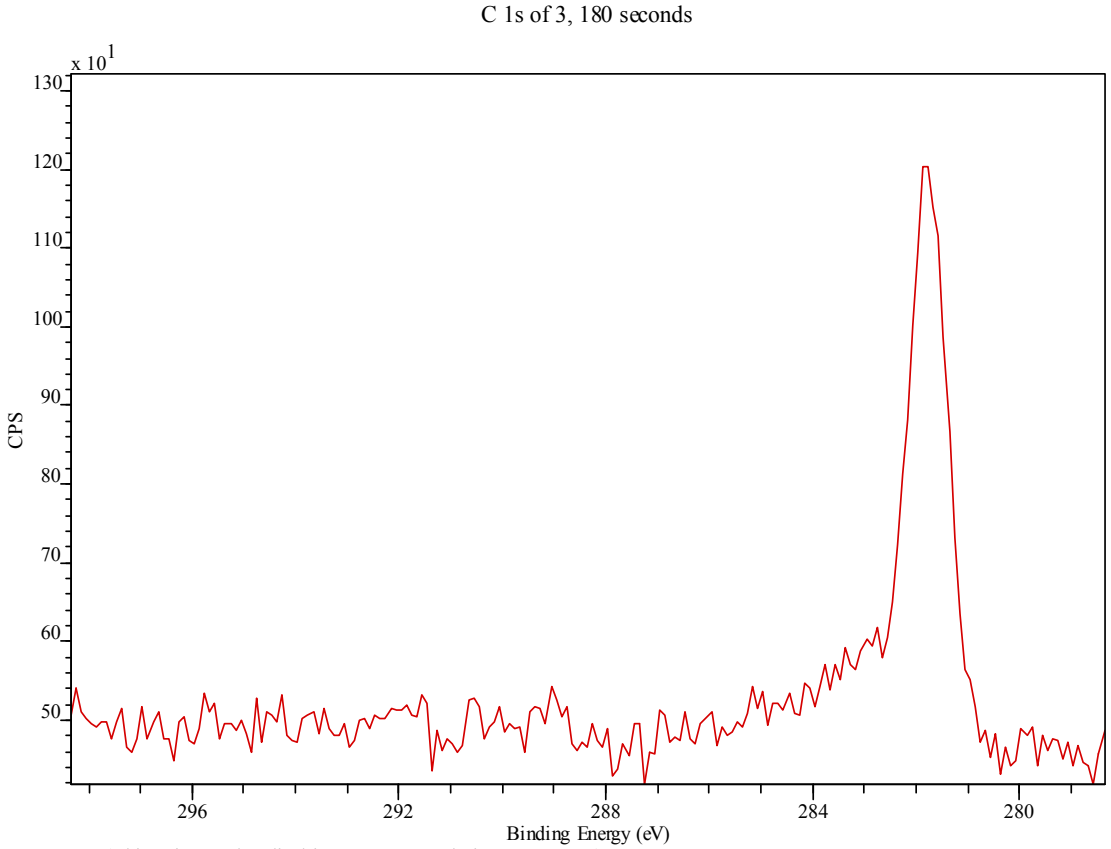


180 seconds of sputtering:

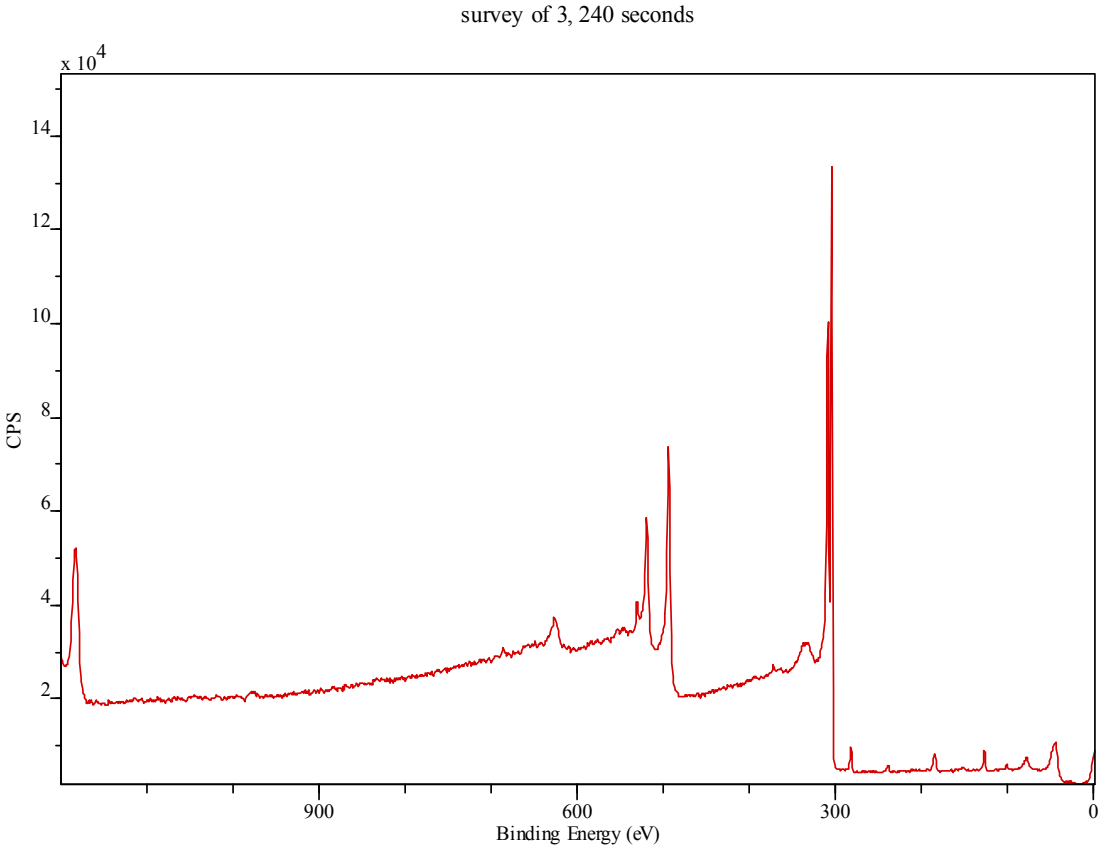

survey of 3, 180 seconds
x 10^4
16
14
12
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

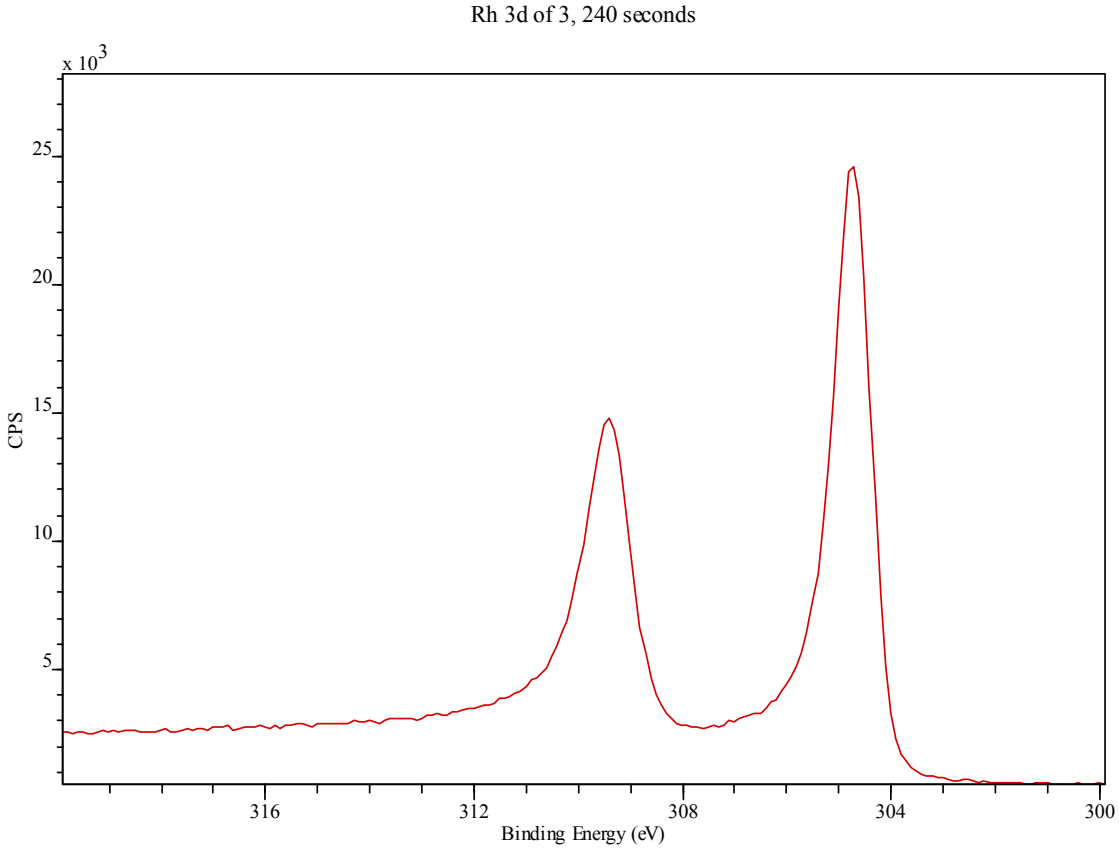

Rh 3d of 3, 180 seconds
x 10^3
25
20
15
10
5
CPS
316
312
308
304
300
Binding Energy (eV)

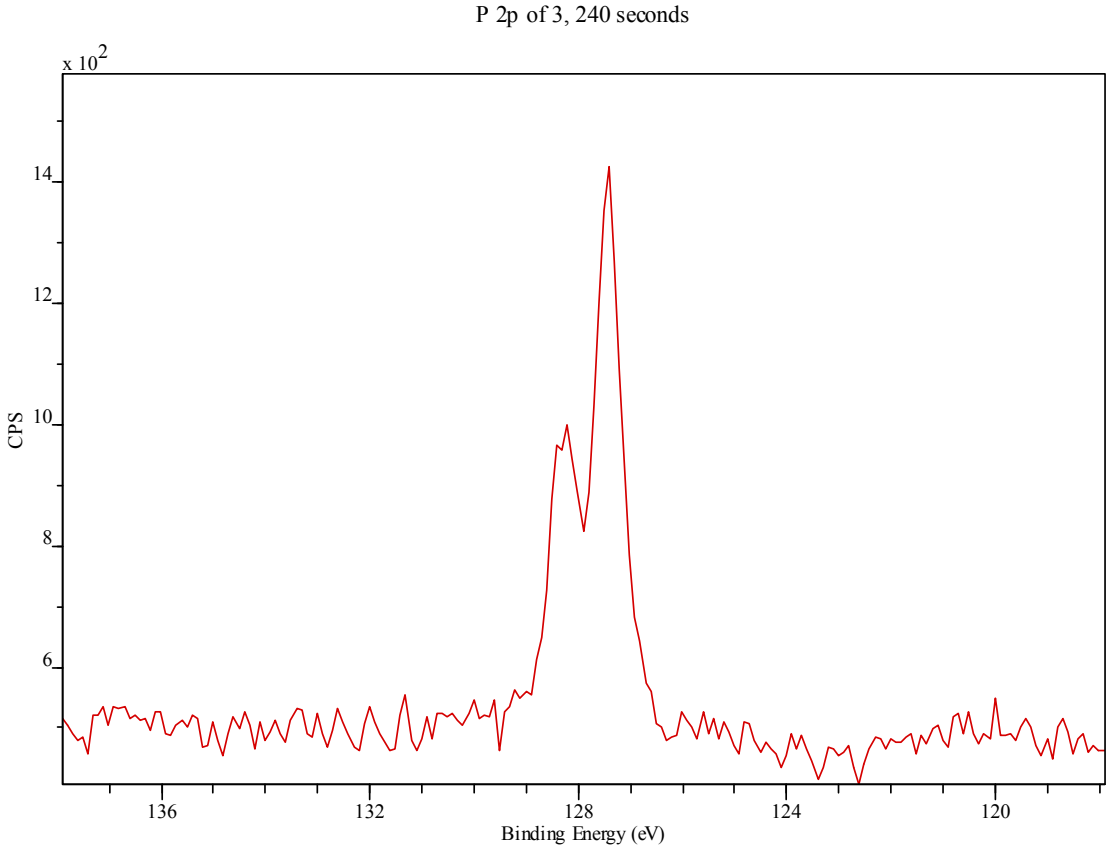

P 2p of 3, 180 seconds
x 10^2
14
12
10
8
6
CPS
136
132
128
124
120
Binding Energy (eV)

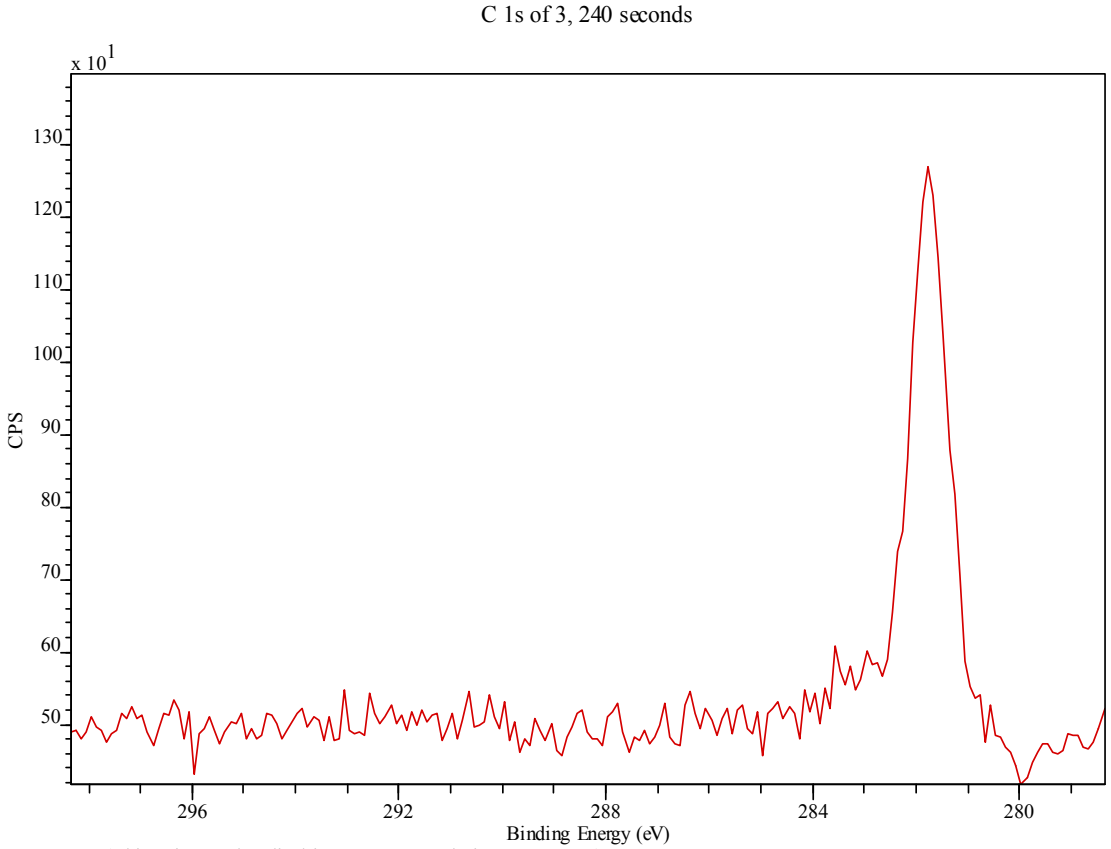


240 seconds of sputtering:

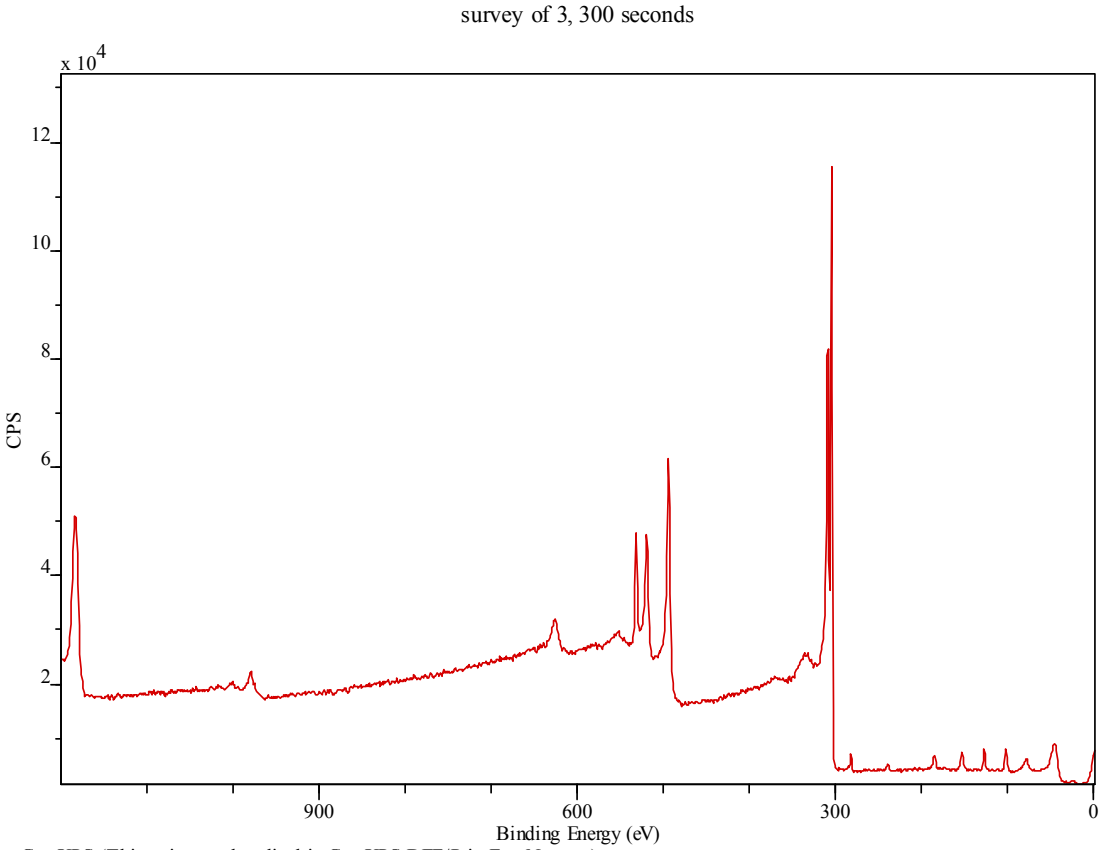


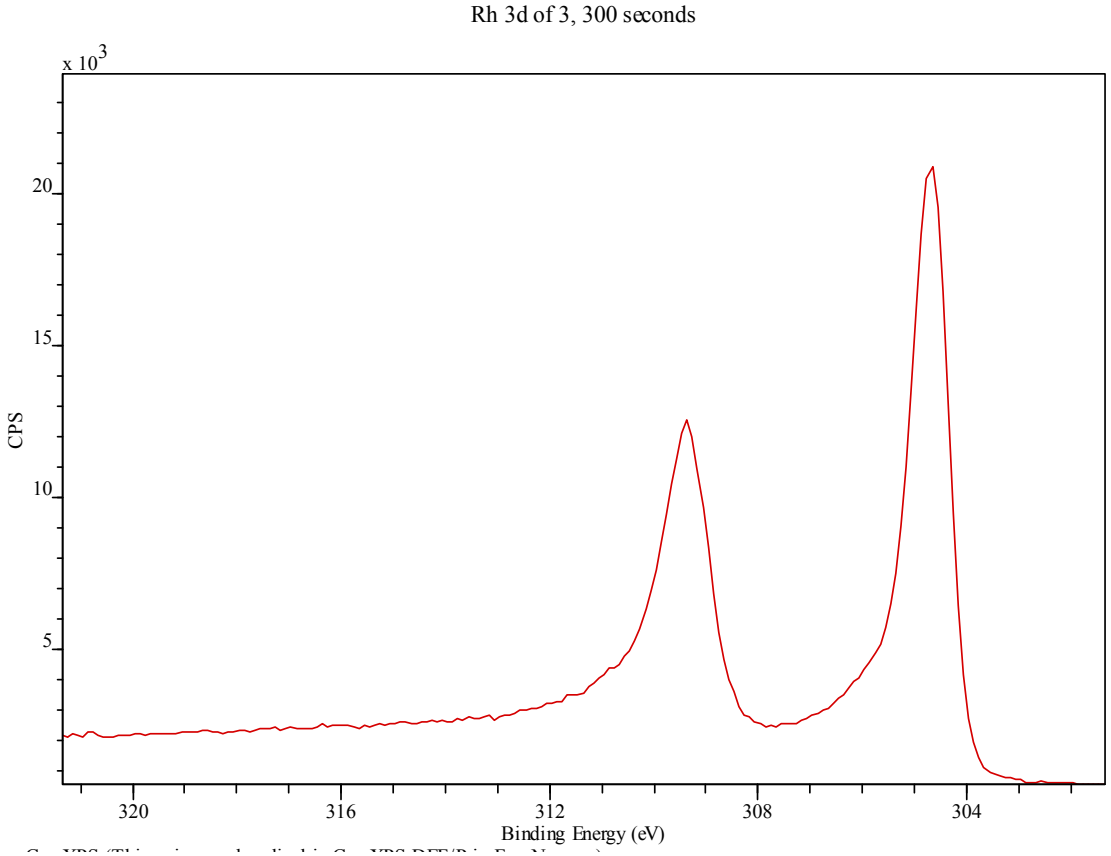


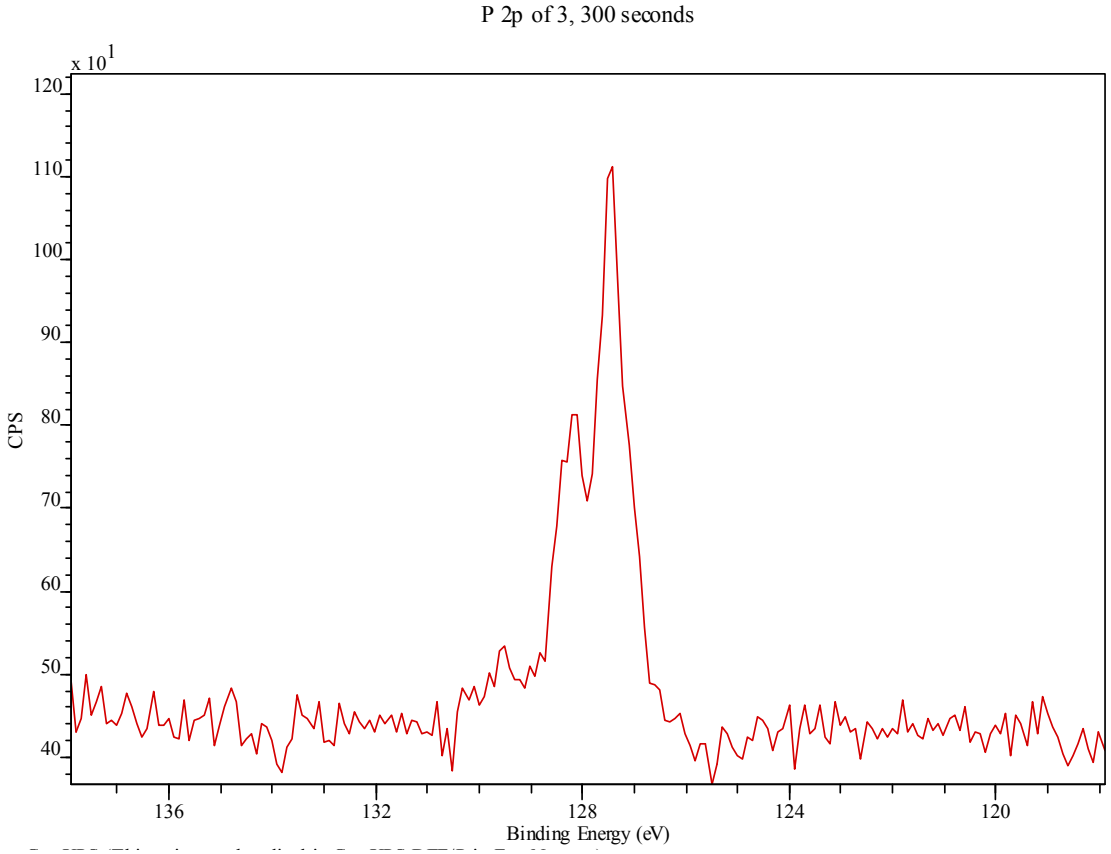

P 2p of 3, 240 seconds
x 10^2
14
12
10
8
6
CPS
136
132
128
124
120
Binding Energy (eV)

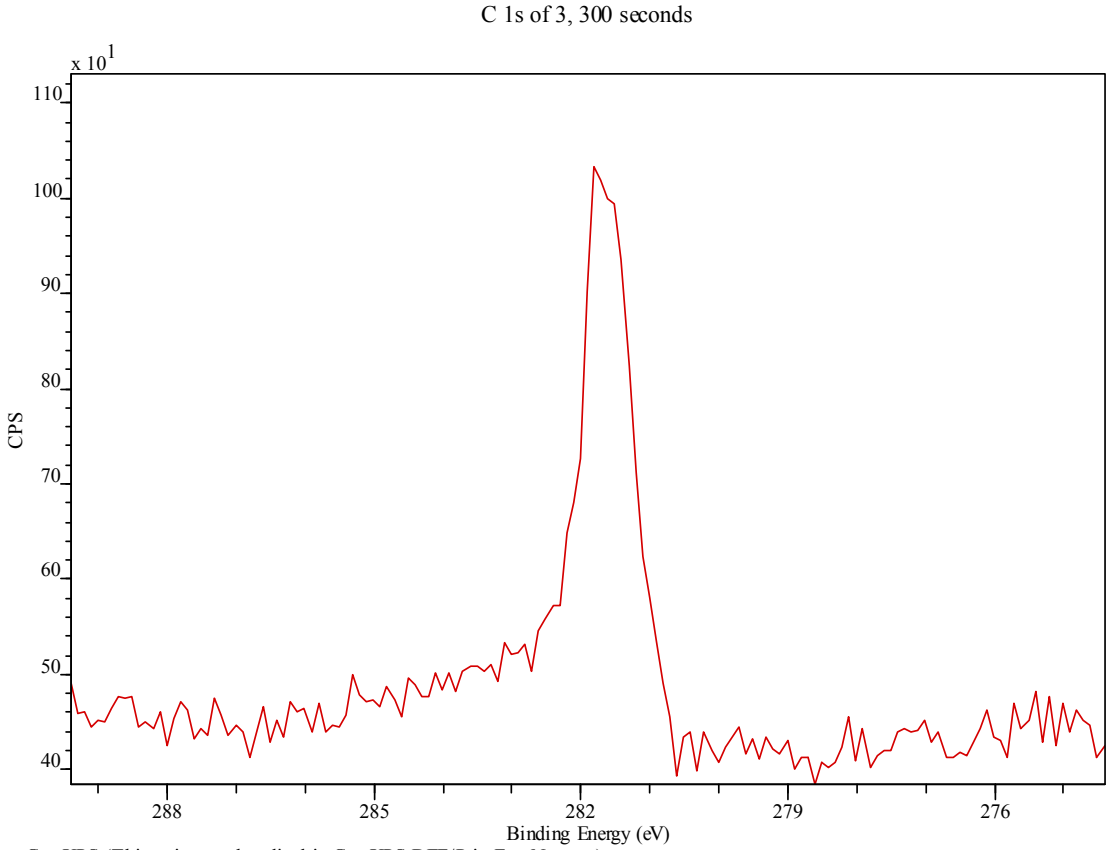


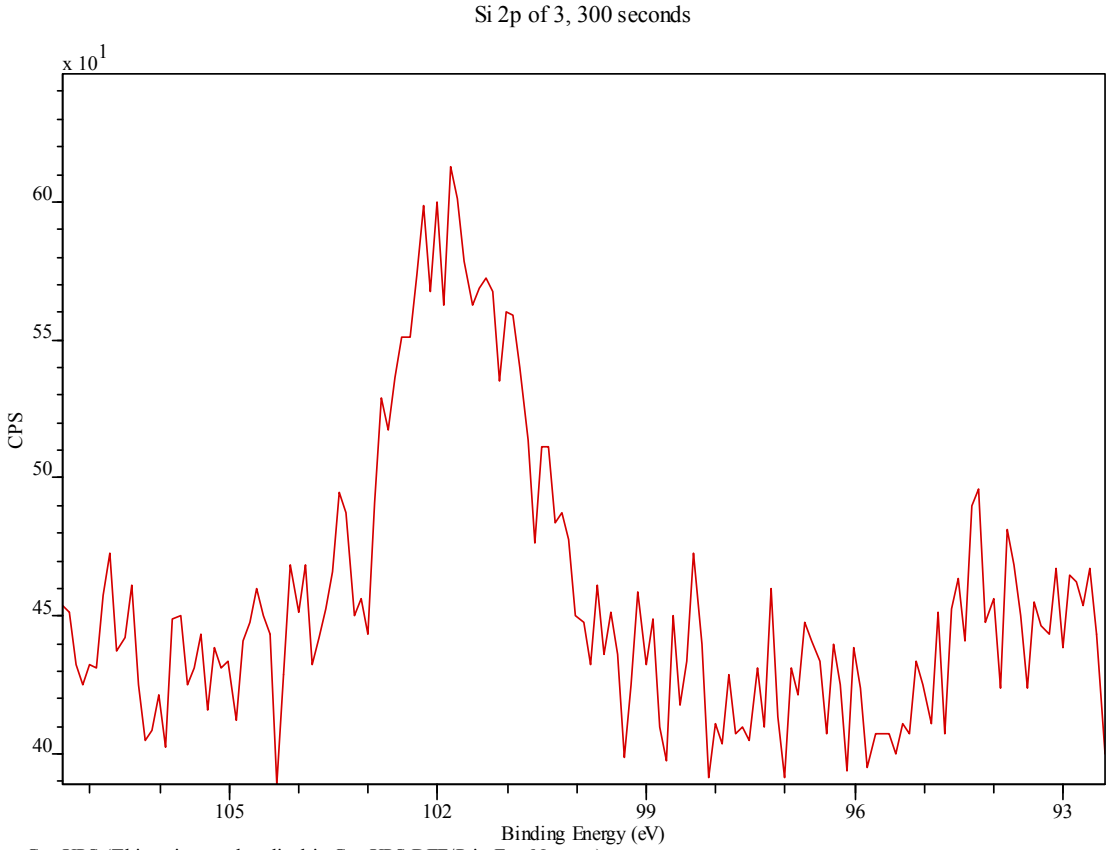
300 seconds of sputtering:


survey of 3, 300 seconds
x 10^4
12
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

