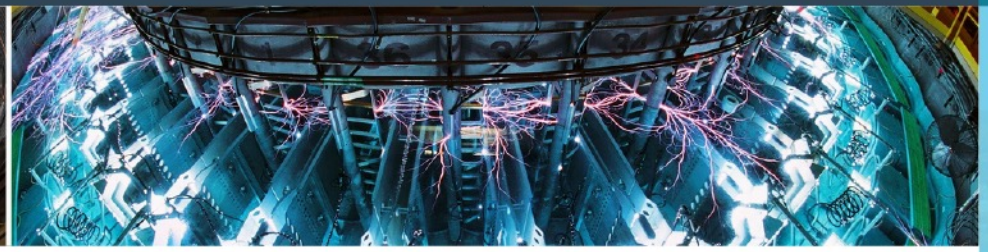
SAND2022-11990C

7th Annual Tritium Science Technical Exchange

Sandia National Laboratories

In situ quantification of the Effect of Ni Surface Impurities on Hydrogen and Deuterium Adsorption Using Environmental-XPS



PRESENTED BY

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U.S. DEPARTMENT OF ENERGY | NNSA

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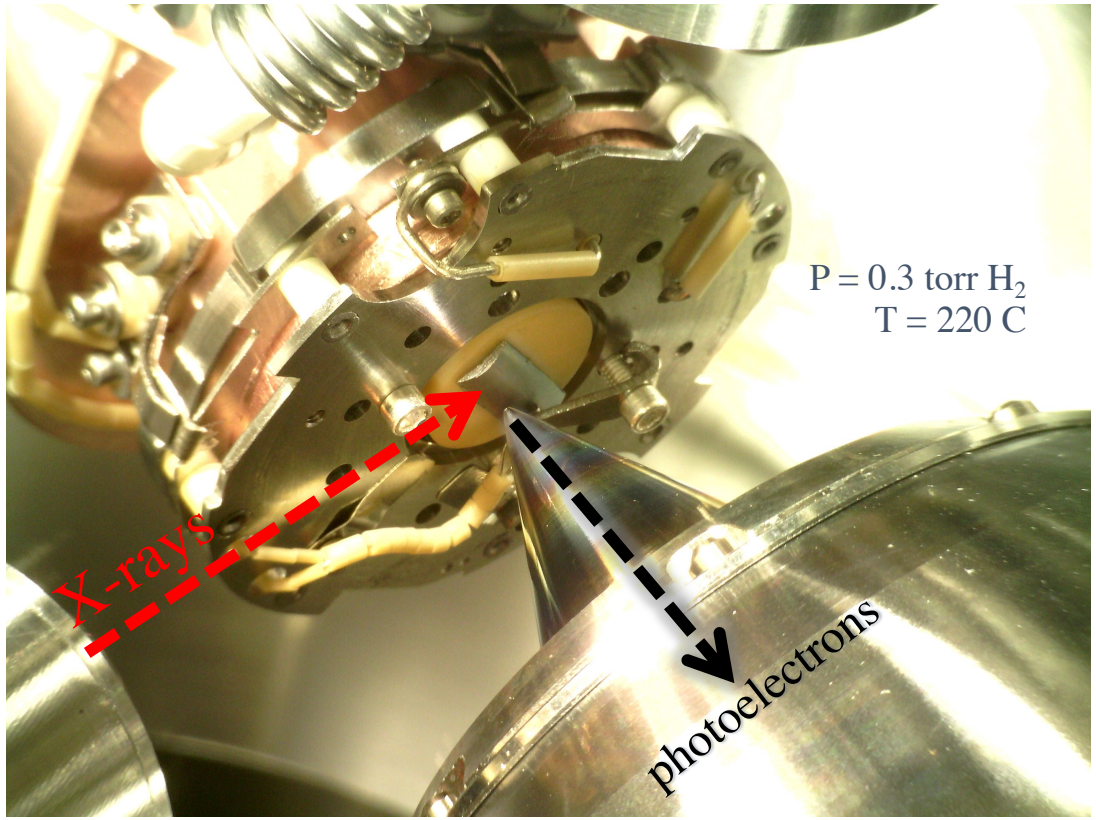
Motivation and Goals of the project