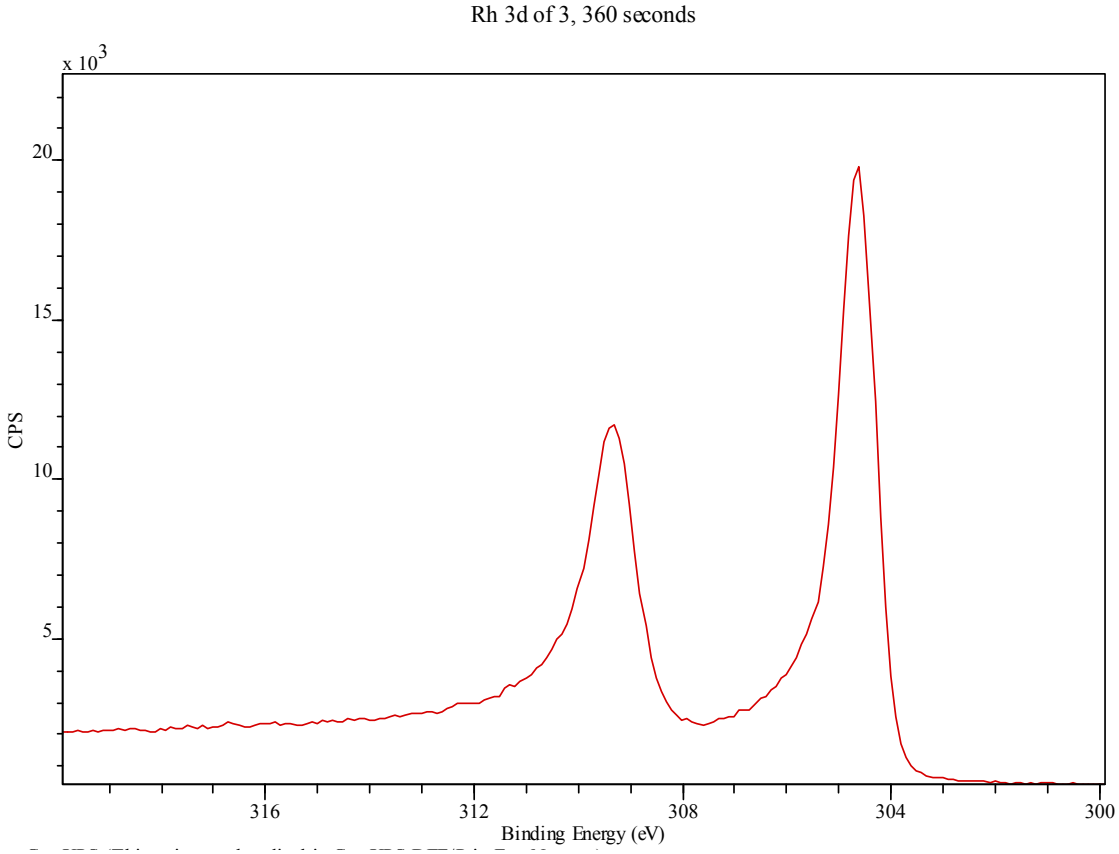

Rh 3d of 3, 300 seconds
x 10^3
20
15
10
5
CPS
320
316
312
308
304
Binding Energy (eV)

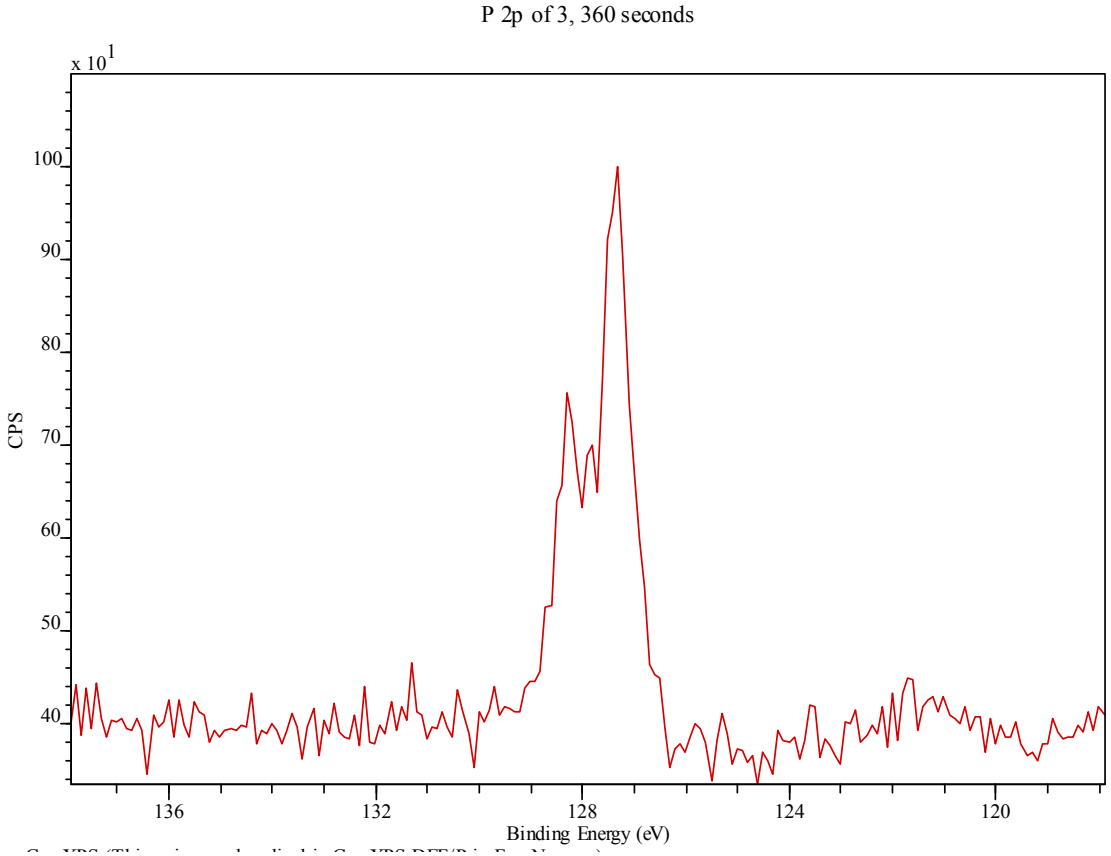

P 2p of 3, 300 seconds
x 10^1
120
110
100
90
80
70
60
50
40
CPS
136
132
128
124
120
Binding Energy (eV)

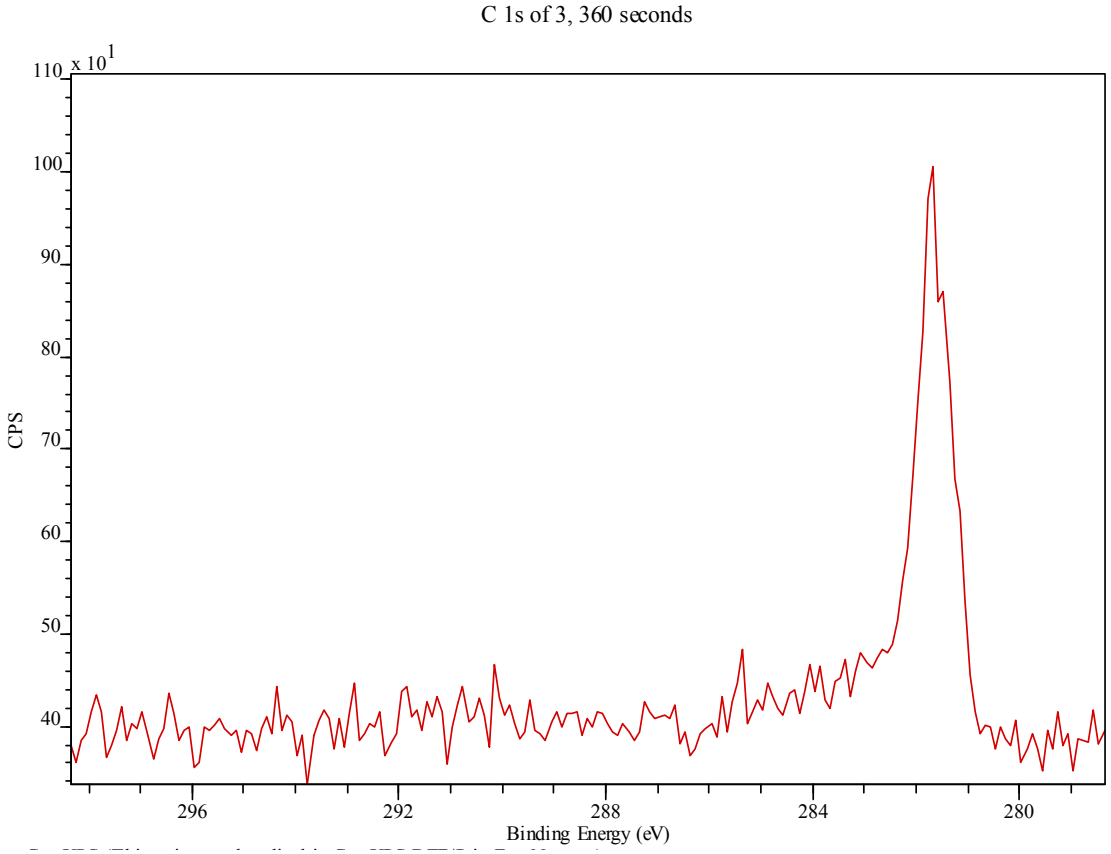

C 1s of 3, 300 seconds
x 10^1
110
100
90
80
70
60
50
40
CPS
288
285
282
279
276
Binding Energy (eV)

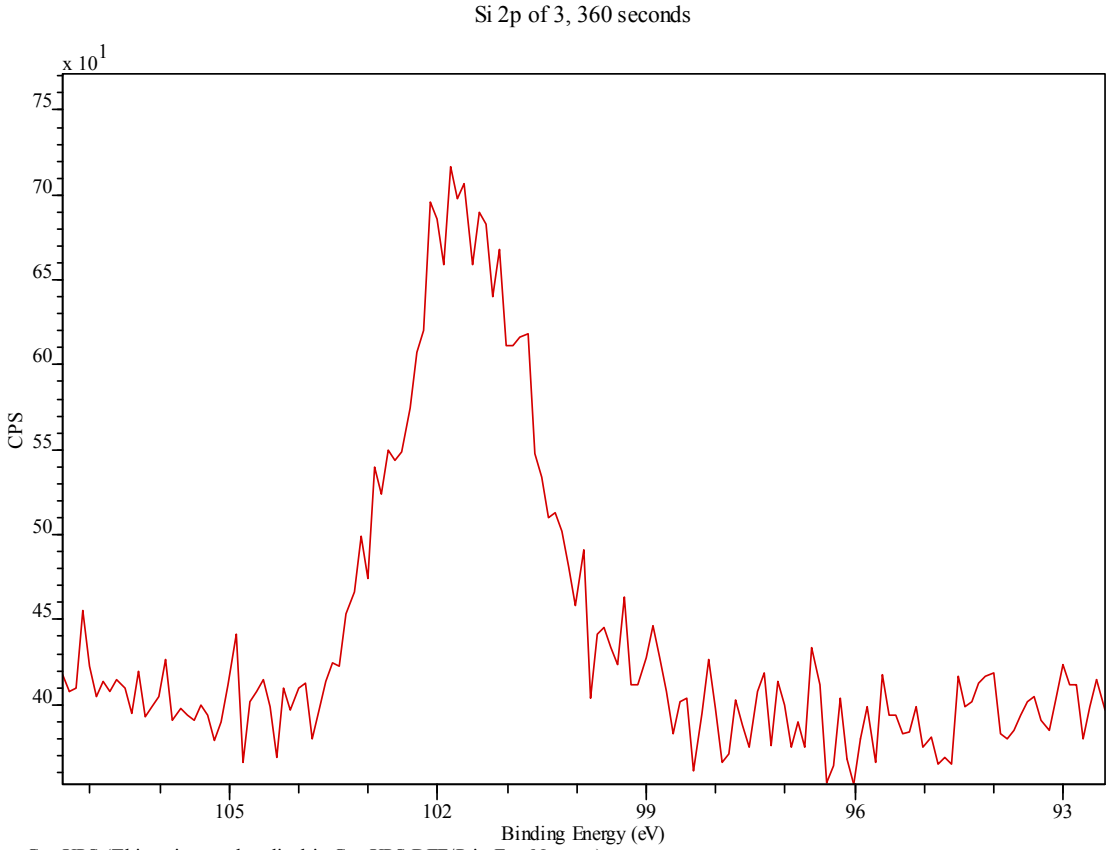


360 seconds of sputtering:

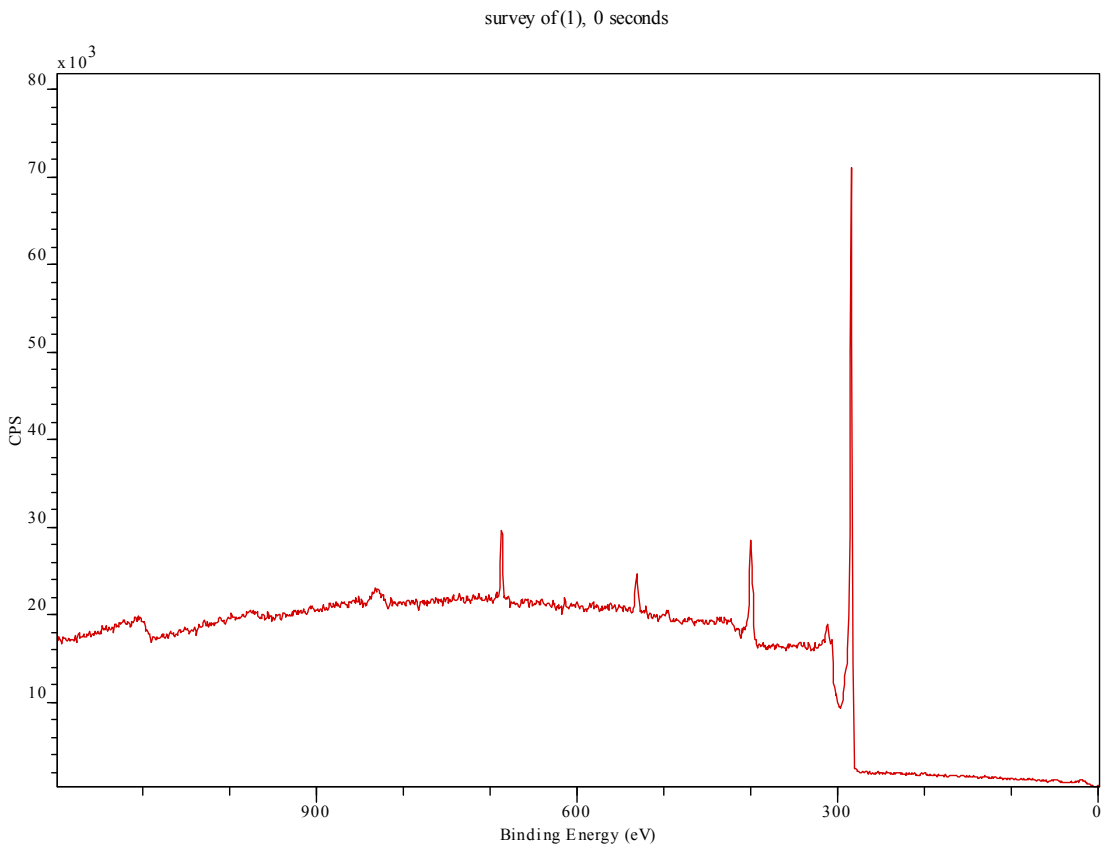

Rh 3d of 3, 360 seconds
x 10^3
20
15
10
5
CPS
316
312
308
304
300
Binding Energy (eV)

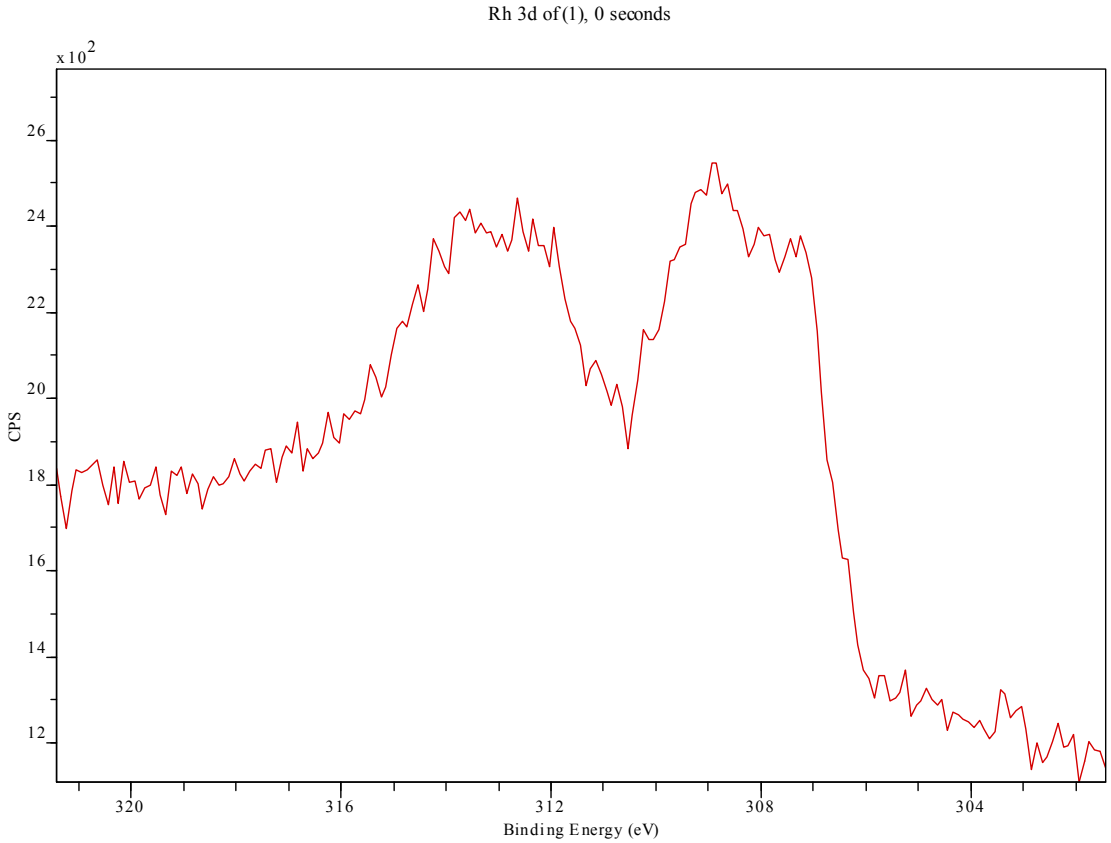

P 2p of 3, 360 seconds
x 10^1
100
90
80
70
60
50
40
CPS
136
132
128
124
120
Binding Energy (eV)

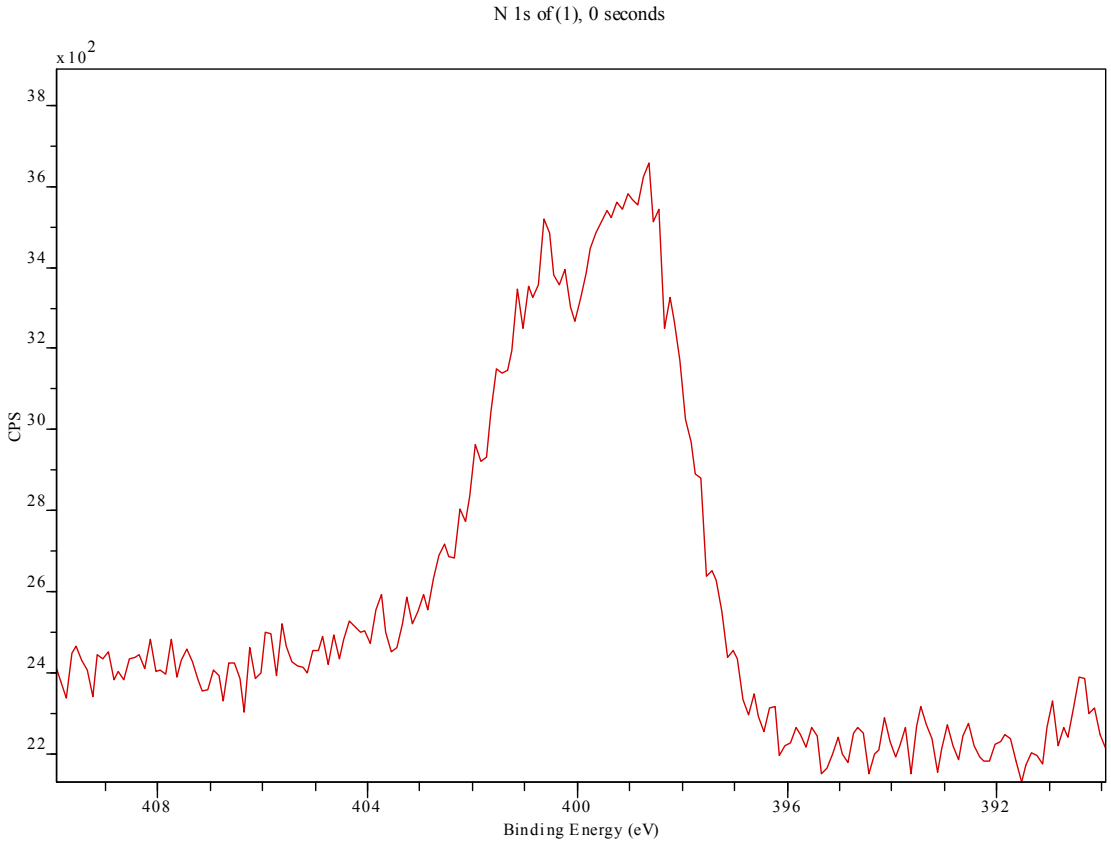

C 1s of 3, 360 seconds
x 10^1
110
100
90
80
70
60
50
40
CPS
296
292
288
284
280
Binding Energy (eV)

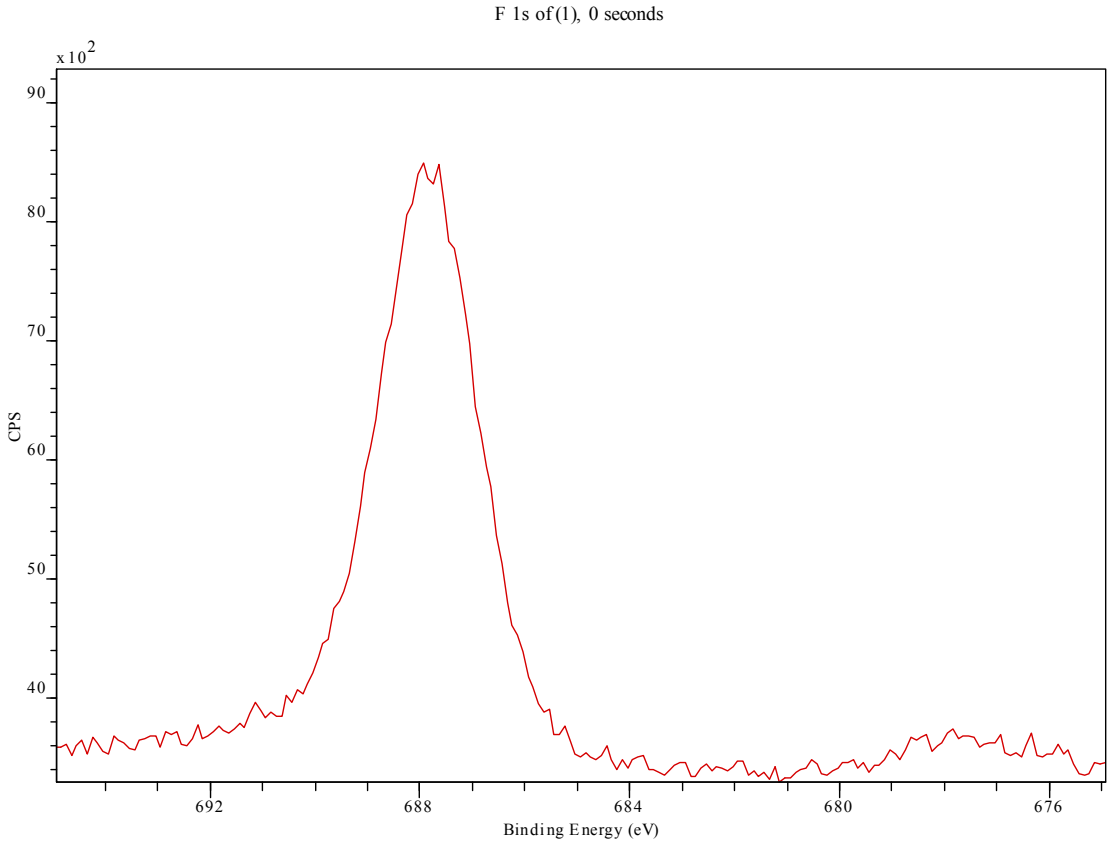

Si 2p of 3, 360 seconds
x 10^1
75
70
65
60
55
50
45
40
CPS
105
102
99
96
93
Binding Energy (eV)

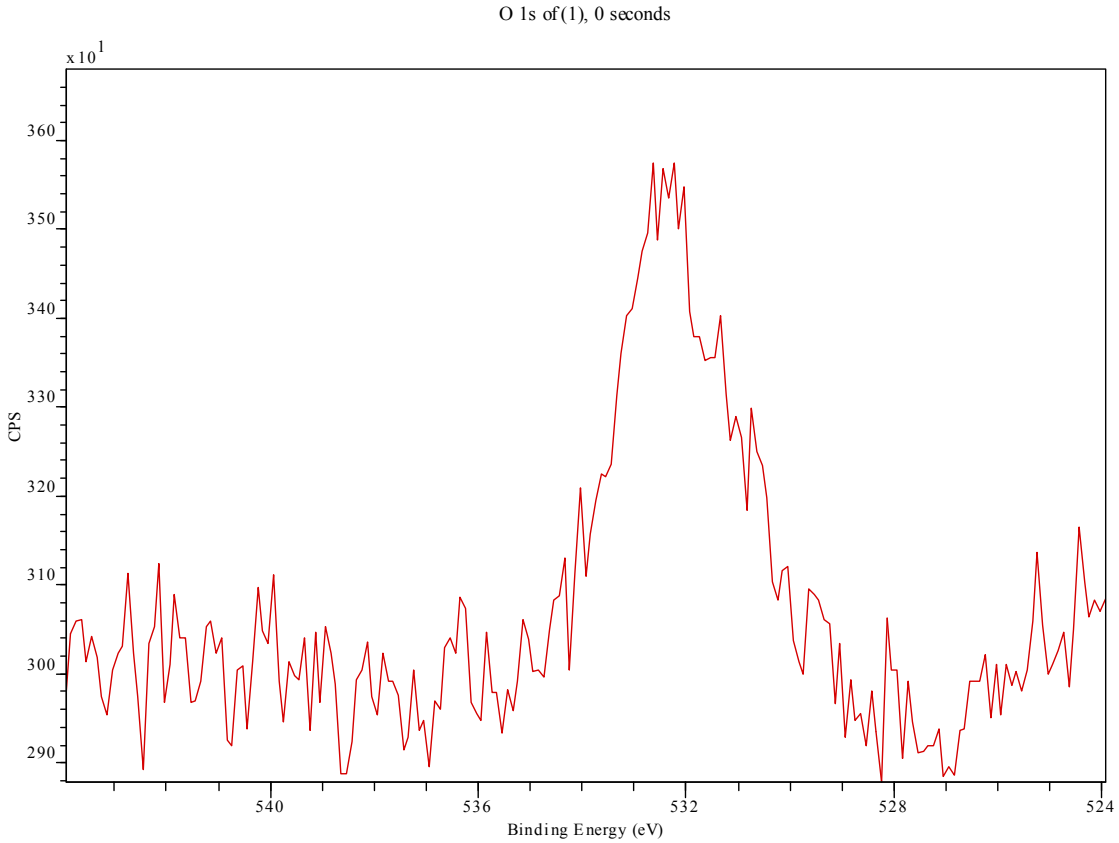
XPS spectroscopy of $[Rh(\eta^2\text{-}C_2H_4)_2(\mu\text{-}3,5\text{-}(CF_3)_2\text{-}Pz)]_2$ (**1**) using argon as the carrier gas

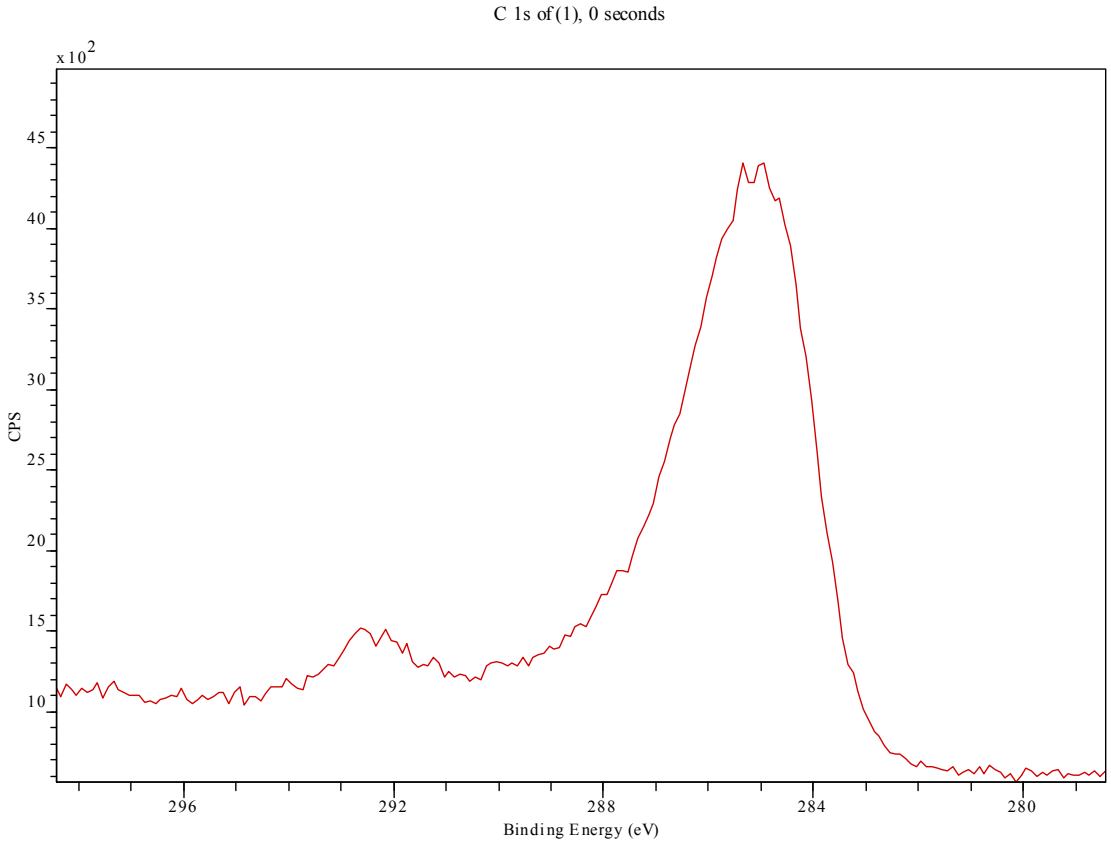


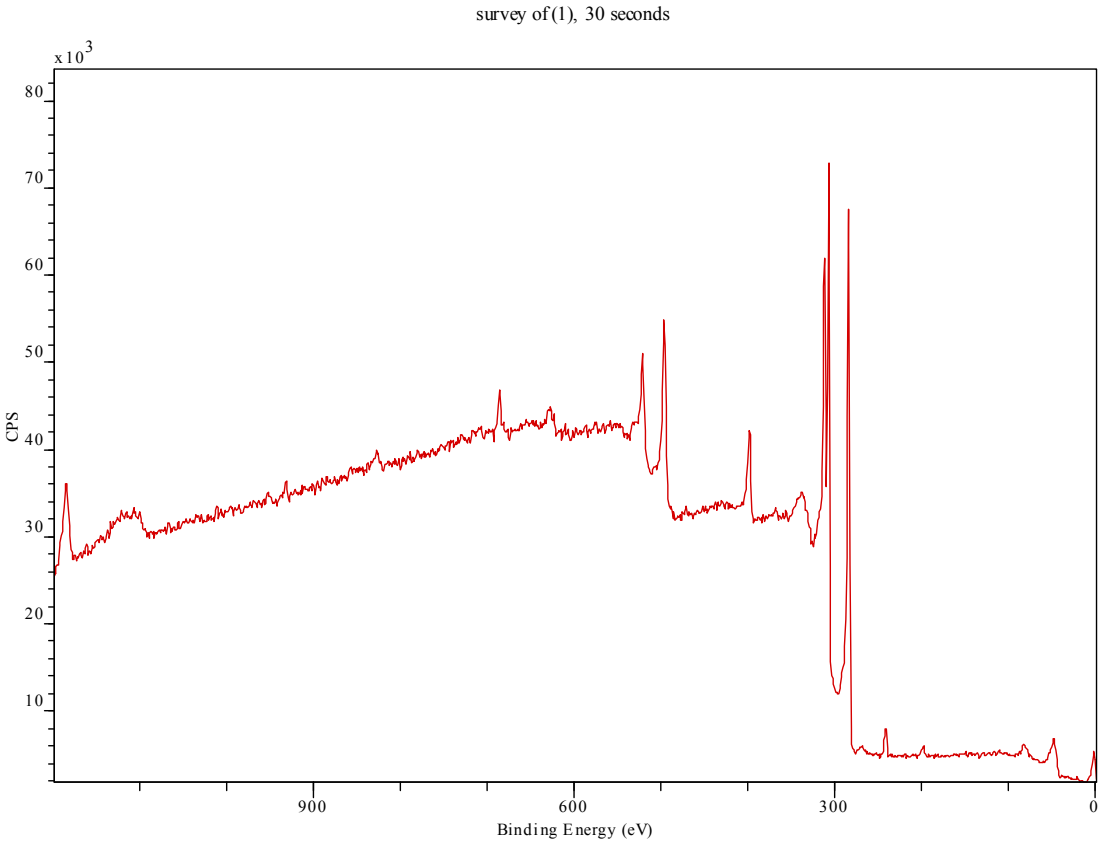

Rh 3d of (1), 0 seconds
x 10^2
26
24
22
20
18
16
14
12
CPS
320
316
312
308
304
Binding Energy (eV)

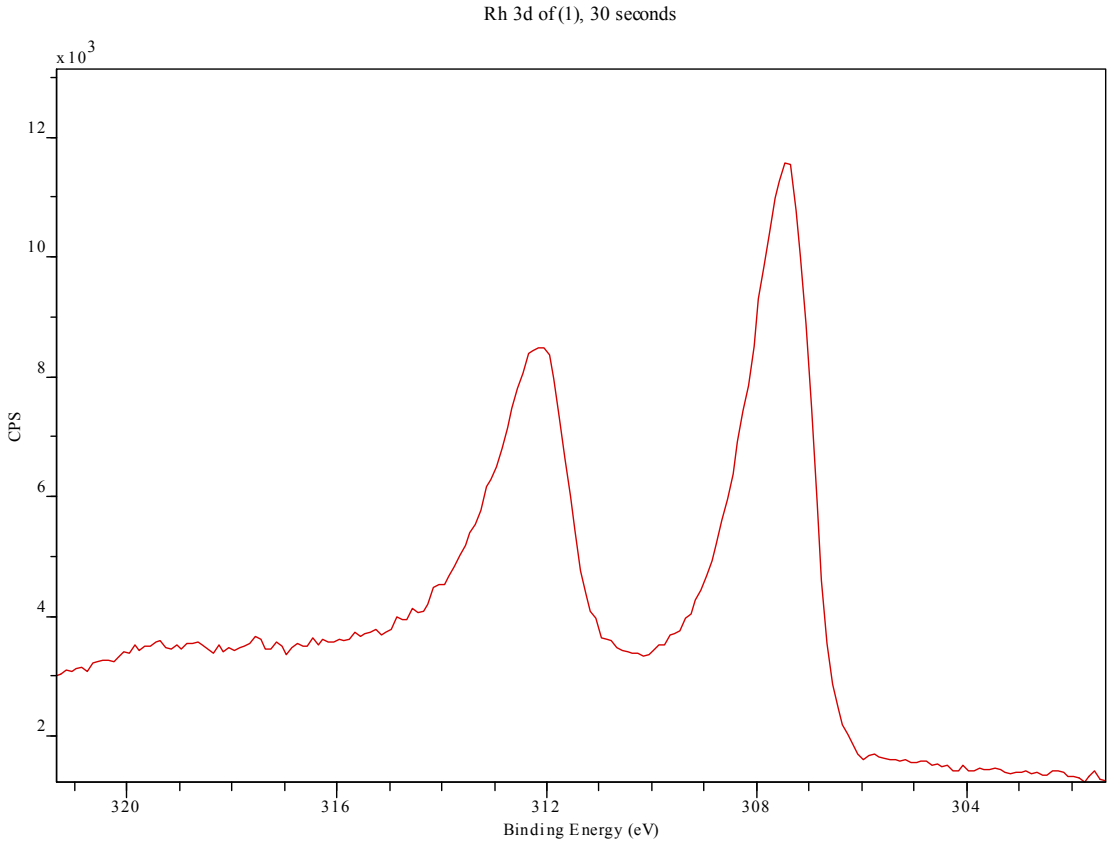

N 1s of (1), 0 seconds
x 10^2
38
36
34
32
30
28
26
24
22
CPS
408
404
400
396
392
Binding Energy (eV)

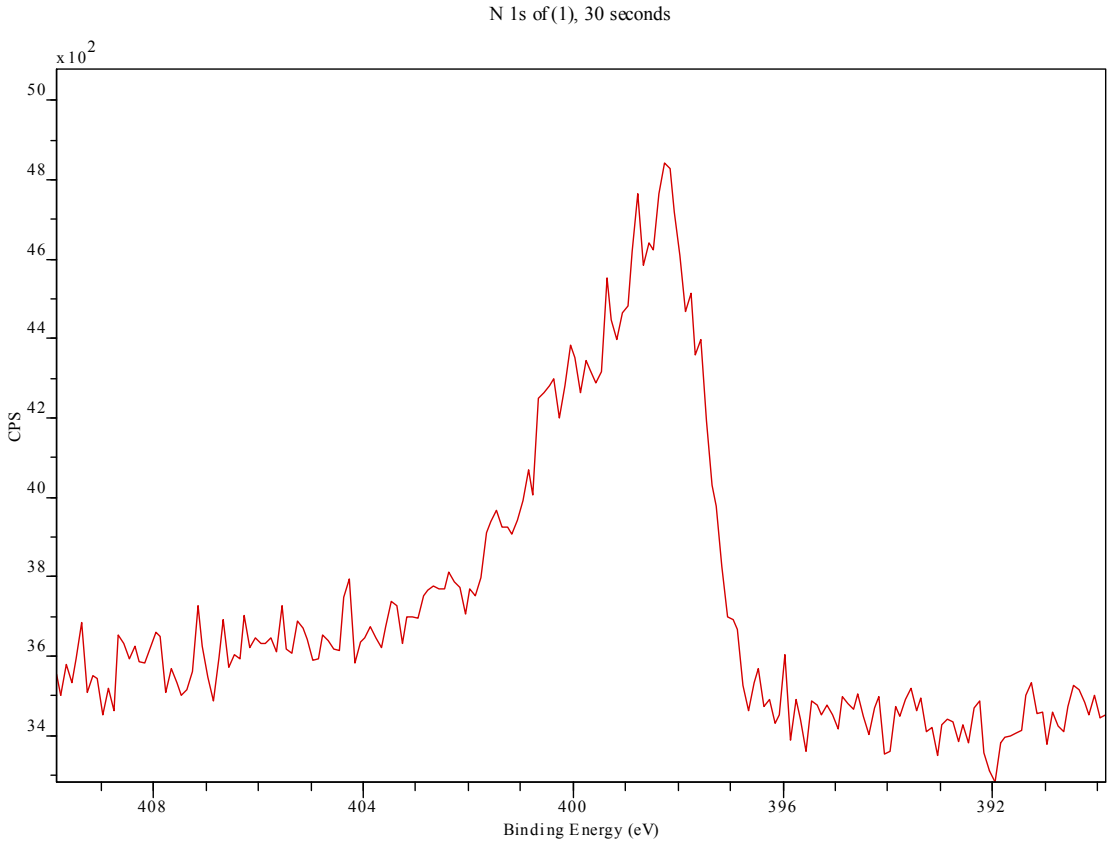


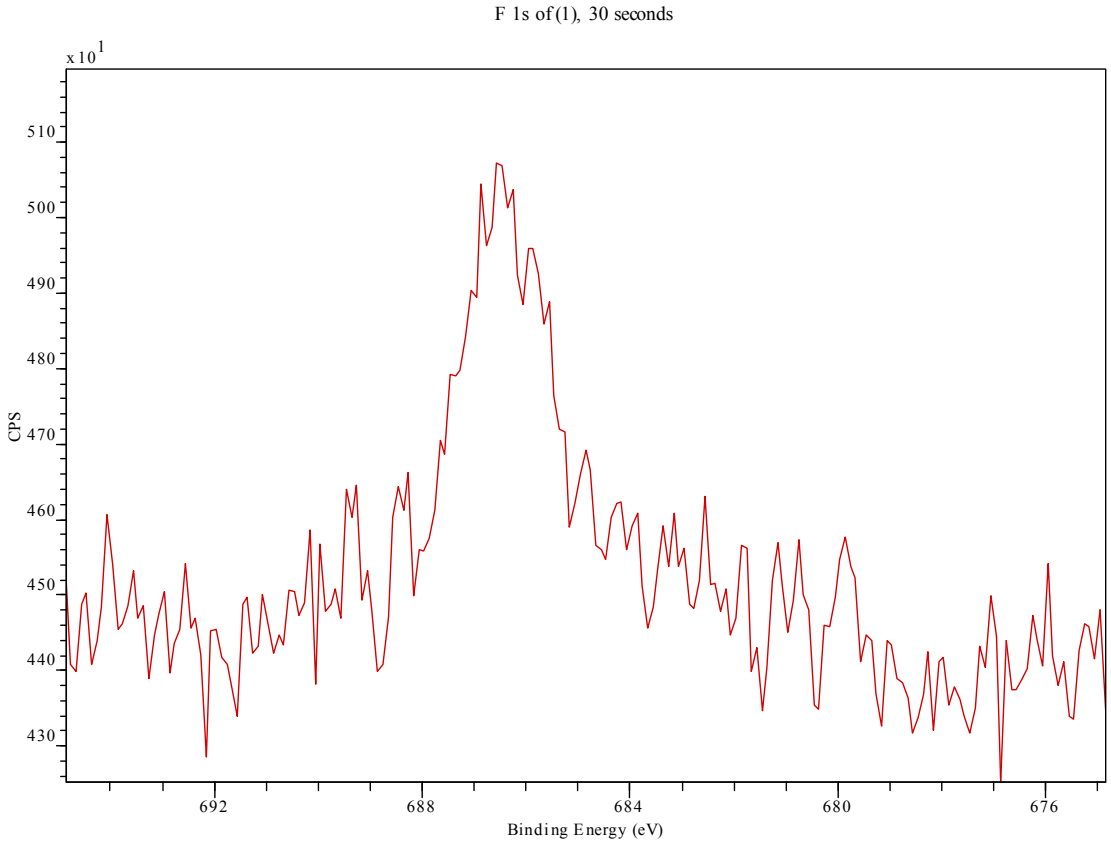

O 1s of(1), 0 seconds
x 10 1
360
350
340
330
320
310
300
290
CPS
540
536
532
528
524
Binding Energy (eV)

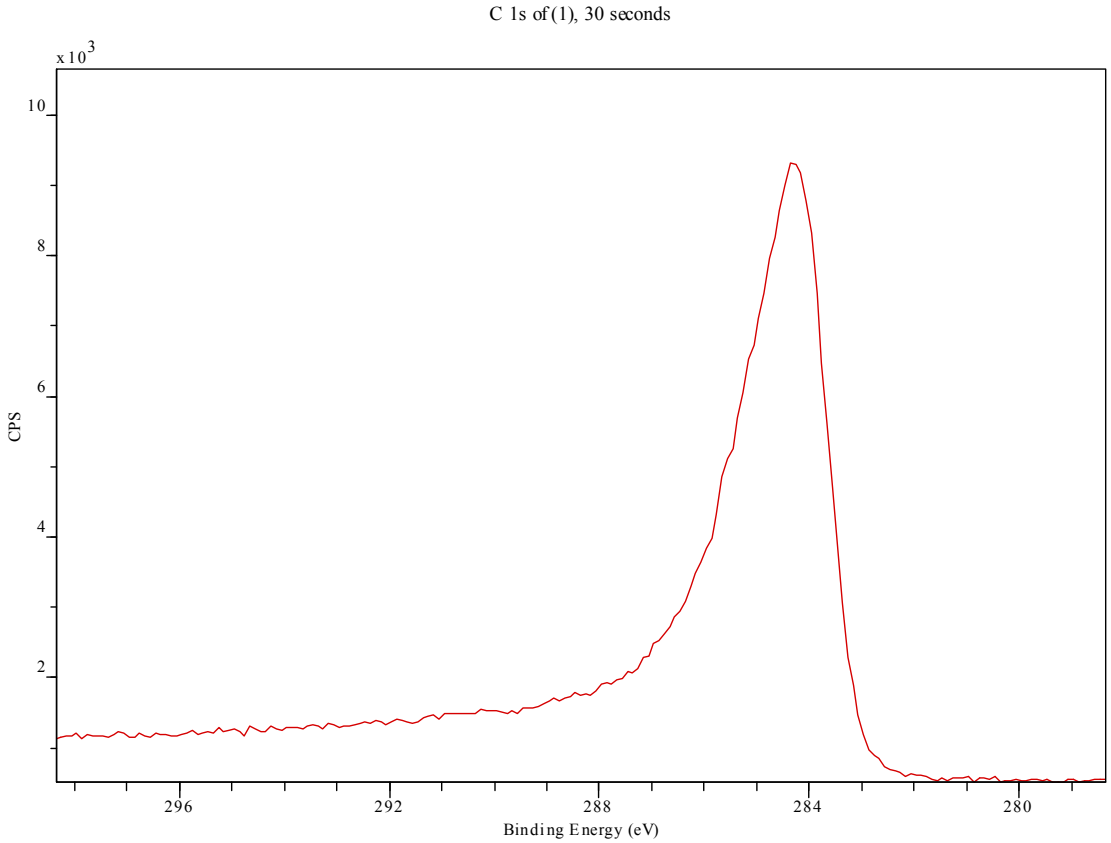


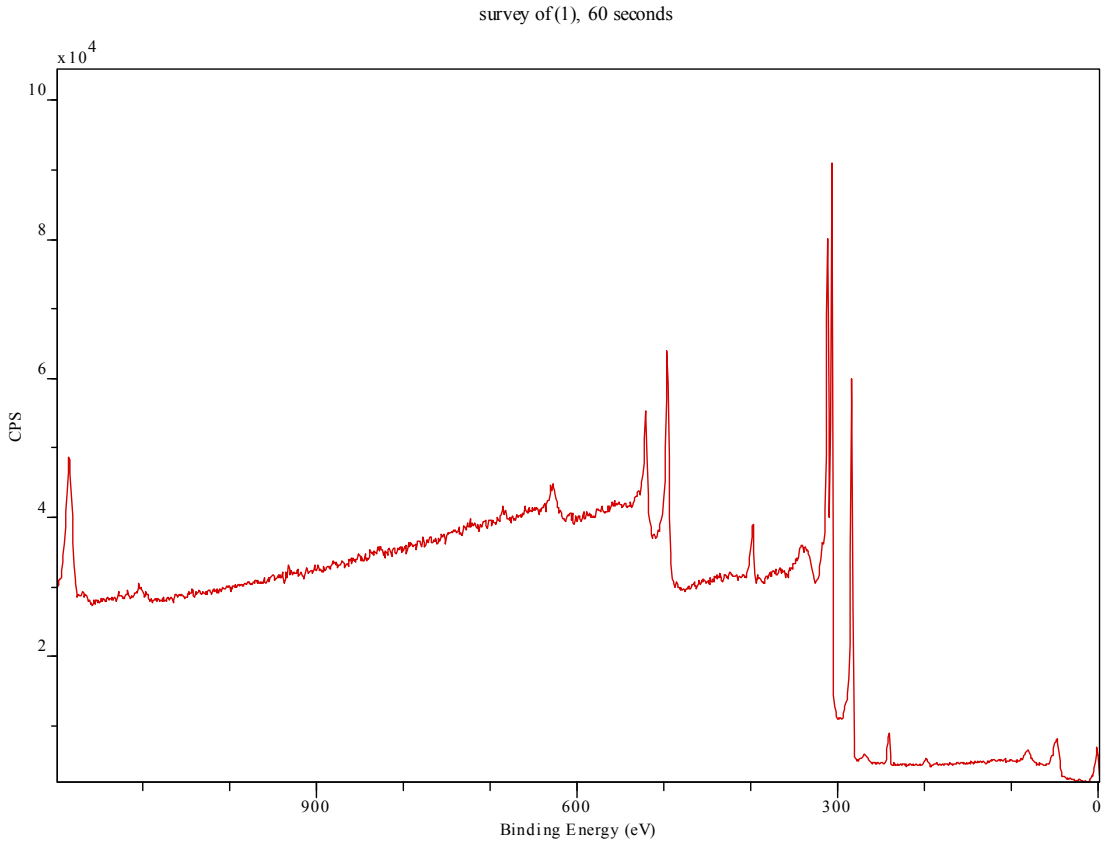

survey of (1), 30 seconds
x 10^3
80
70
60
50
40
30
20
10
CPS
900
600
300
0
Binding Energy (eV)

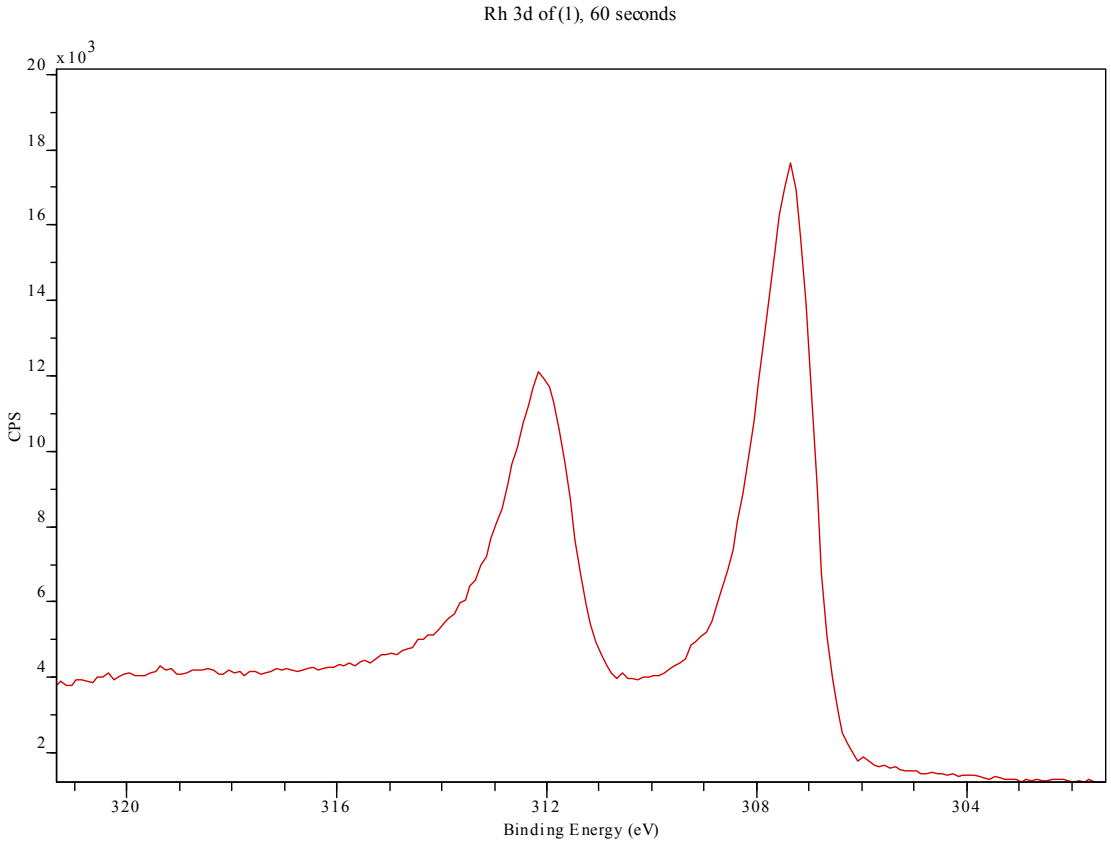


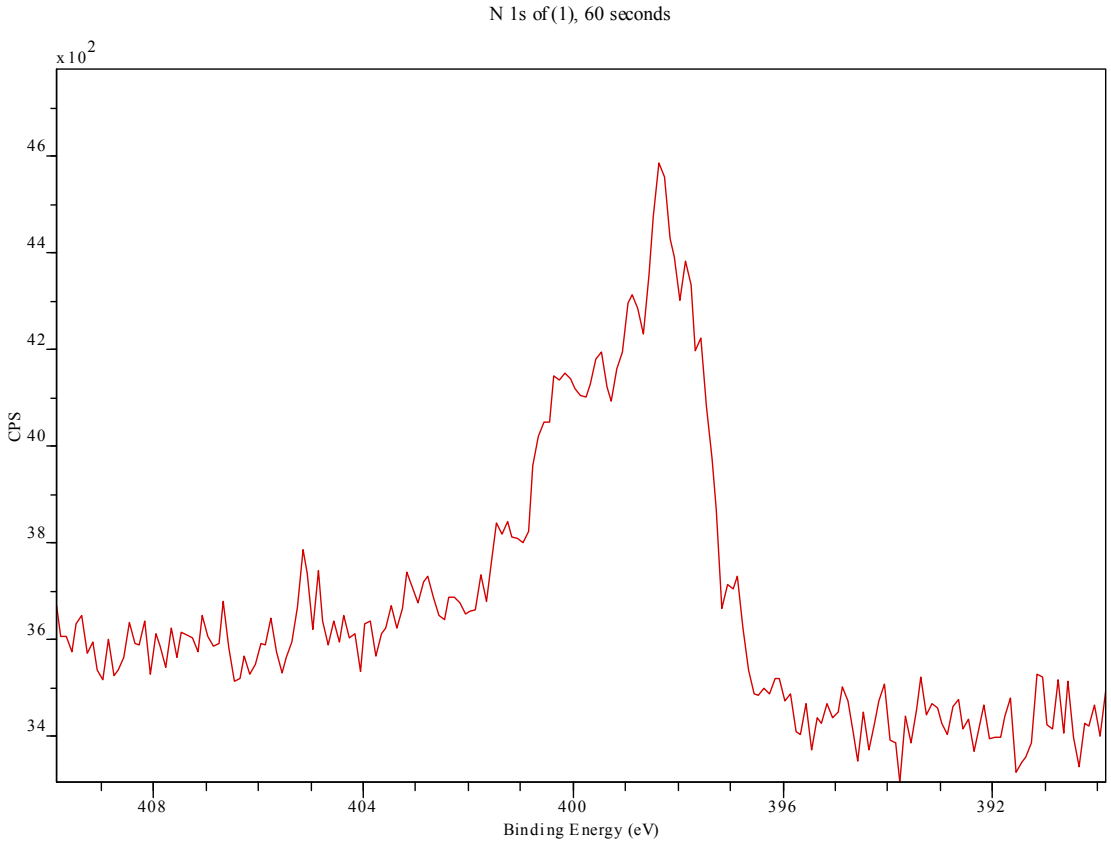


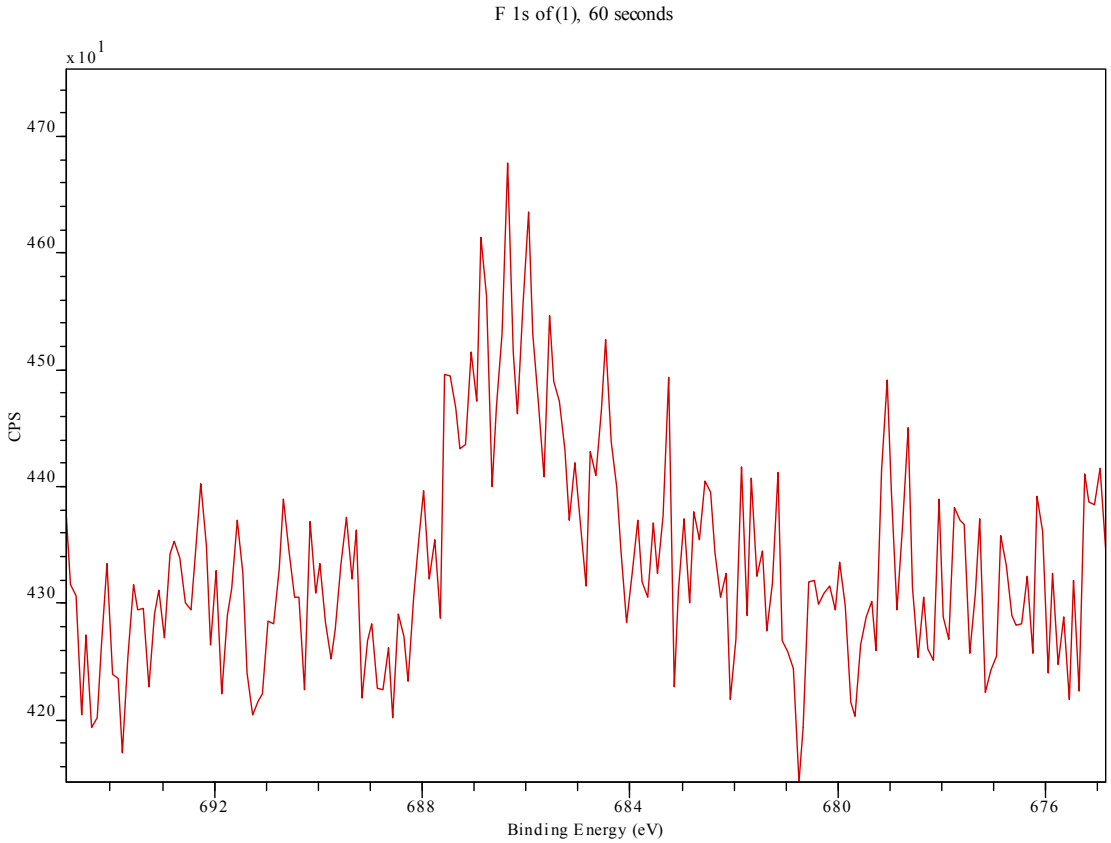

F 1s of (1), 30 seconds
x 10 1
510
500
490
480
470
460
450
440
430
CPS
692
688
684
680
676
Binding Energy (eV)

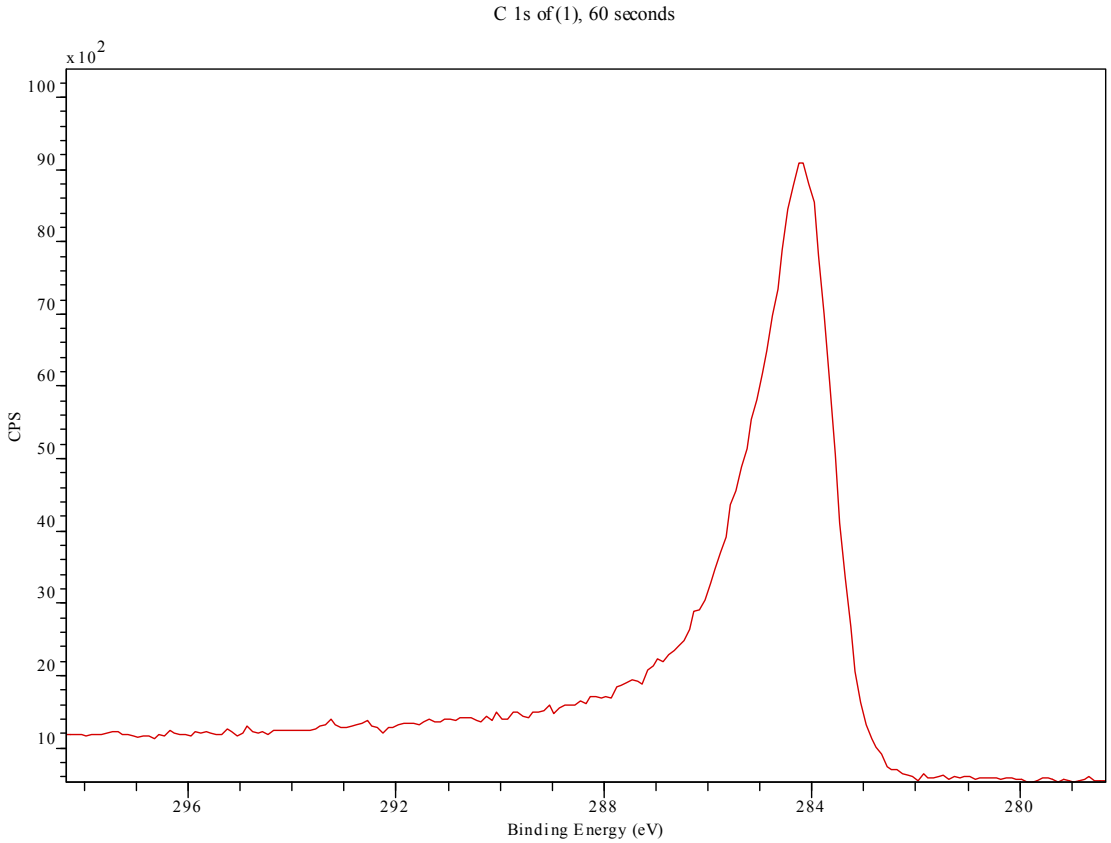

C 1s of (1), 30 seconds
x 10^3
10
8
6
4
2
CPS
296
292
288
284
280
Binding Energy (eV)

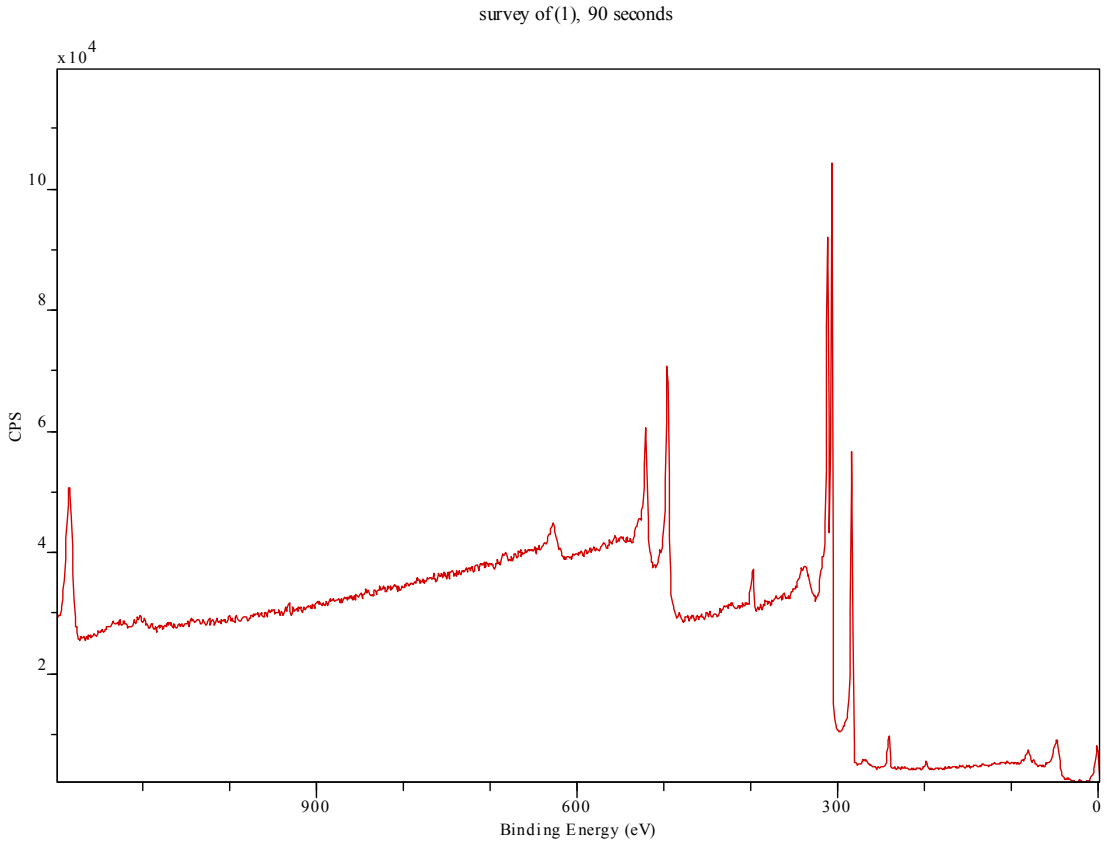

survey of (1), 60 seconds
x 10^4
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

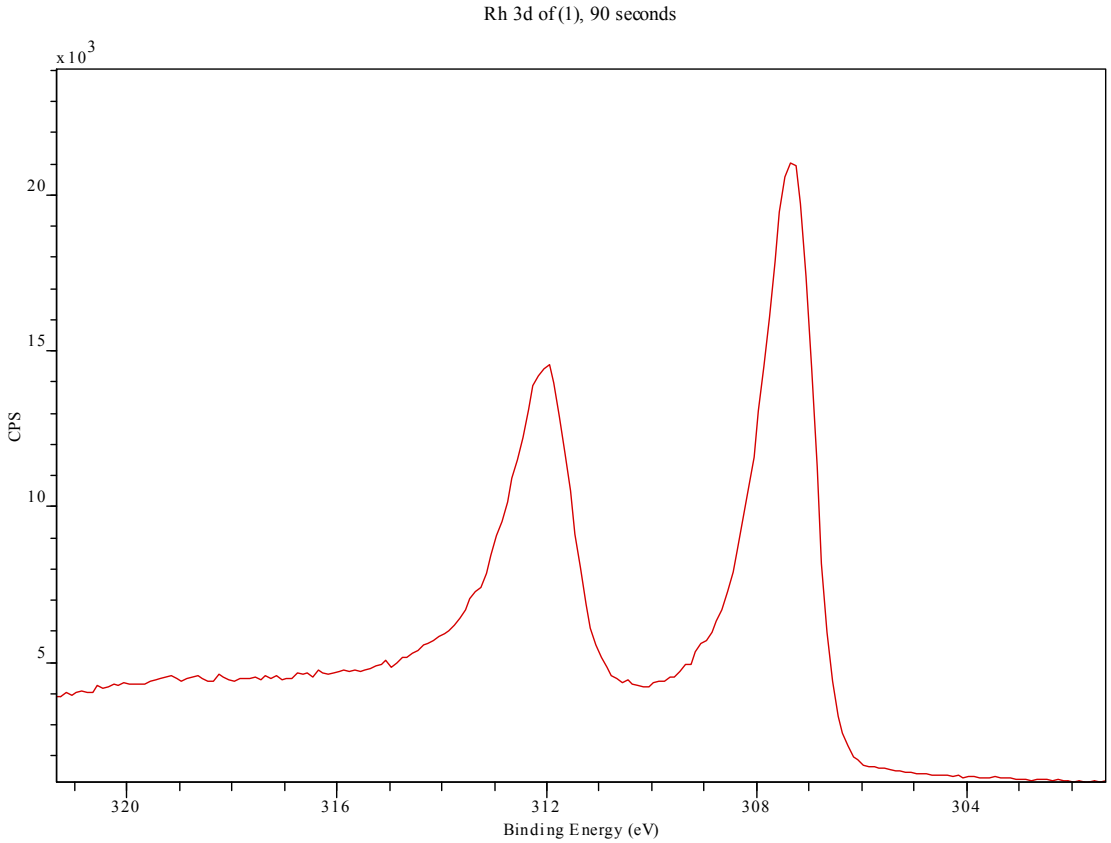


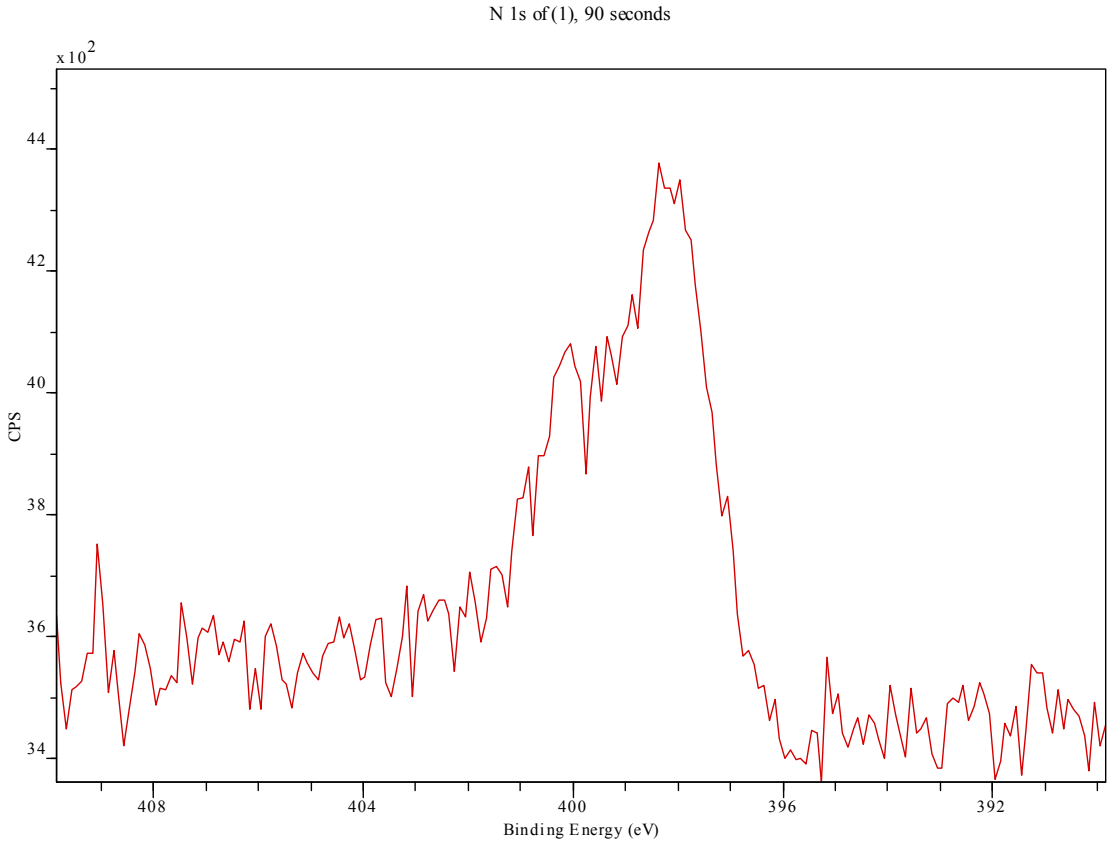

N 1s of (1), 60 seconds
x 10 2
46
44
42
CPS 40
38
36
34
408
404
400
396
392
Binding Energy (eV)

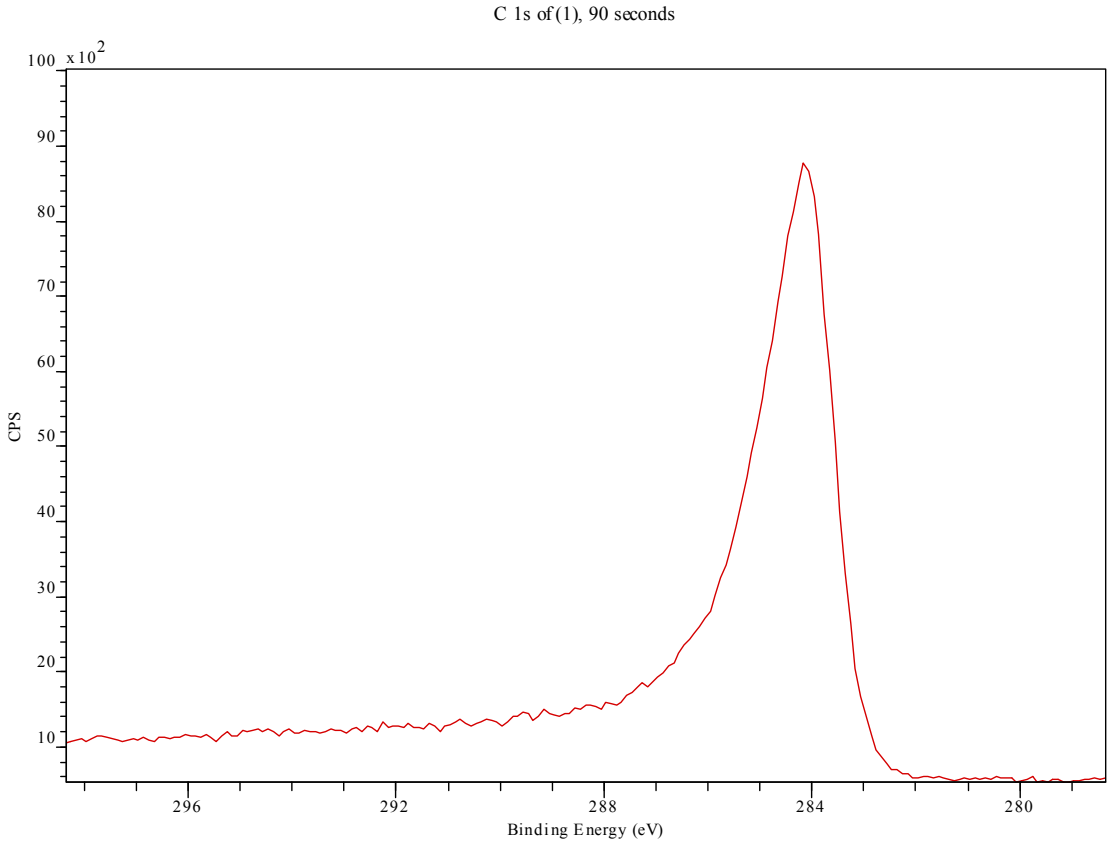

F 1s of (1), 60 seconds
x 10 1
470
460
450
440
430
420
CPS
692
688
684
680
676
Binding Energy (eV)

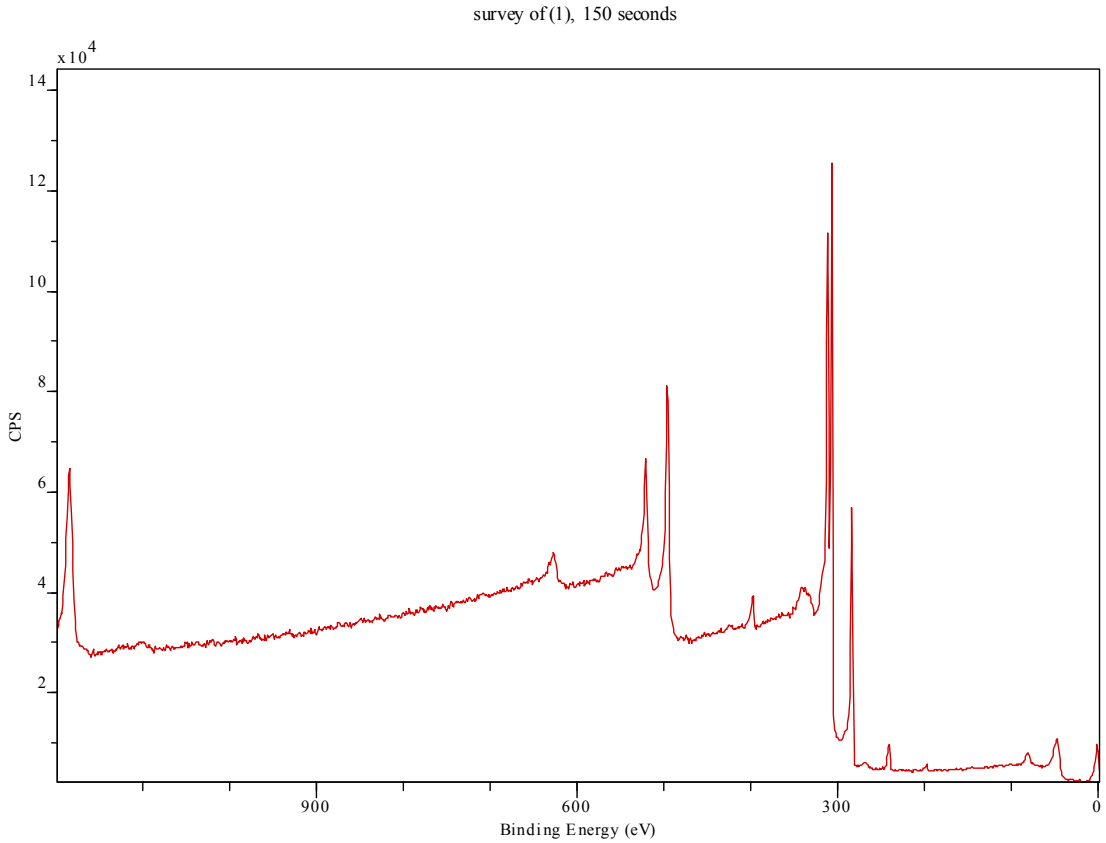


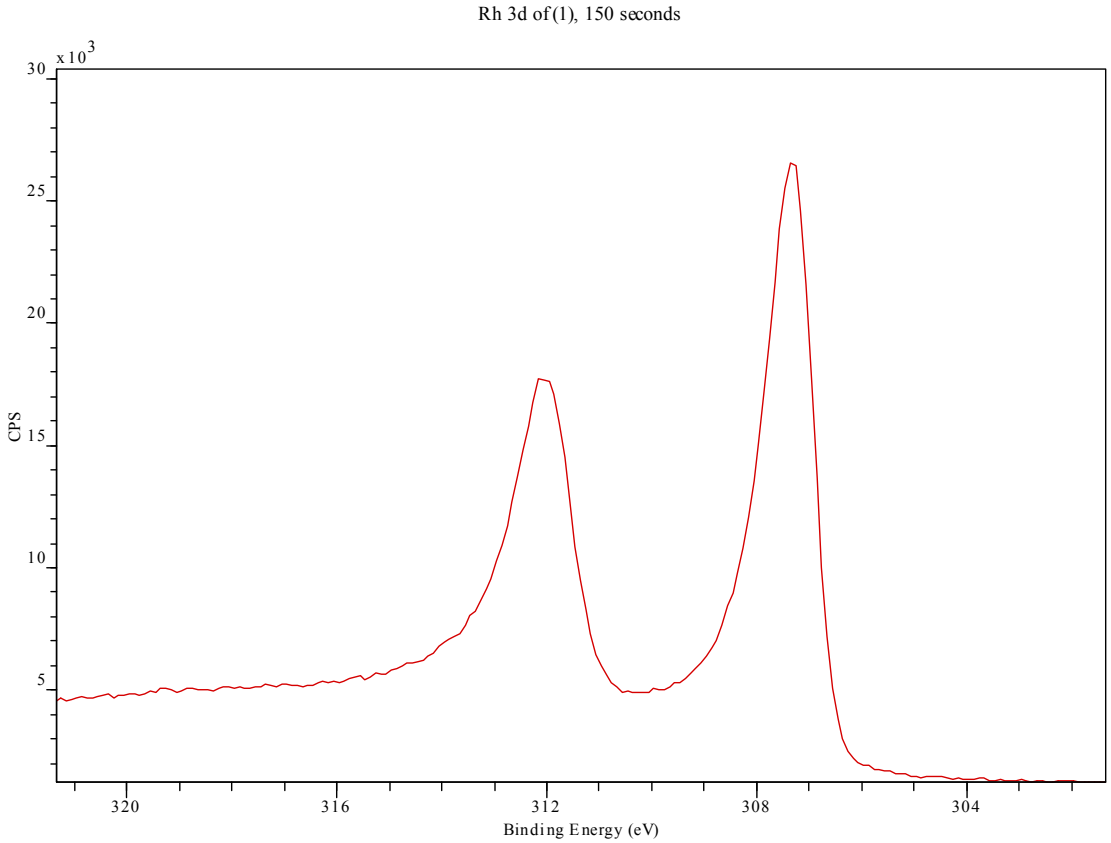

survey of (1), 90 seconds
x 10^4
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

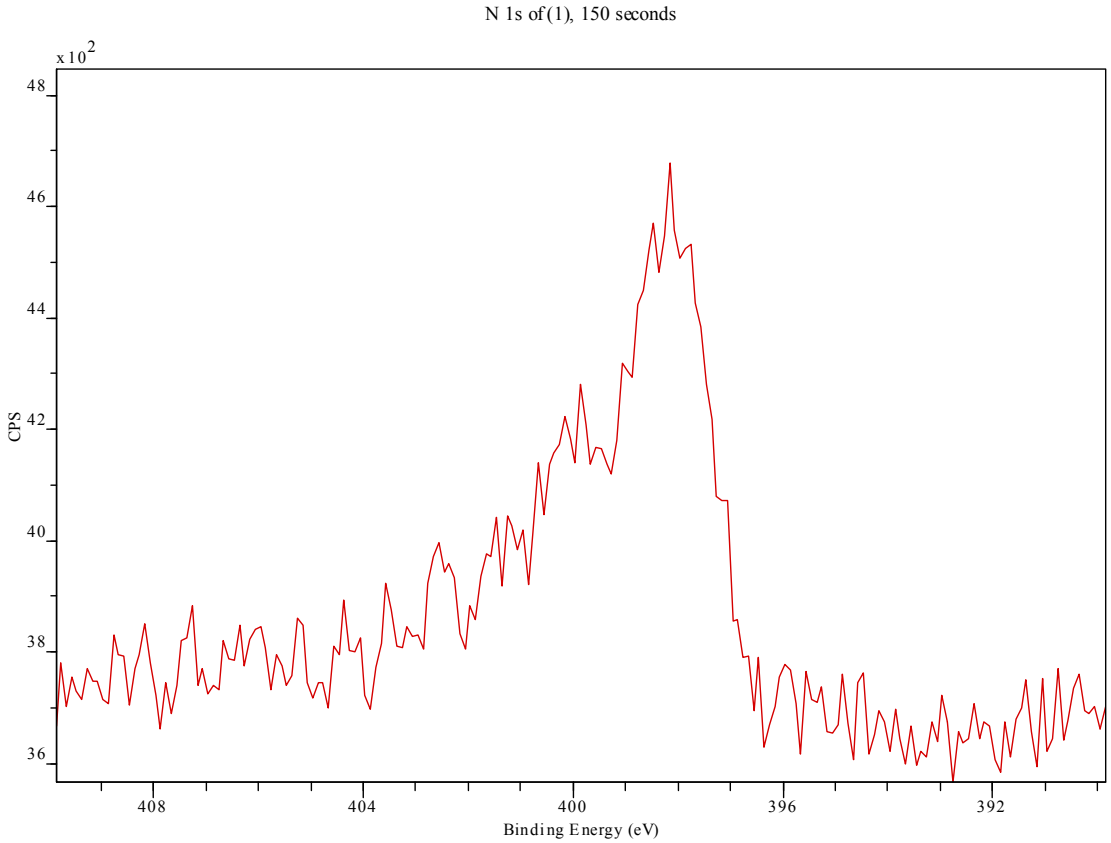

Rh 3d of (1), 90 seconds
x 10 3
20
15
10
5
CPS
320
316
312
308
304
Binding Energy (eV)

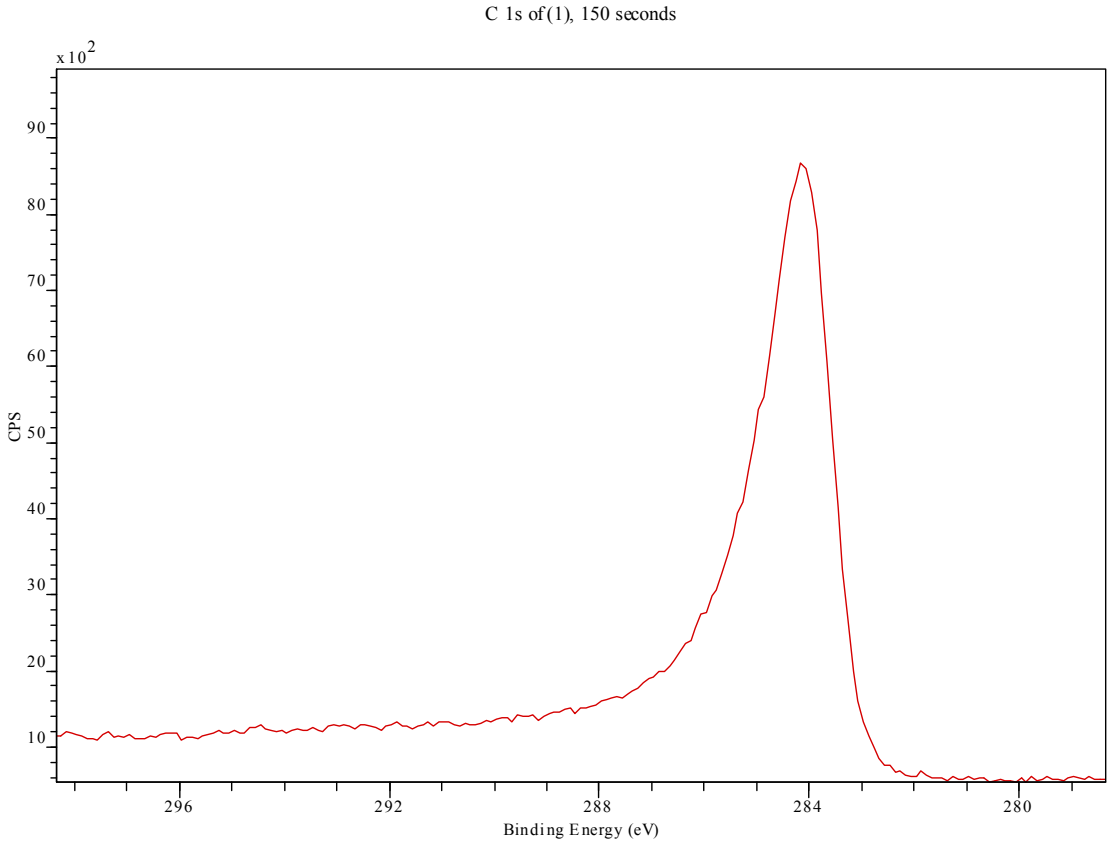


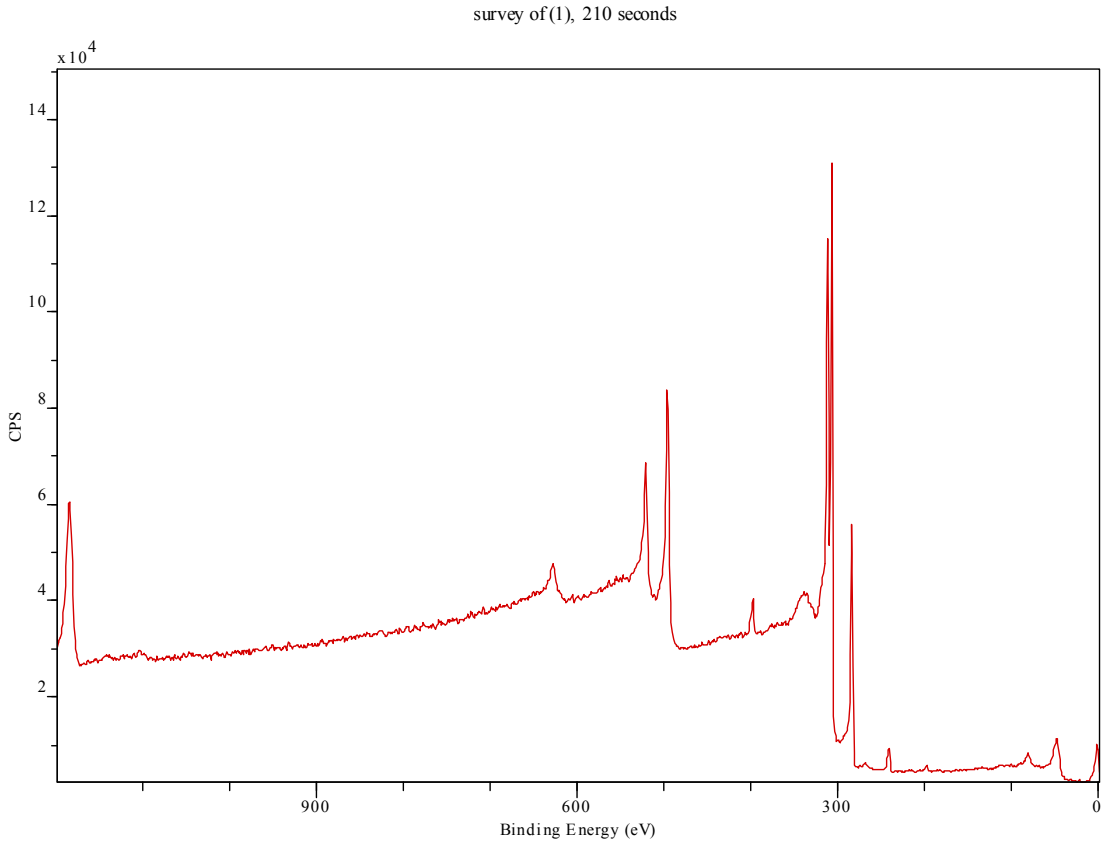

C 1s of (1), 90 seconds
100 x10^2
90
80
70
60
50
40
30
20
10
CPS
296
292
288
284
280
Binding Energy (eV)

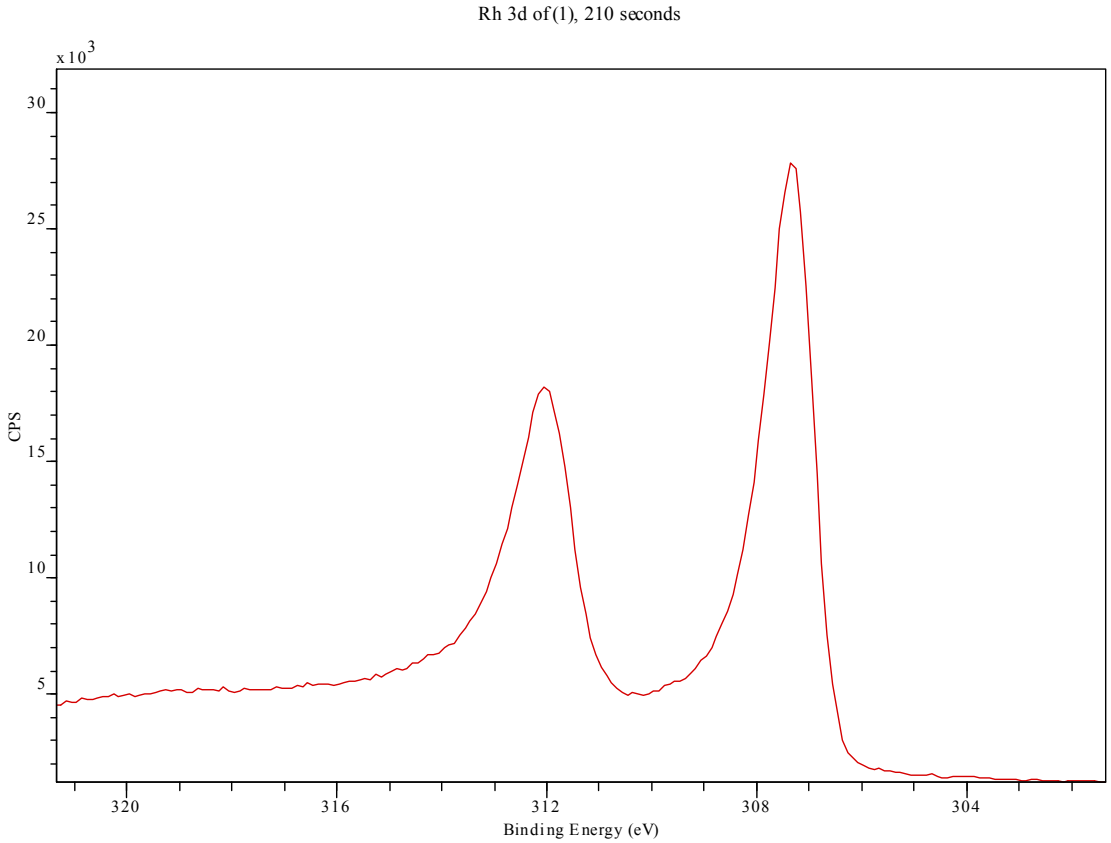

survey of (1), 150 seconds
x 10^4
14
12
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

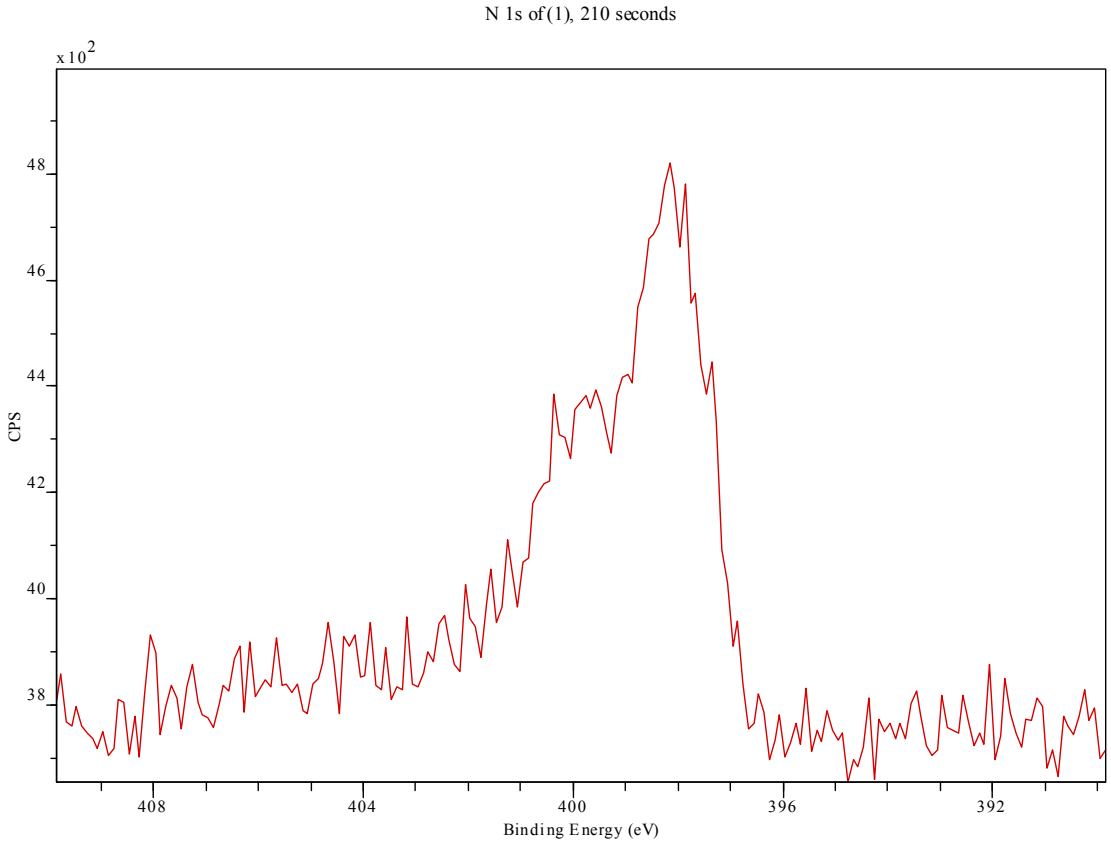

Rh 3d of (1), 150 seconds
x 10^3
30
25
20
15
10
5
CPS
320
316
312
308
304
Binding Energy (eV)

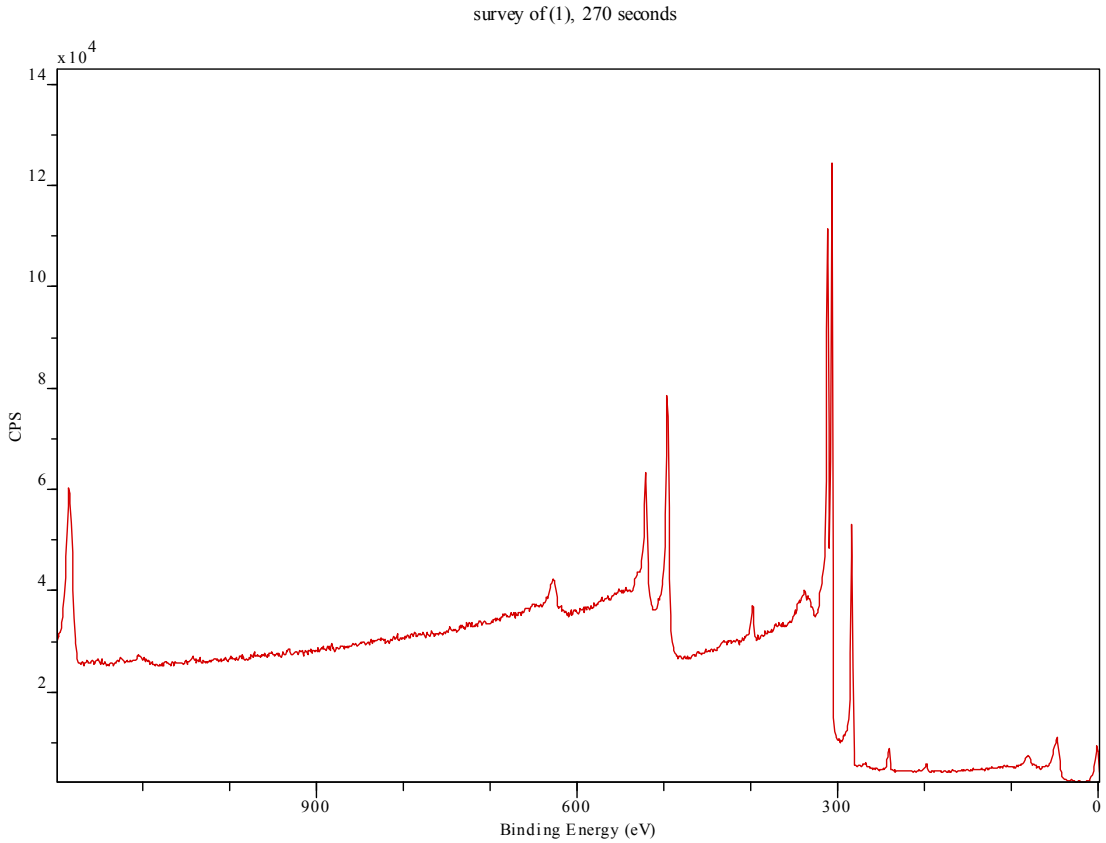

N 1s of (1), 150 seconds
x 10^2
48
46
44
42
40
38
36
CPS
408
404
400
396
392
Binding Energy (eV)

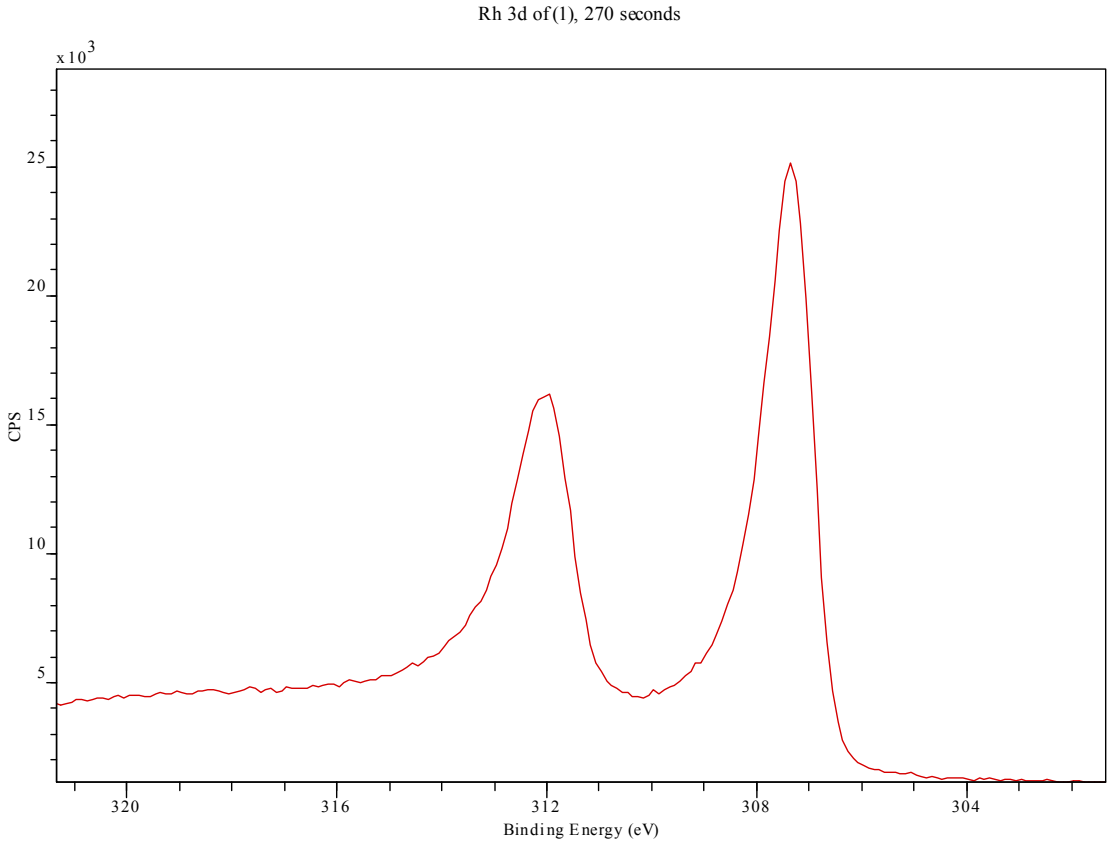


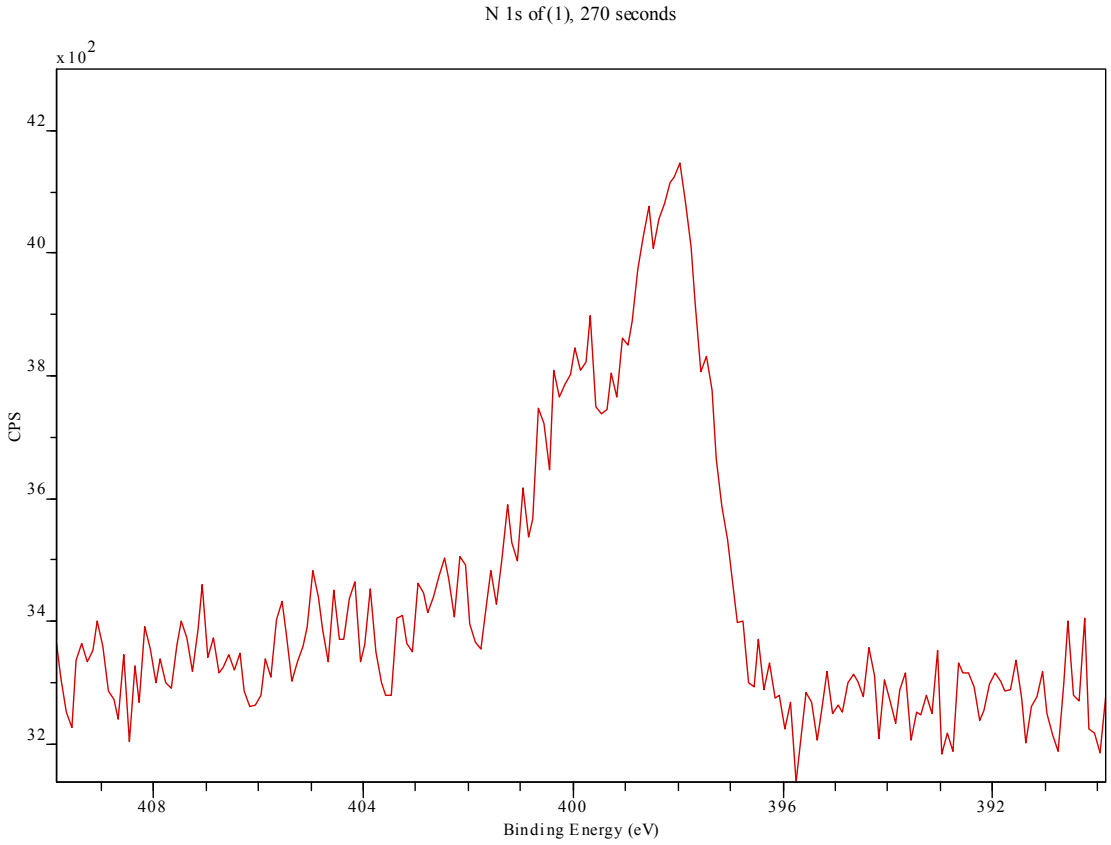

survey of (1), 210 seconds
x 10^4
14
12
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

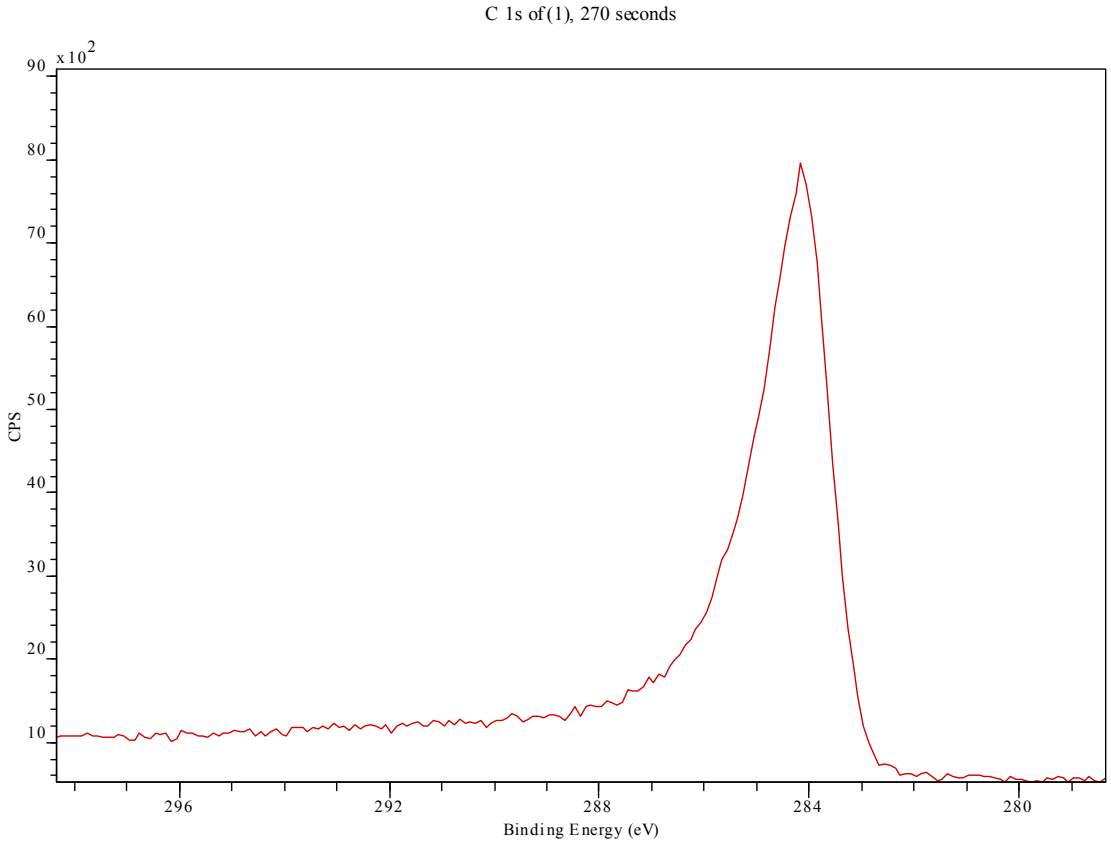

Rh 3d of(1), 210 seconds
x 10^3
30
25
20
15
10
5
CPS
320
316
312
308
304
Binding Energy (eV)

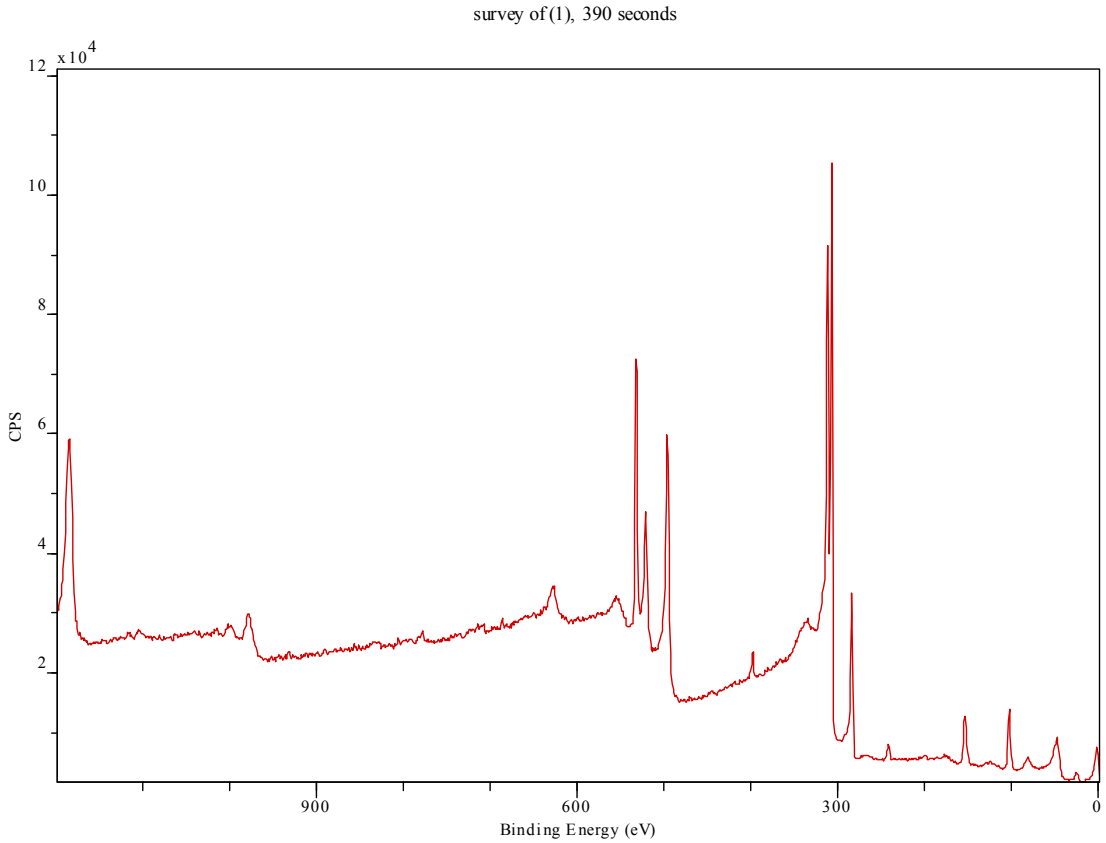

N 1s of (1), 210 seconds
x 10^2
48
46
44
42
40
38
CPS
408
404
400
396
392
Binding Energy (eV)

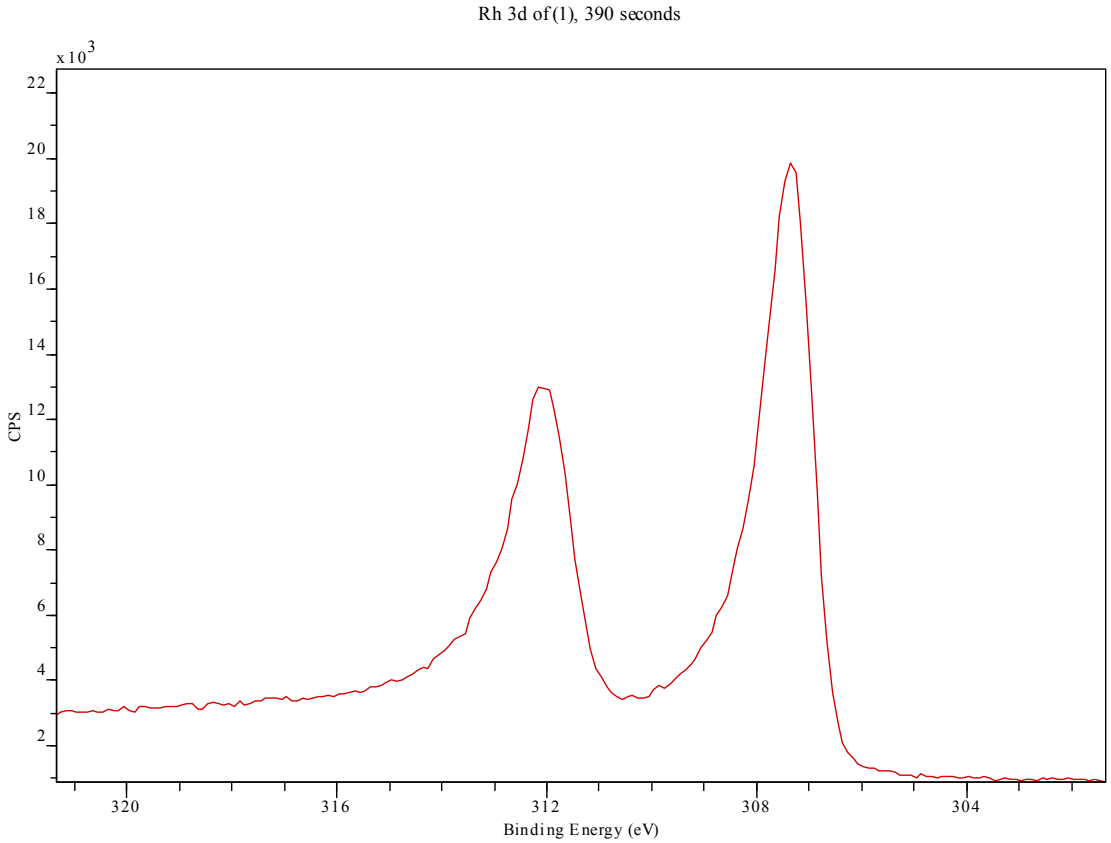

survey of (1), 270 seconds
x 10^4
14
12
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

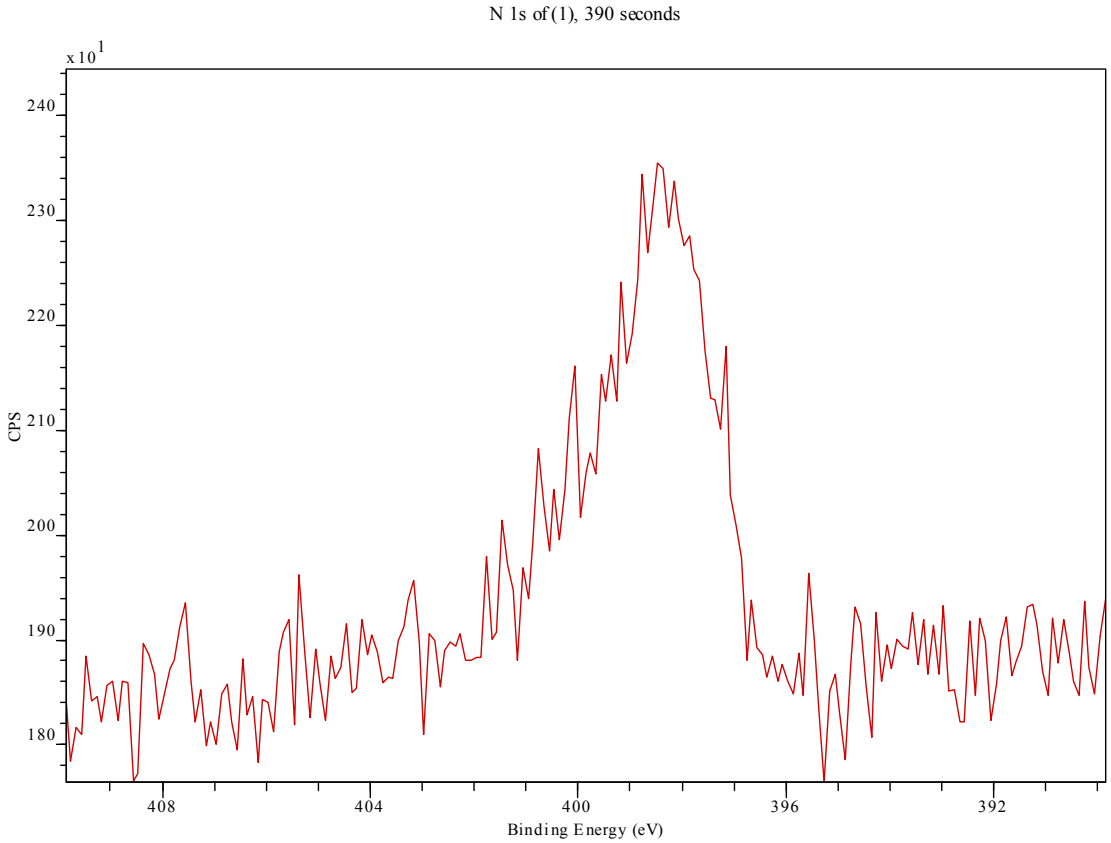

Rh 3d of (1), 270 seconds
x 10 3
25
20
15
10
5
CPS
320
316
312
308
304
Binding Energy (eV)

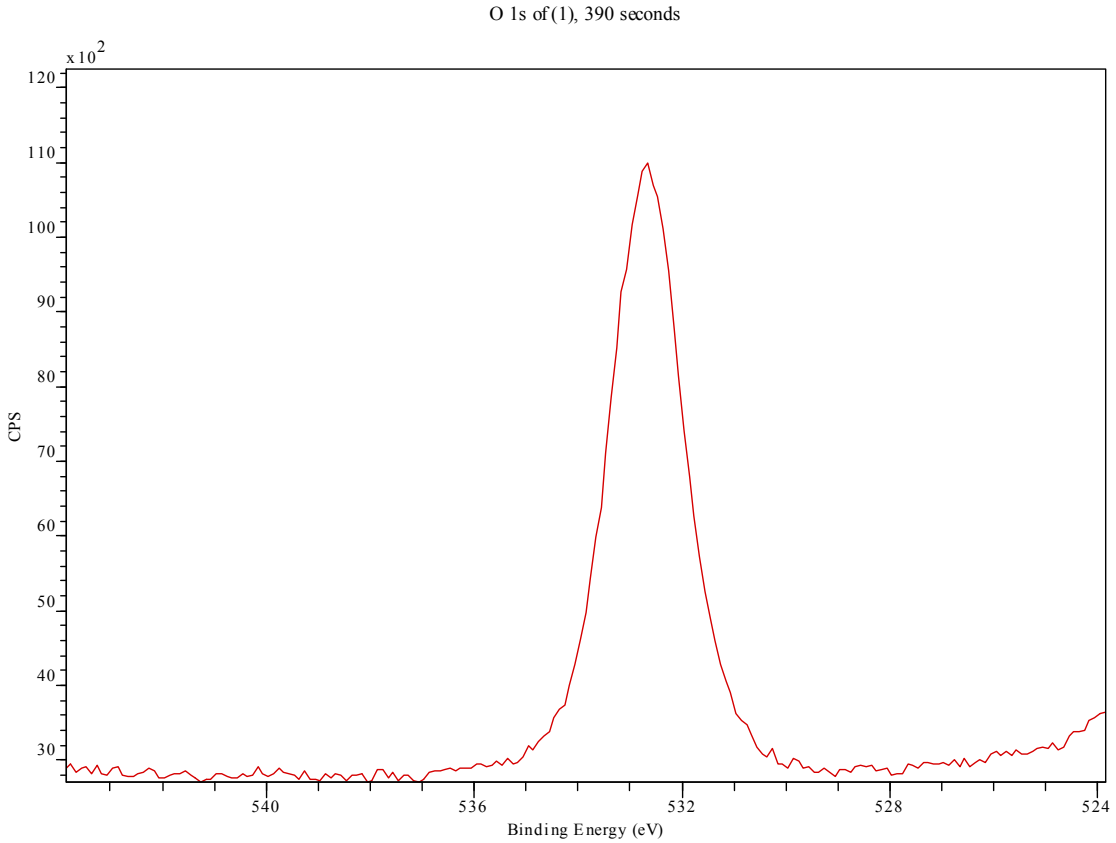


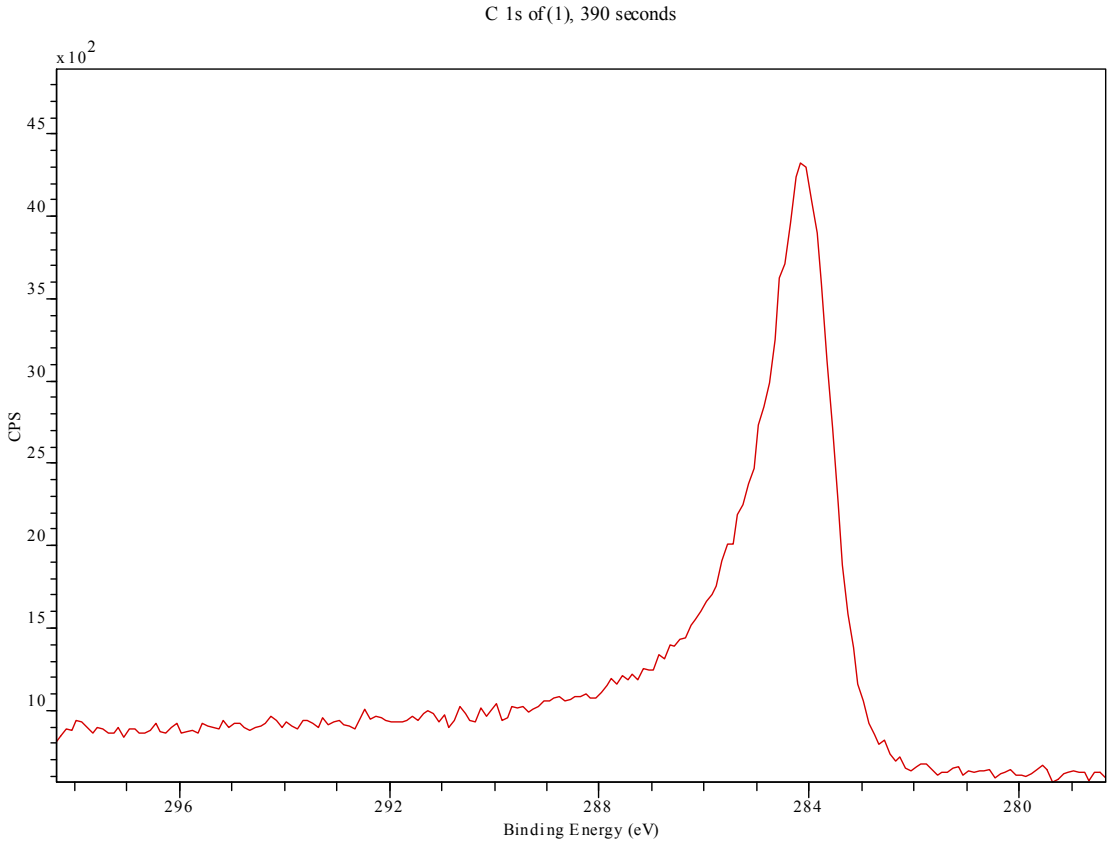


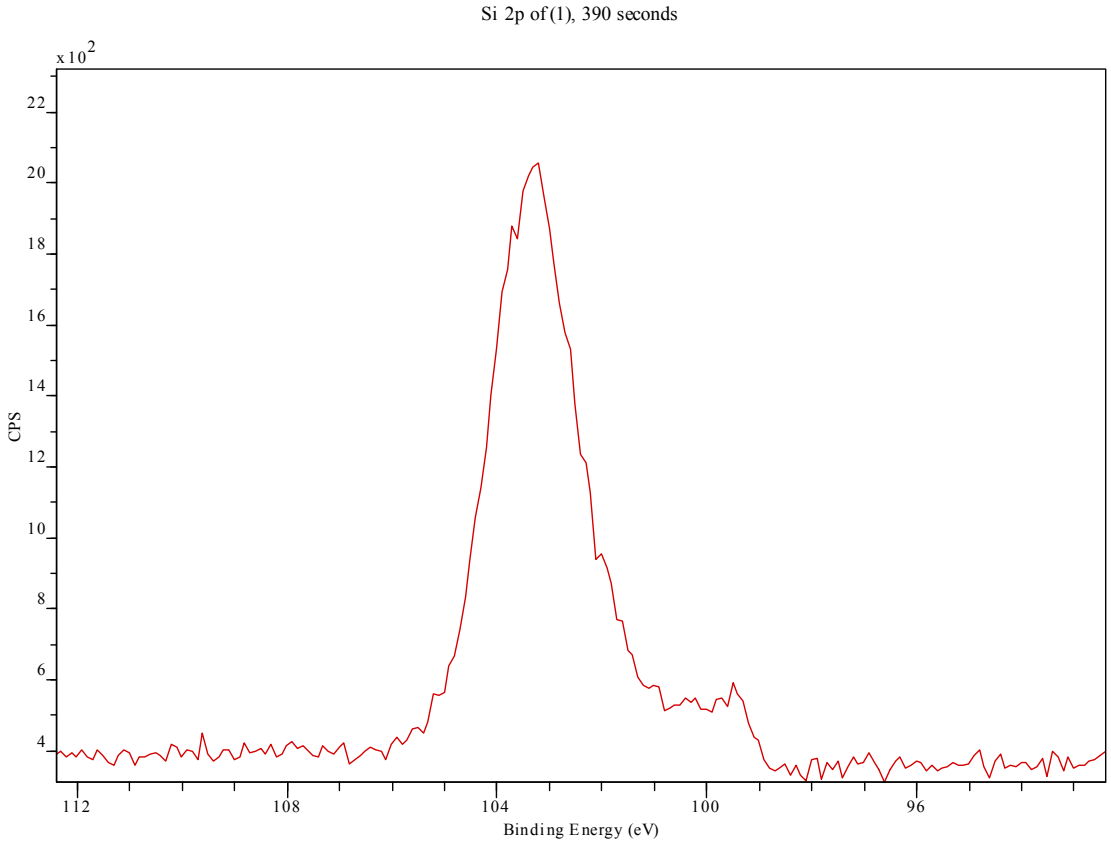

survey of (1), 390 seconds
x10^4
12
10
8
6
4
2
CPS
900
600
300
0
Binding Energy (eV)

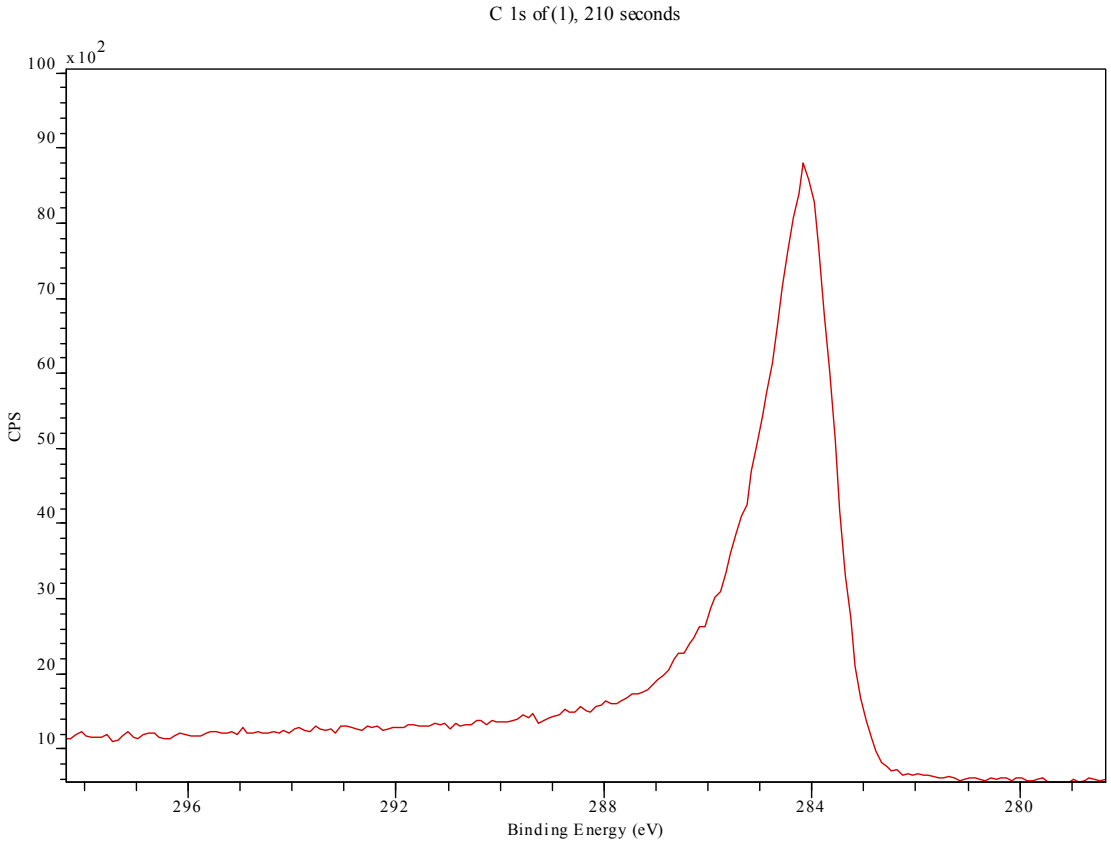

Rh 3d of (1), 390 seconds
x 10^3
22
20
18
16
14
12
10
8
6
4
2
CPS
320
316
312
308
304
Binding Energy (eV)


N 1s of (1), 390 seconds
x 10 1
240
230
220
210
200
190
180
CPS
408
404
400
396
392
Binding Energy (eV)

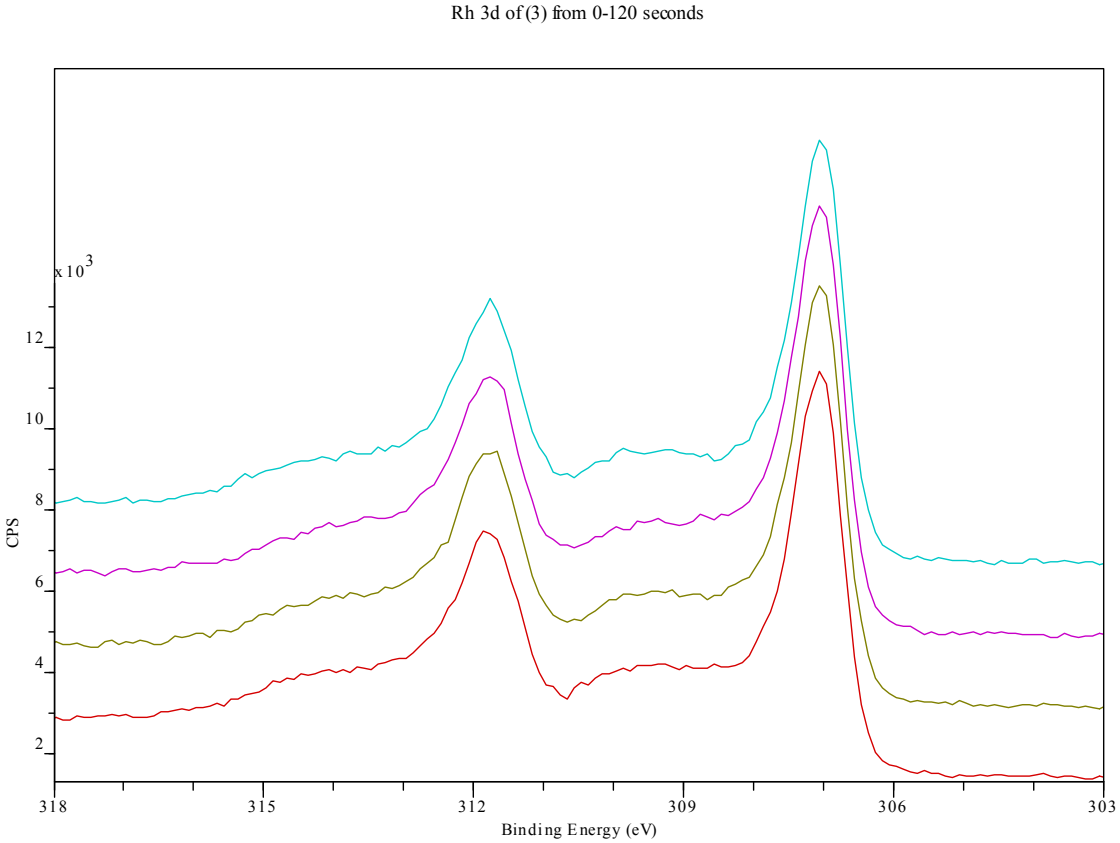

O 1s of (1), 390 seconds
x 10^2
120
110
100
90
80
70
60
50
40
30
CPS
540
536
532
528
524
Binding Energy (eV)

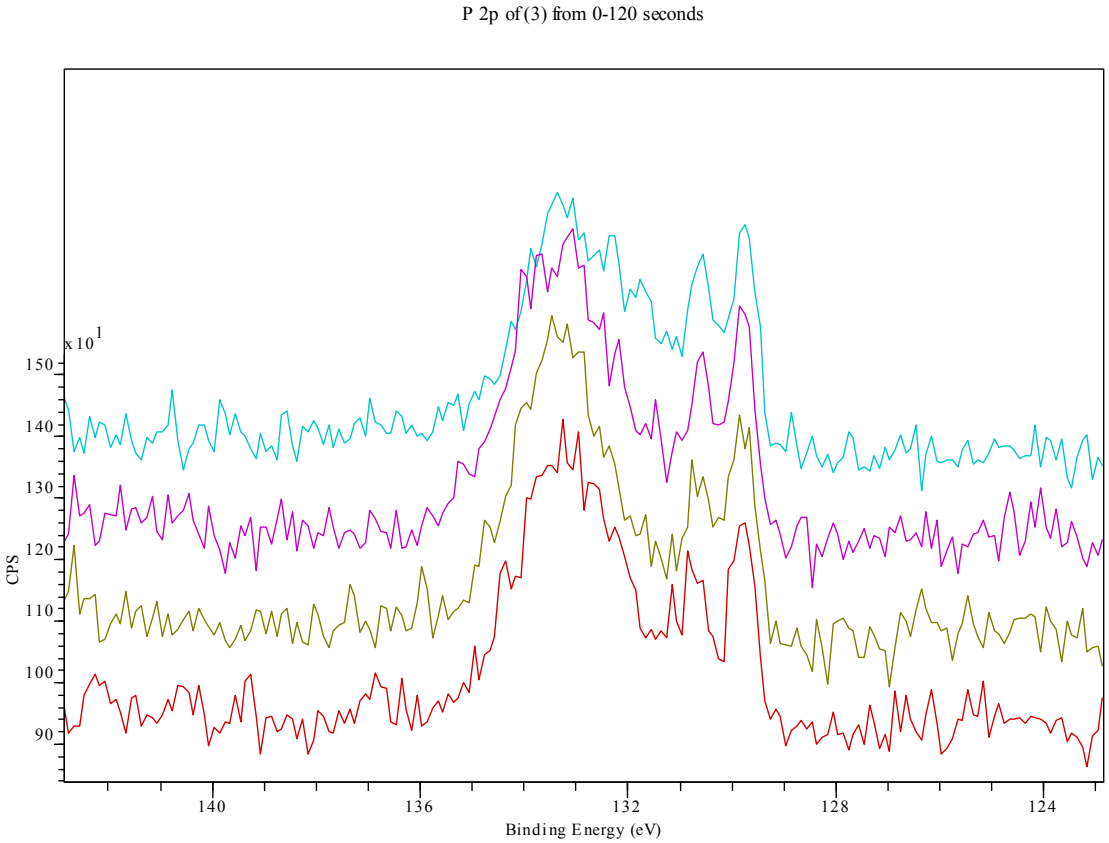

C 1s of (1), 390 seconds
x 10^2
45
40
35
30
25
20
15
10
CPS
296
292
288
284
280
Binding Energy (eV)

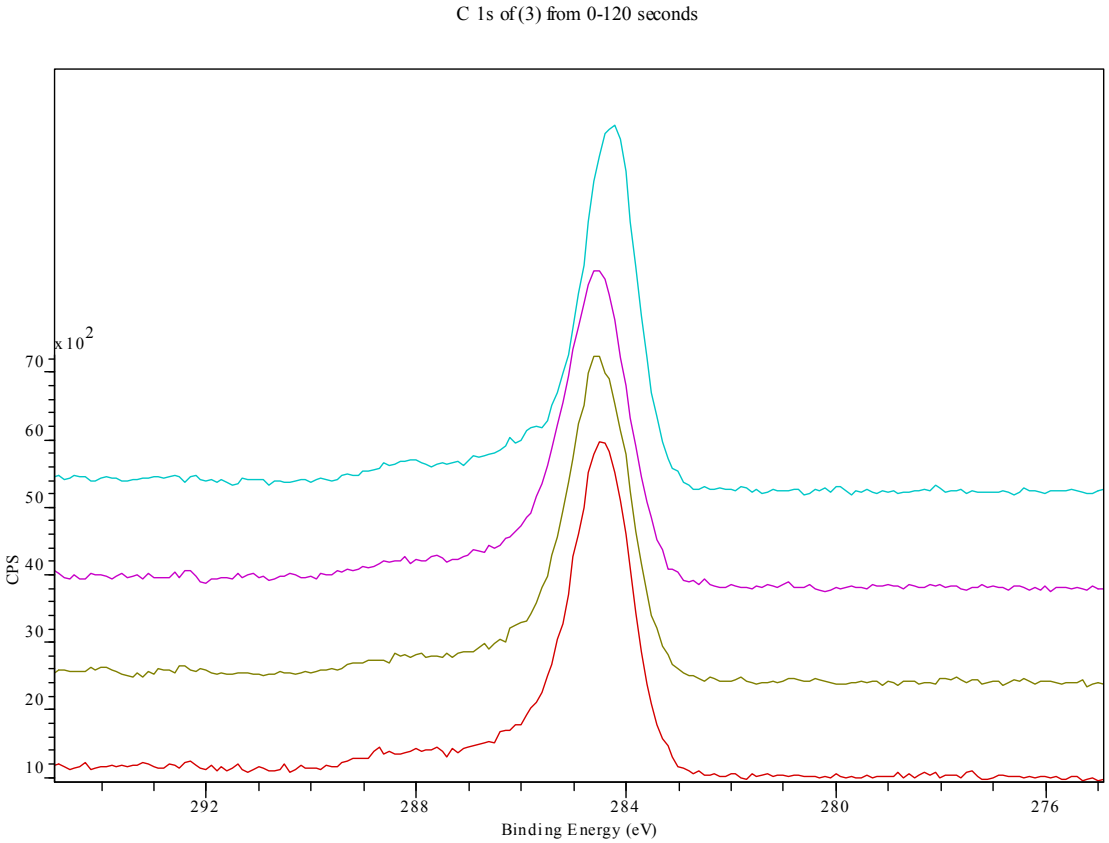

Si 2p of (1), 390 seconds
x 10^2
22
20
18
16
14
12
10
8
6
4
CPS
112
108
104
100
96
Binding Energy (eV)


C 1s of (1), 210 seconds
x 10^2
100
90
80
70
60
50
40
30
20
10
CPS
296
292
288
284
280
Binding Energy (eV)

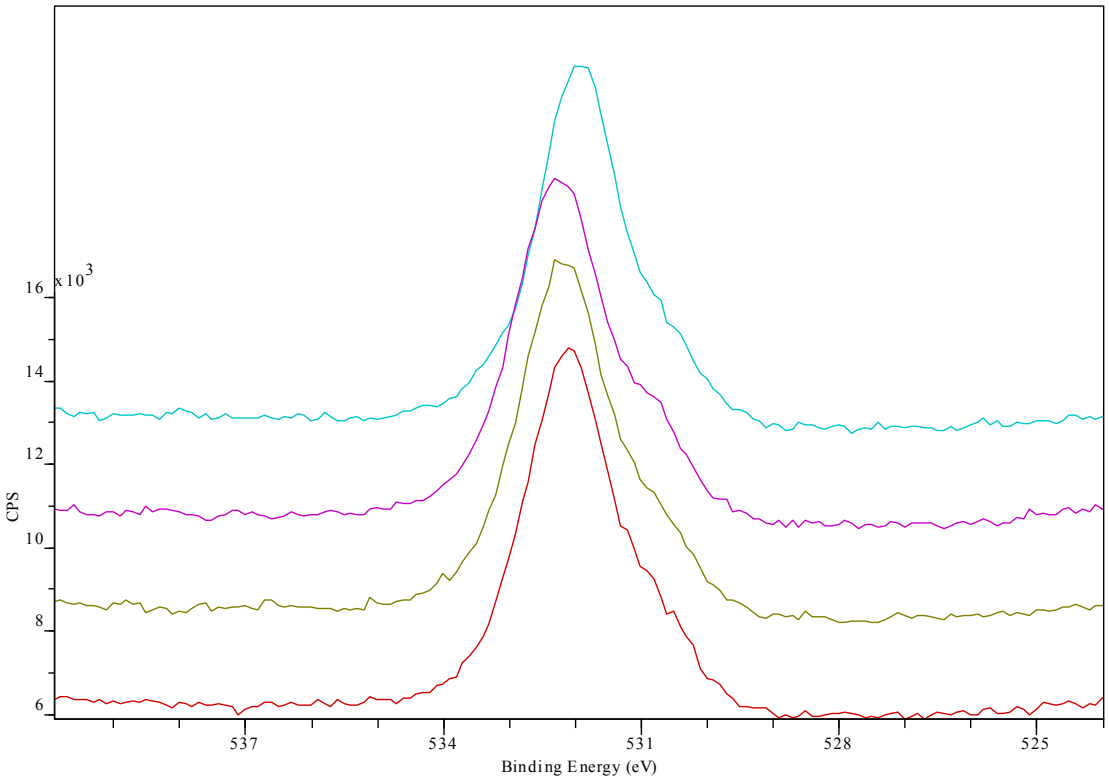
XPS spectroscopy of [Rh(3,5-$(CF_3)_2$-Pz)$(PMe_3)_3$] (**3**) using argon as the carrier gas

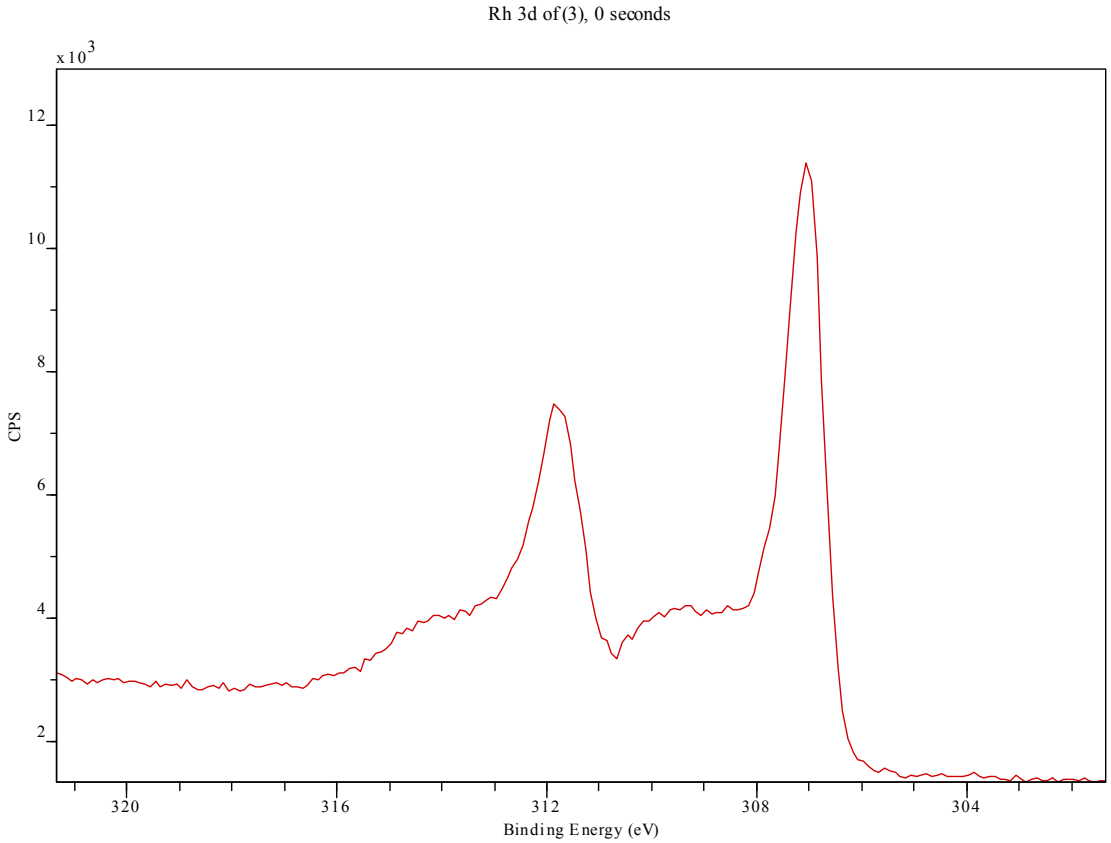


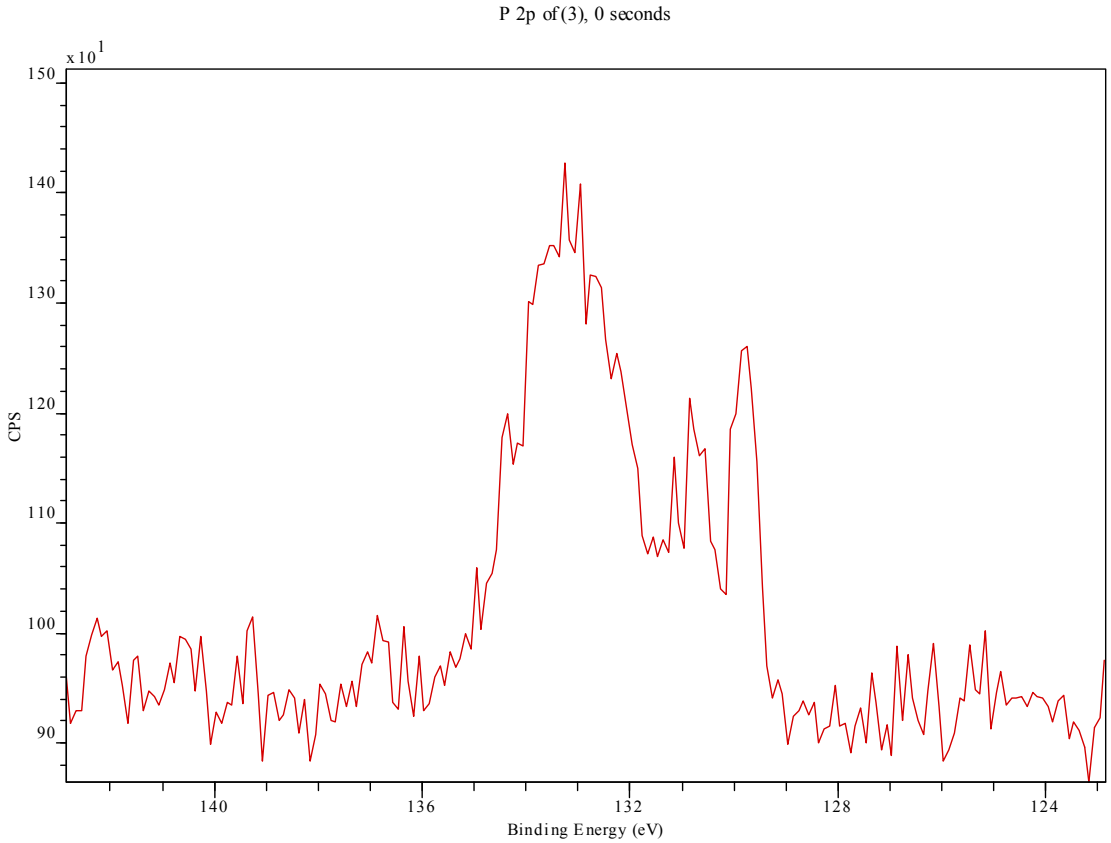

P 2p of (3) from 0-120 seconds
x 10 1
150
140
130
120
110
100
90
CPS
140
136
132
128
124
Binding Energy (eV)

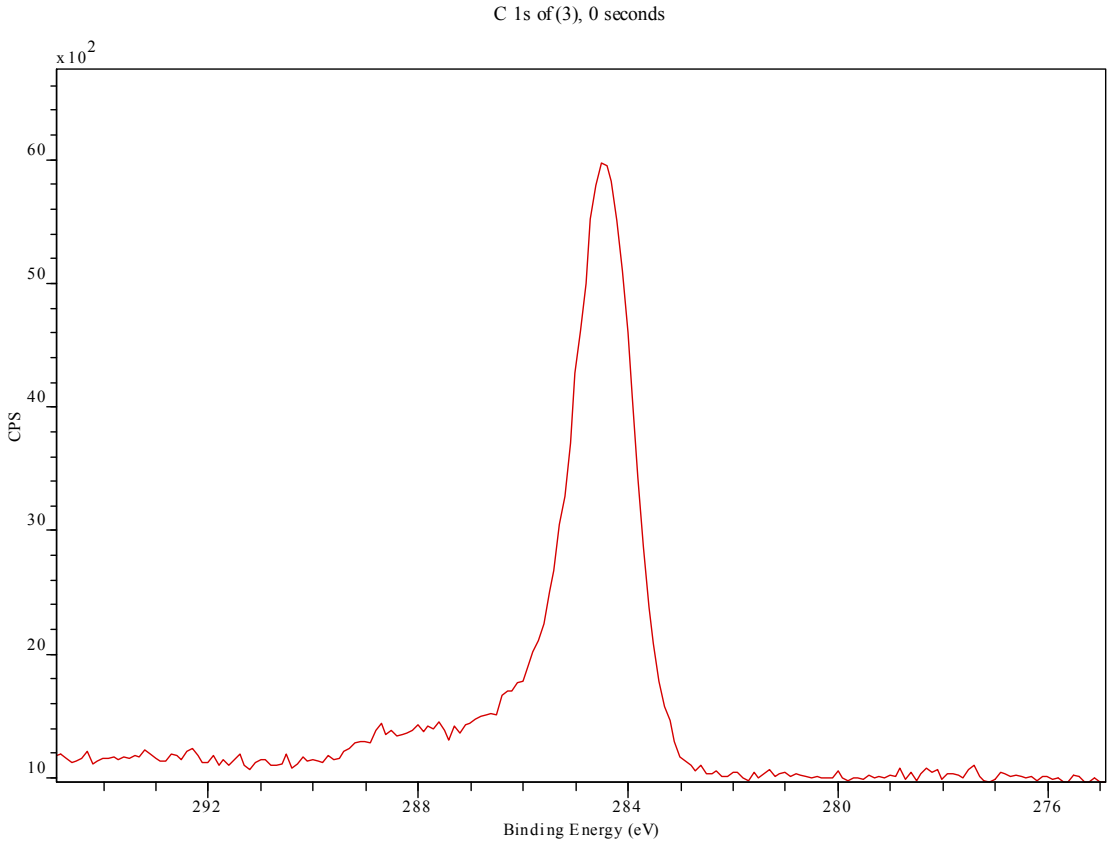

C 1s of (3) from 0-120 seconds
x 10^2
70
60
50
40
30
20
10
CPS
292
288
284
280
276
Binding Energy (eV)

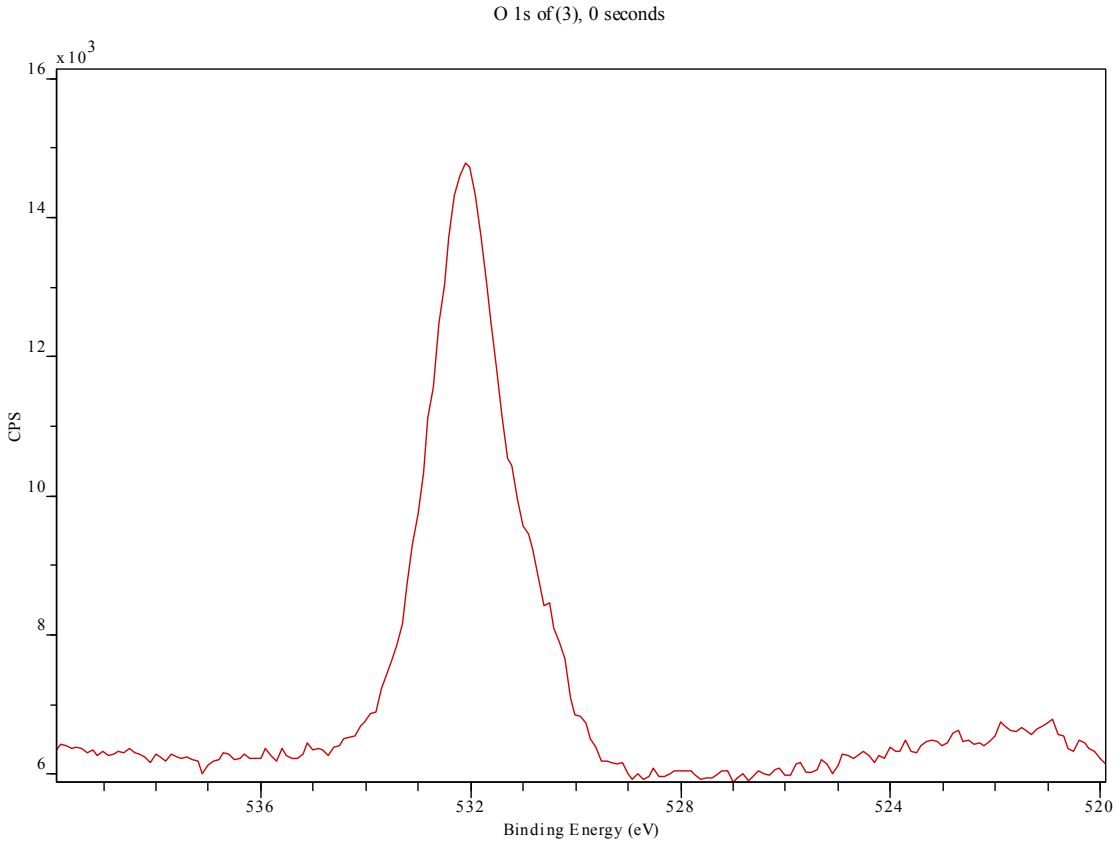
O 1s of (3) from 0-120 seconds

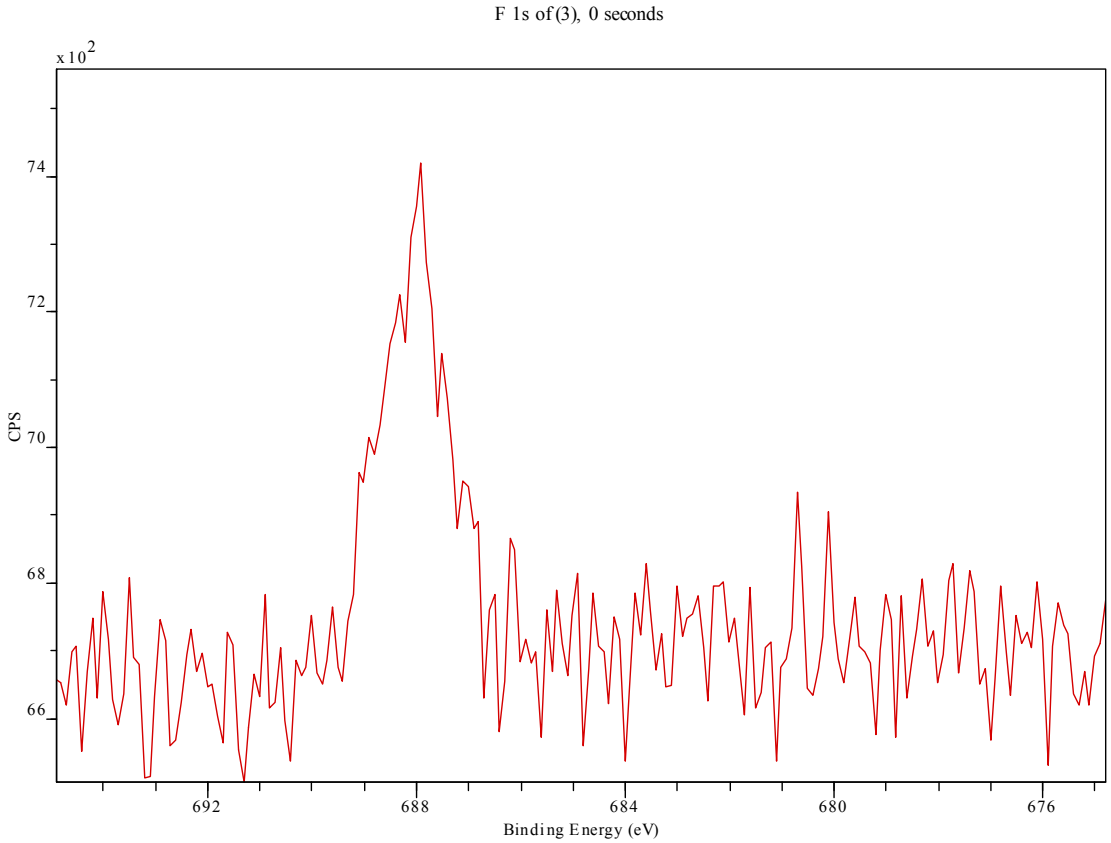


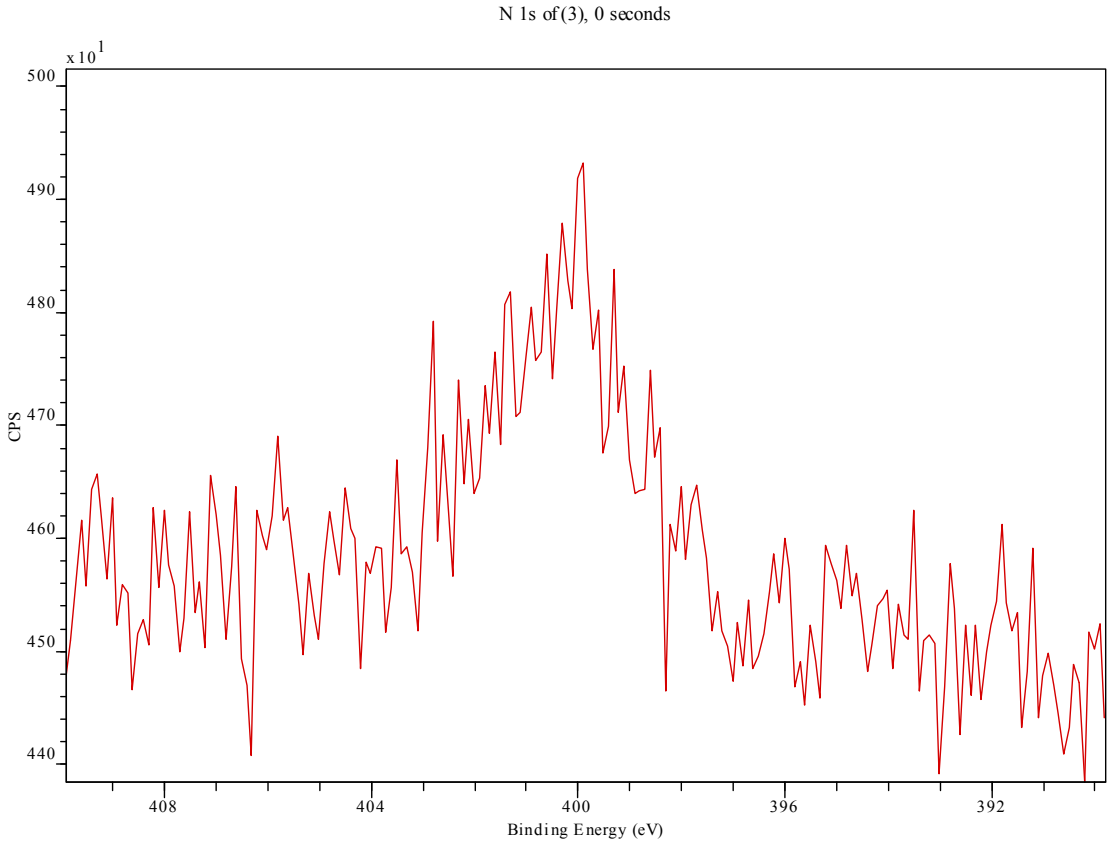

Rh 3d of(3), 0 seconds
x 10^3
12
10
8
6
4
2
CPS
320
316
312
308
304
Binding Energy (eV)

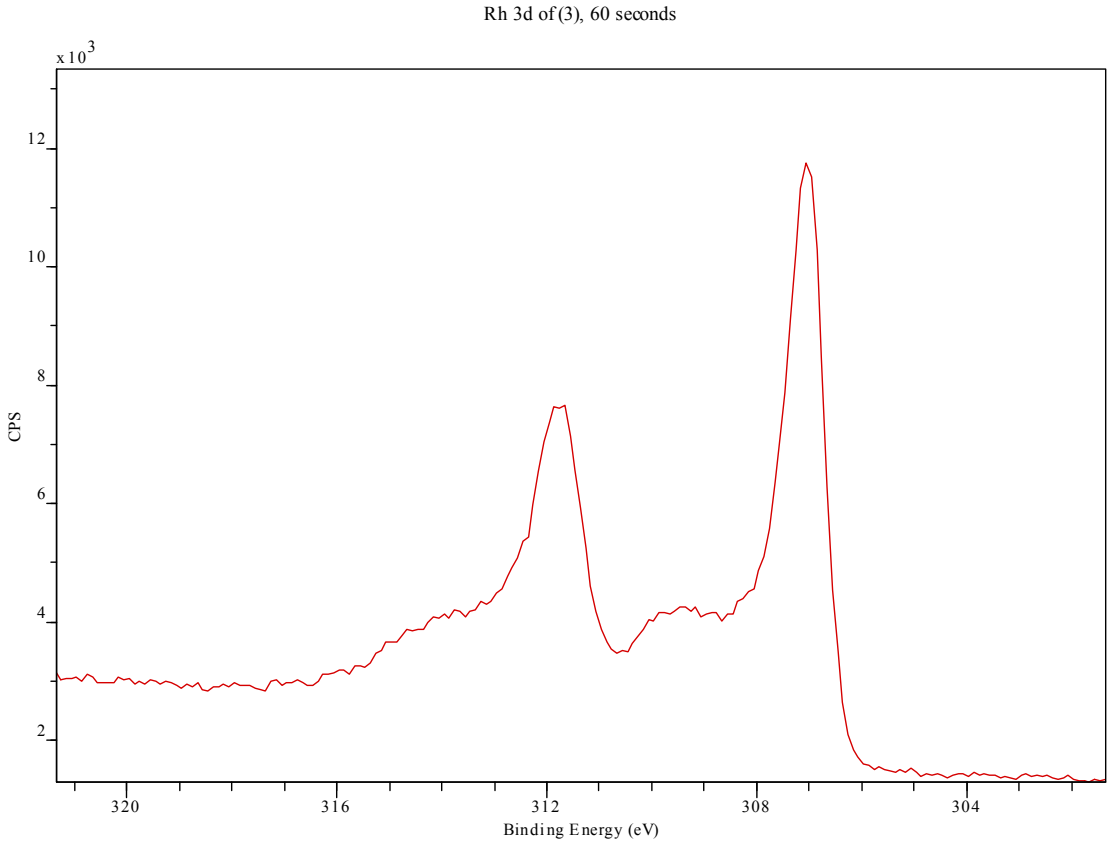

P 2p of(3), 0 seconds
x 10 1
150
140
130
120
110
100
90
CPS
140
136
132
128
124
Binding Energy (eV)

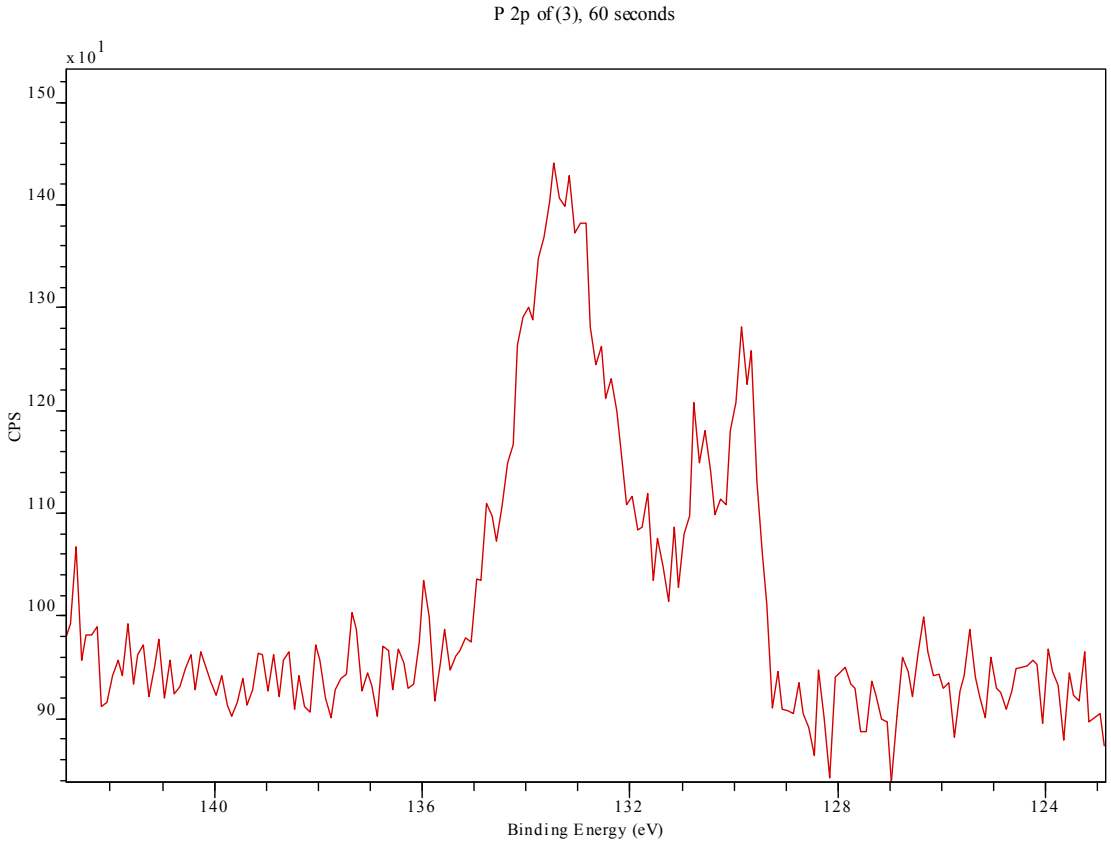

C 1s of (3), 0 seconds
x 10^2
60
50
40
30
20
10
CPS
292
288
284
280
276
Binding Energy (eV)

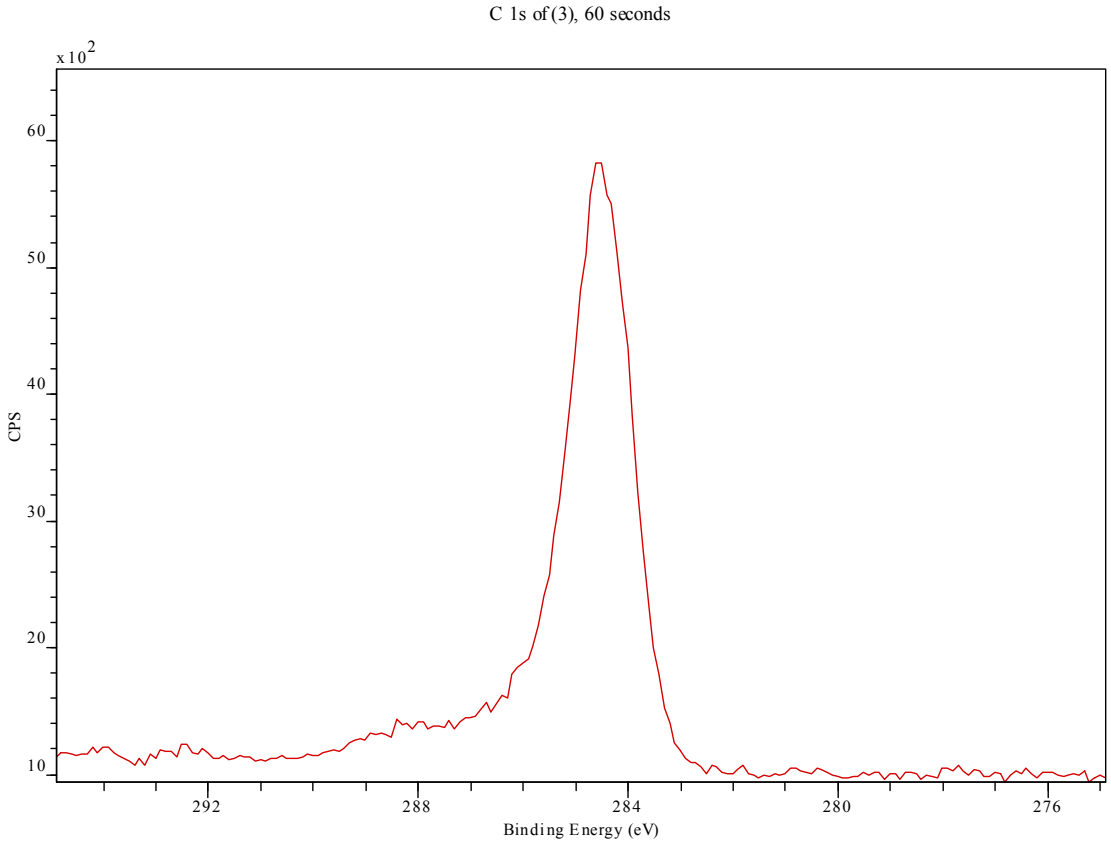

O 1s of (3), 0 seconds
x 10^3
16
14
12
10
8
6
CPS
536
532
528
524
520
Binding Energy (eV)

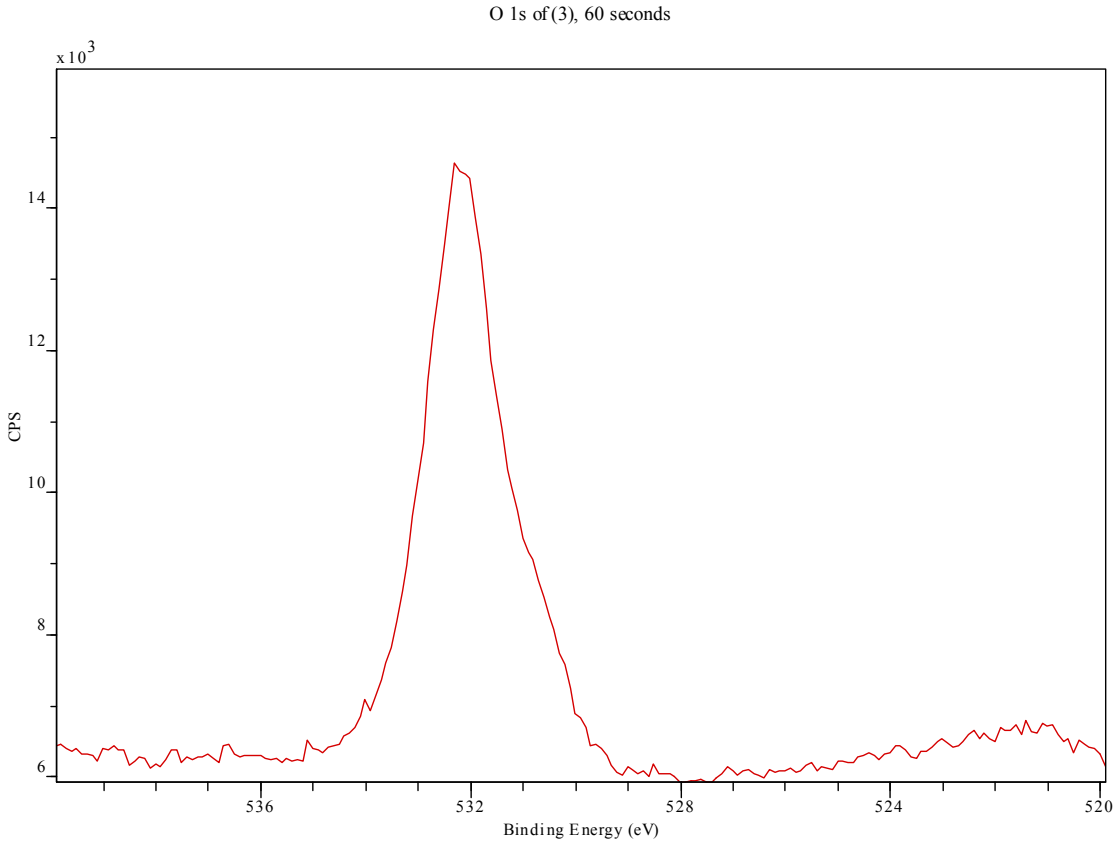


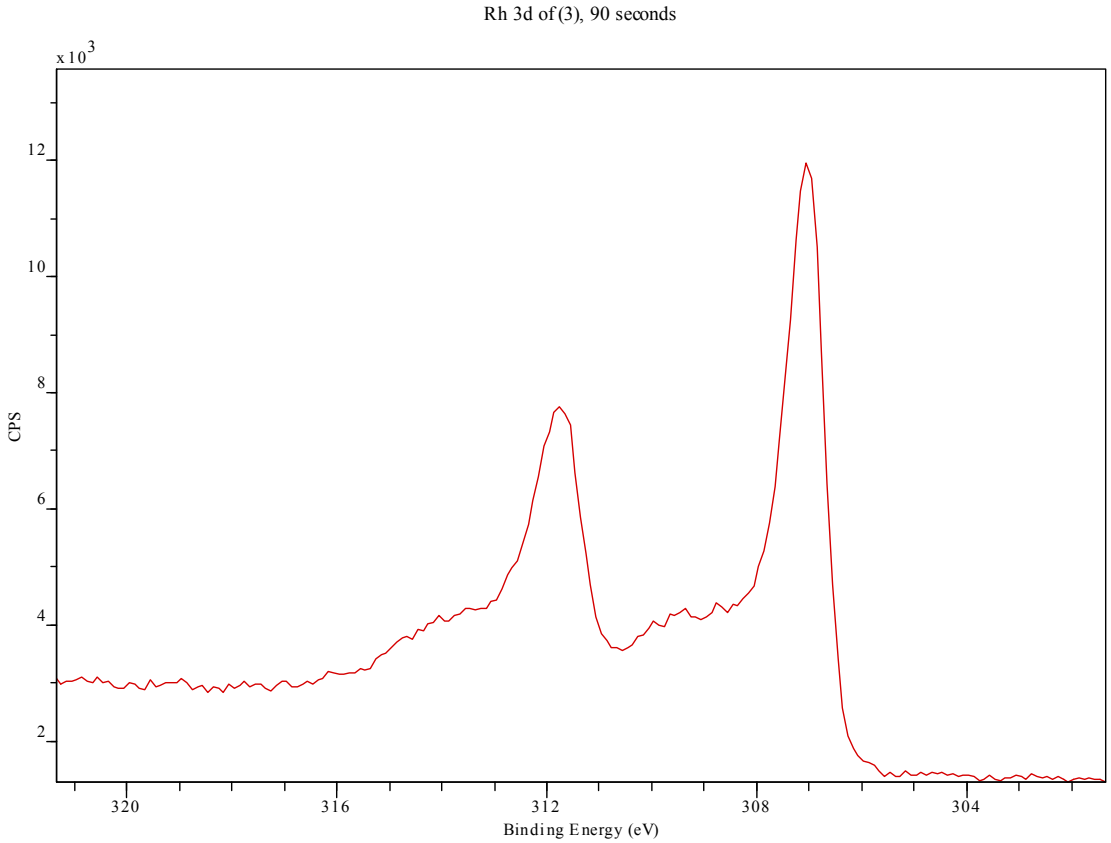

N 1s of (3), 0 seconds
x 10 1
500
490
480
470
460
450
440
CPS
408
404
400
396
392
Binding Energy (eV)

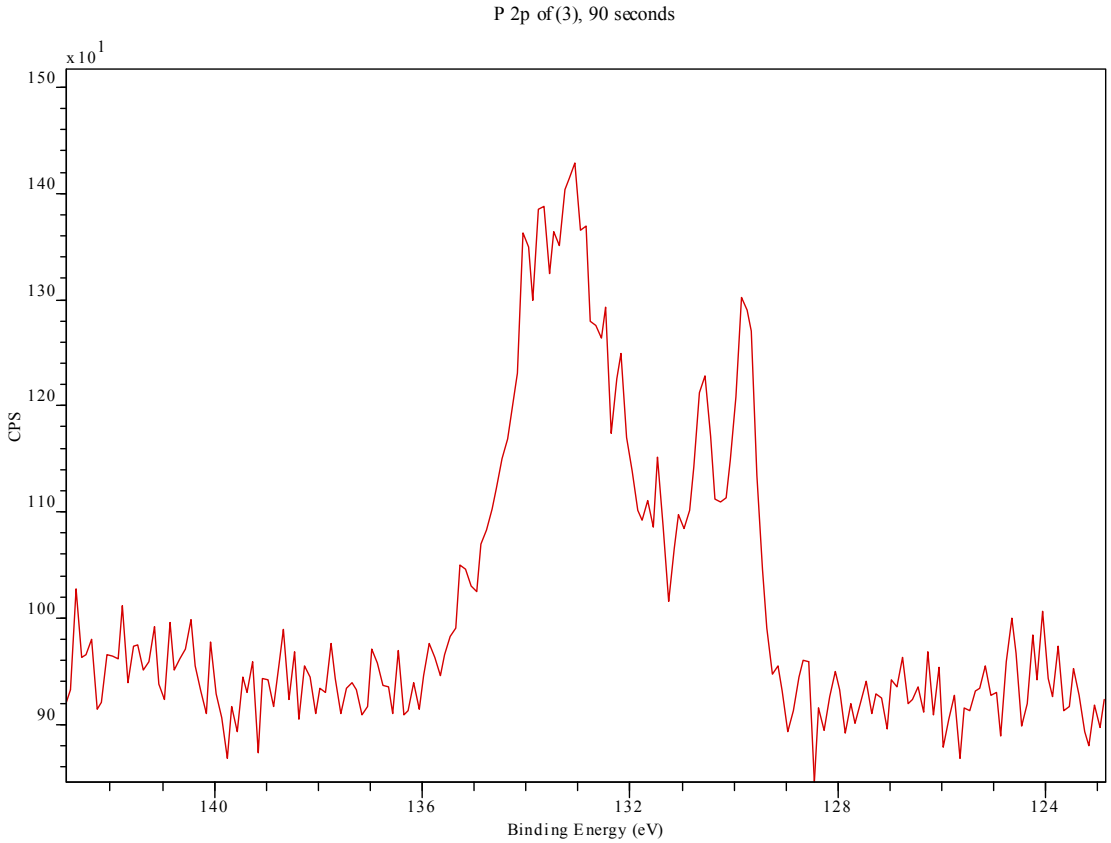

Rh 3d of (3), 60 seconds
x 10^3
12
10
8
6
4
2
CPS
320
316
312
308
304
Binding Energy (eV)

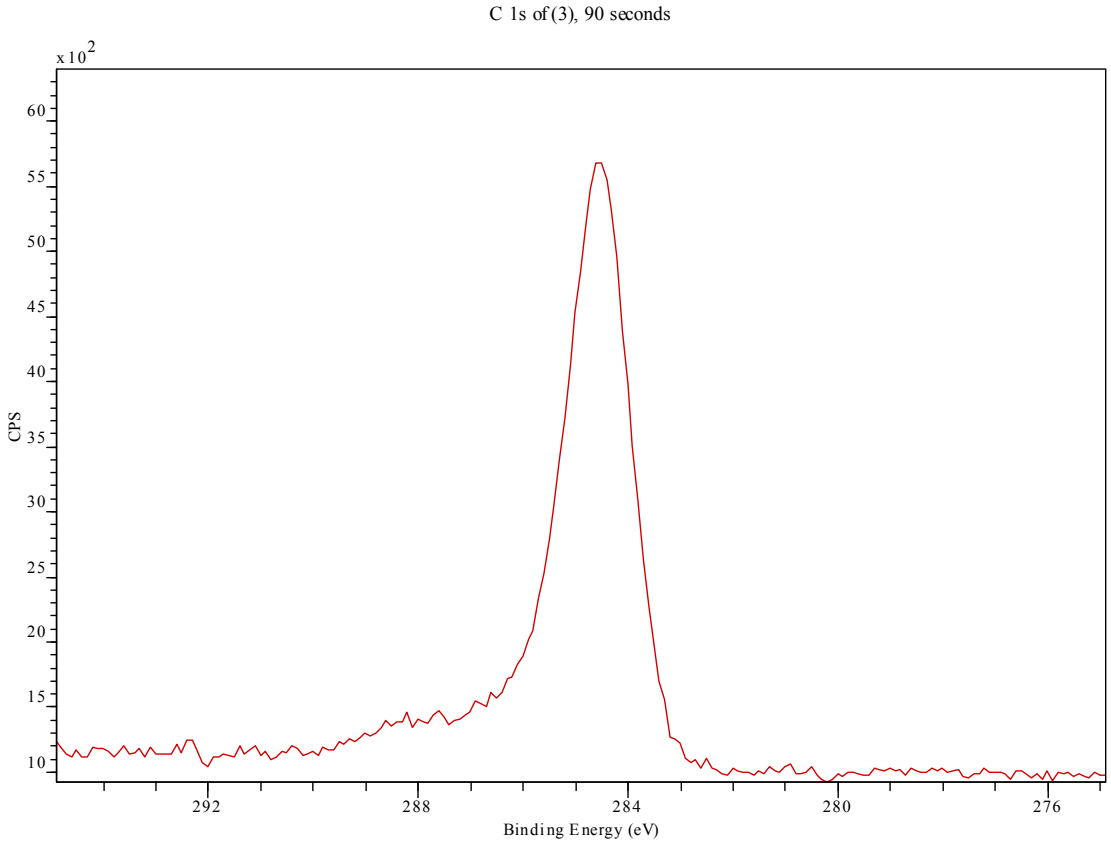

P 2p of (3), 60 seconds
x 10 1
150
140
130
120
110
100
90
CPS
140
136
132
128
124
Binding Energy (eV)

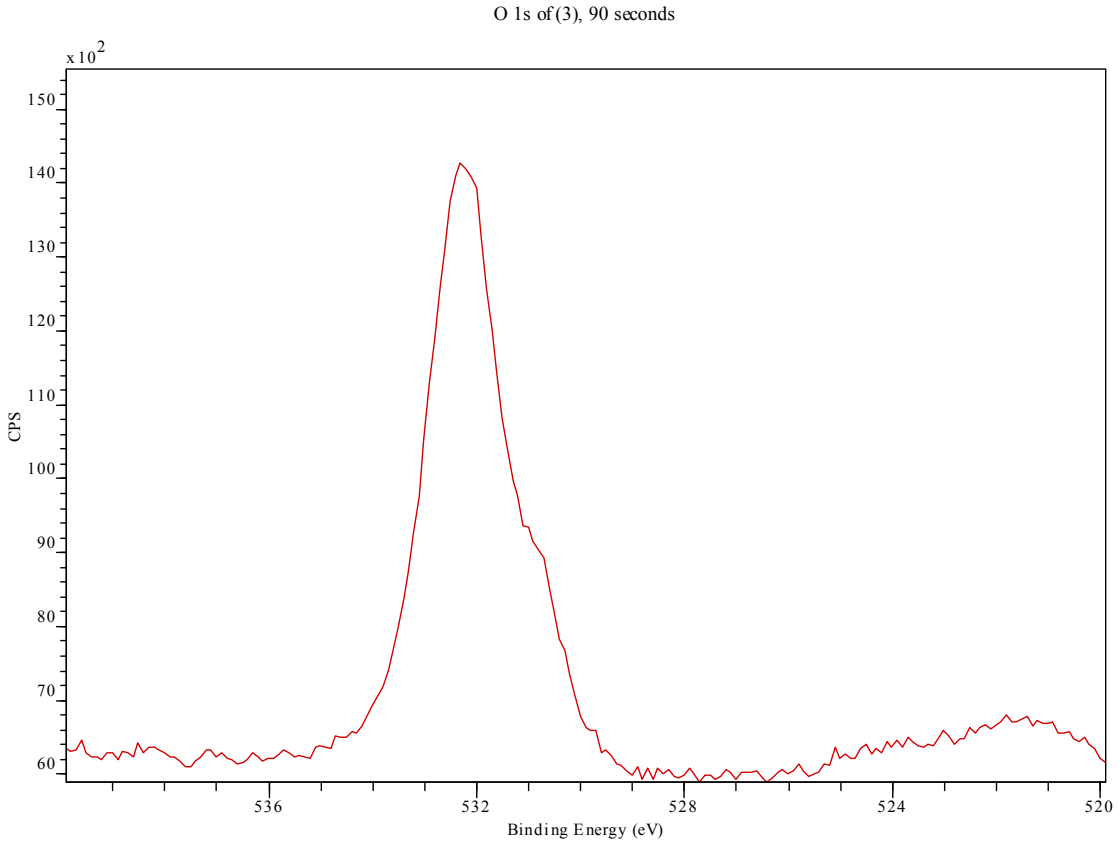

C 1s of (3), 60 seconds
x 10^2
60
50
40
30
20
10
CPS
292
288
284
280
276
Binding Energy (eV)

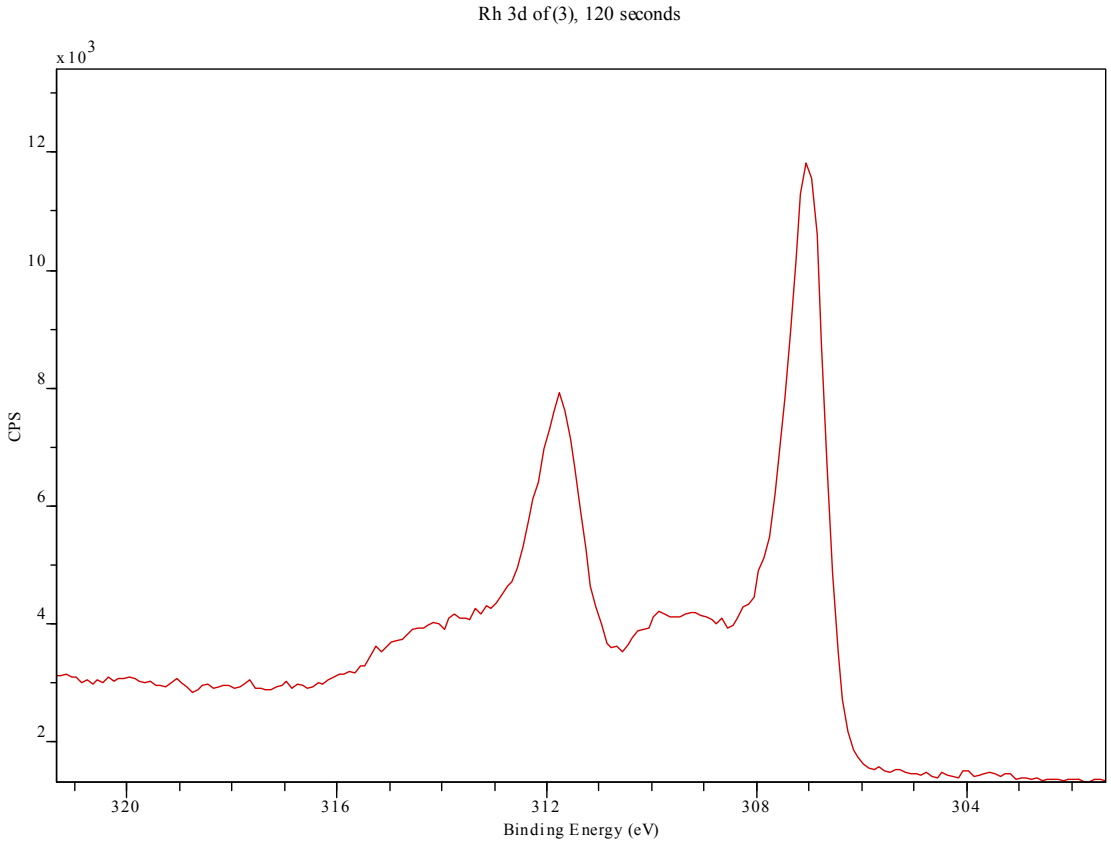

O 1s of (3), 60 seconds
x 10^3
14
12
10
8
6
CPS
536
532
528
524
520
Binding Energy (eV)

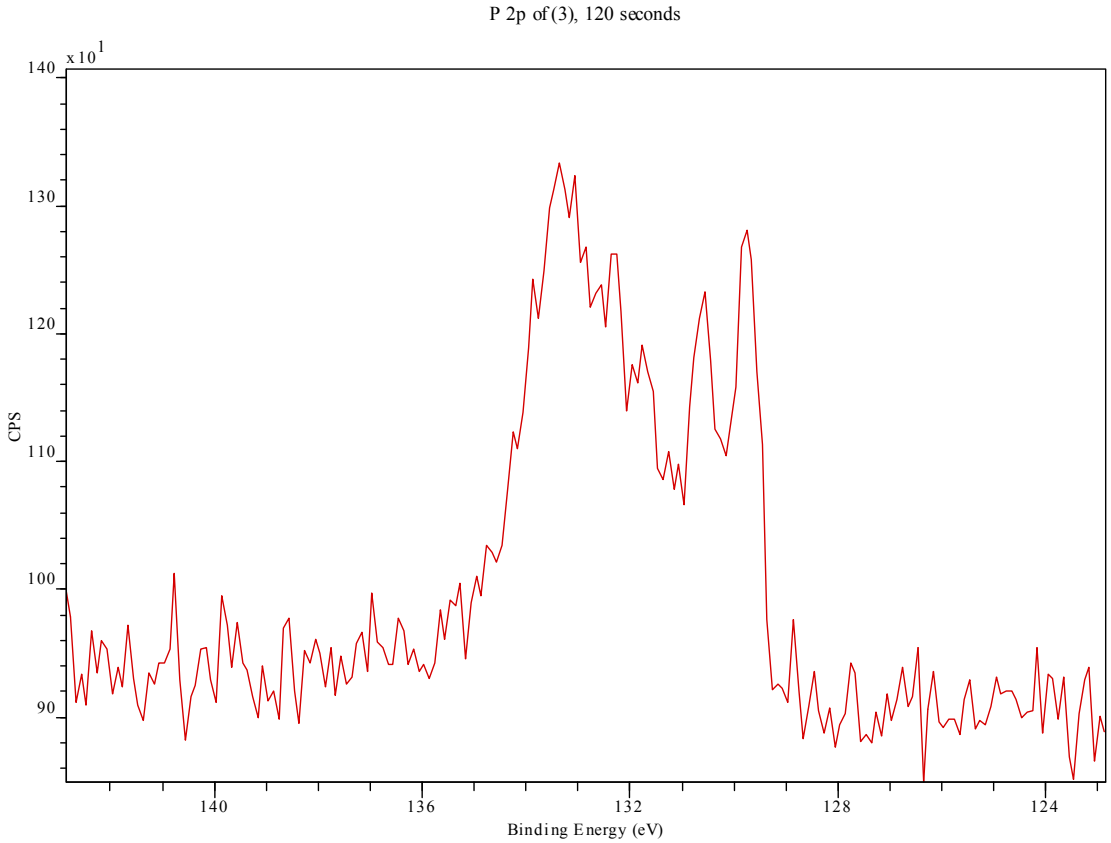

Rh 3d of (3), 90 seconds
x 10^3
12
10
8
6
4
2
CPS
320
316
312
308
304
Binding Energy (eV)

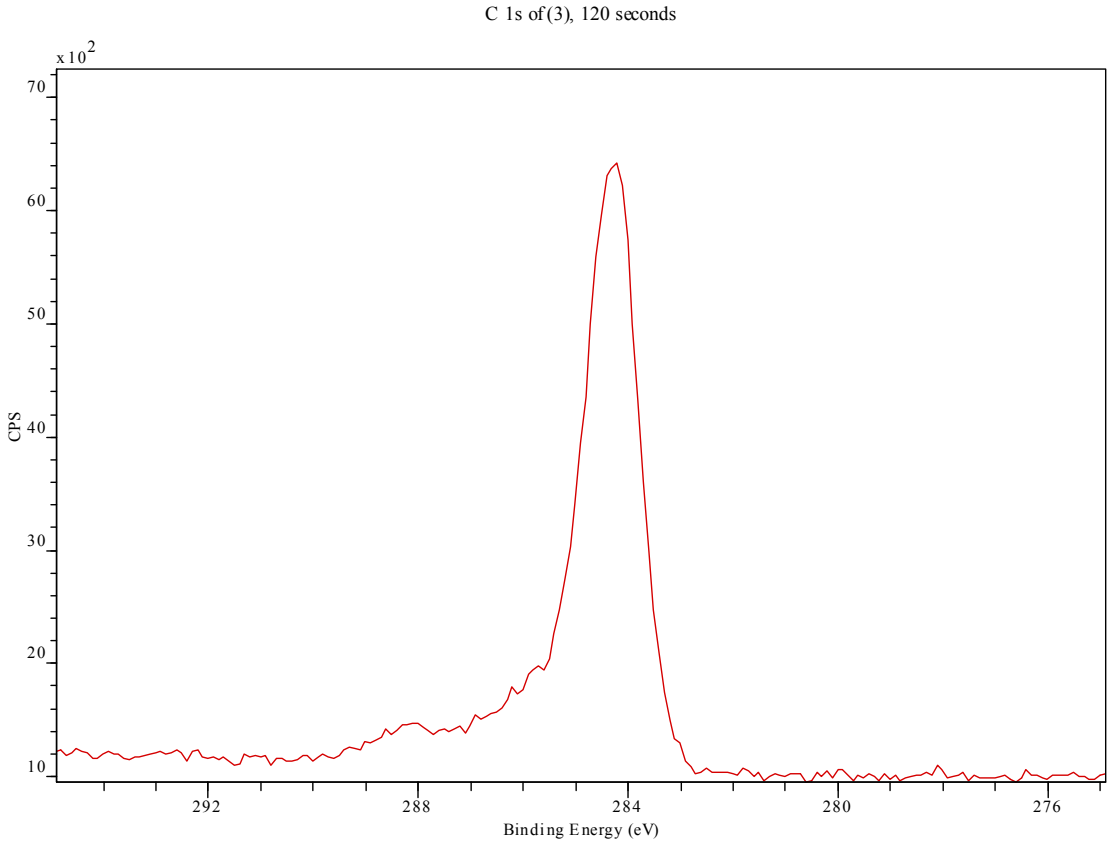

P 2p of (3), 90 seconds
x 10 1
150
140
130
120
110
100
90
CPS
140
136
132
128
124
Binding Energy (eV)


C 1s of (3), 90 seconds
x 10^2
60
55
50
45
40
35
30
25
20
15
10
CPS
292
288
284
280
276
Binding Energy (eV)


O 1s of (3), 90 seconds
x 10^2
150
140
130
120
110
100
90
80
70
60
CPS
536
532
528
524
520
Binding Energy (eV)






C 1s of (3), 120 seconds
x 10^2
70
60
50
40
30
20
10
CPS
292
288
284
280
276
Binding Energy (eV)