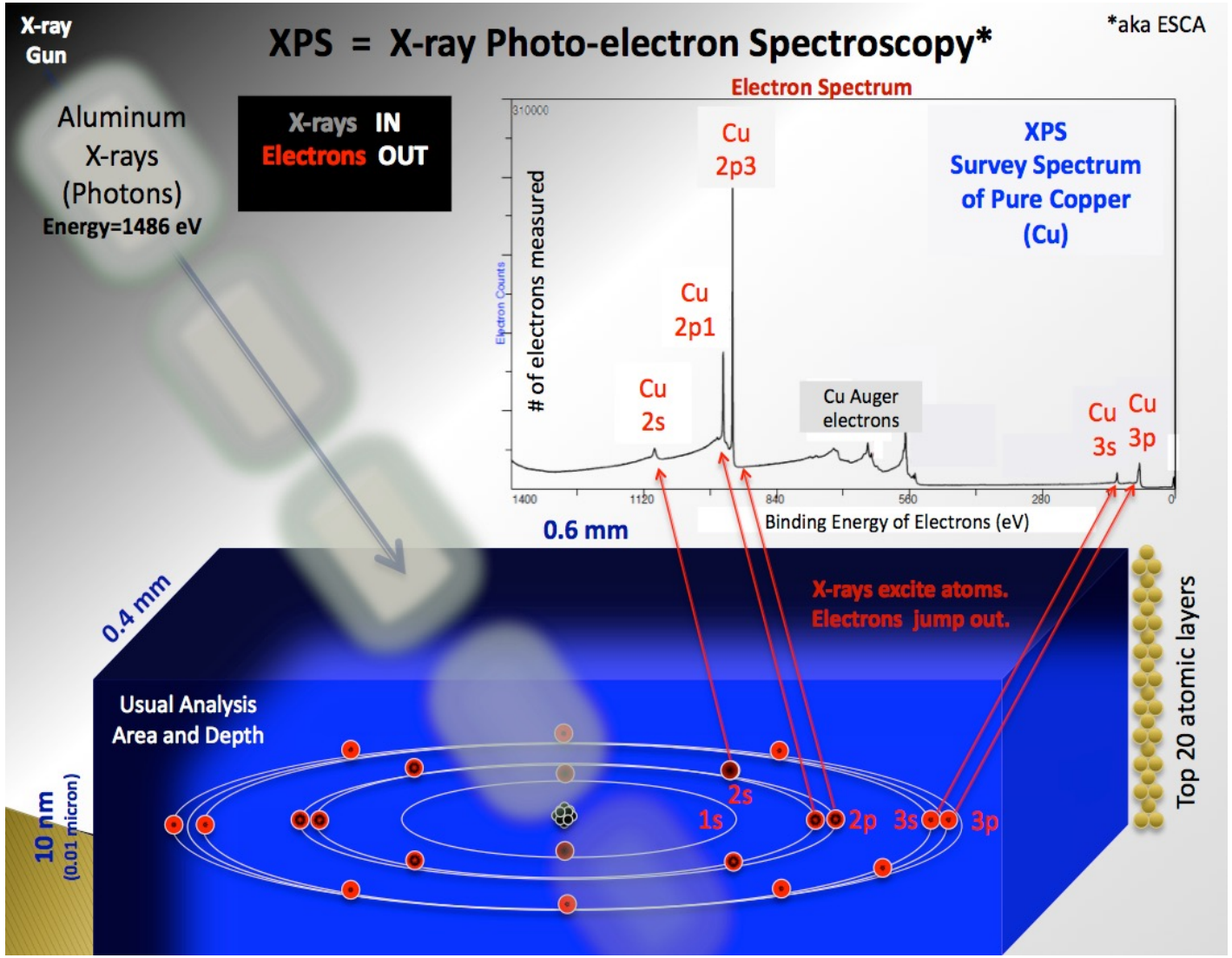
- What is the effect on hydration of surface oxidation and ever-present surface impurities such as carbon?
- Environmental X-ray Photoelectron Spectroscopy (eXPS) overcomes the pressure limitations of traditional XPS and allow **characterizing Ni coating surface, oxidation products, and impurities under hydrogen**
- Sample provided: a prototypical coated cladding sample:
  - Nickel-plated zircaloy tube



Coated cladding at the environmental XPS at SNL/CA

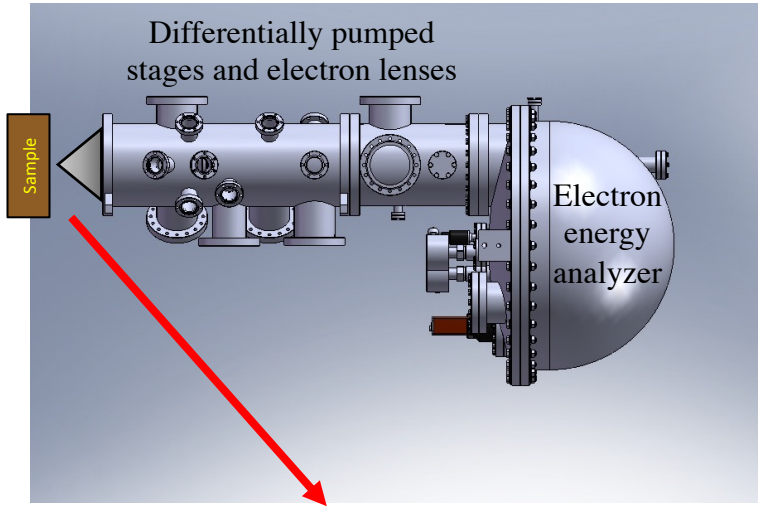
Note: funding arrived March 2022

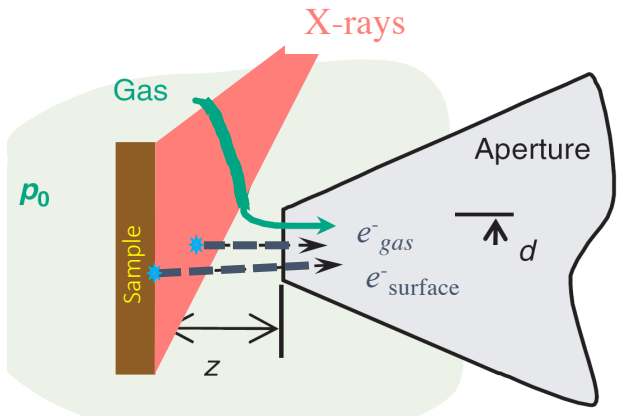
X-ray Photoelectron Spectroscopy



Source: Wikipedia

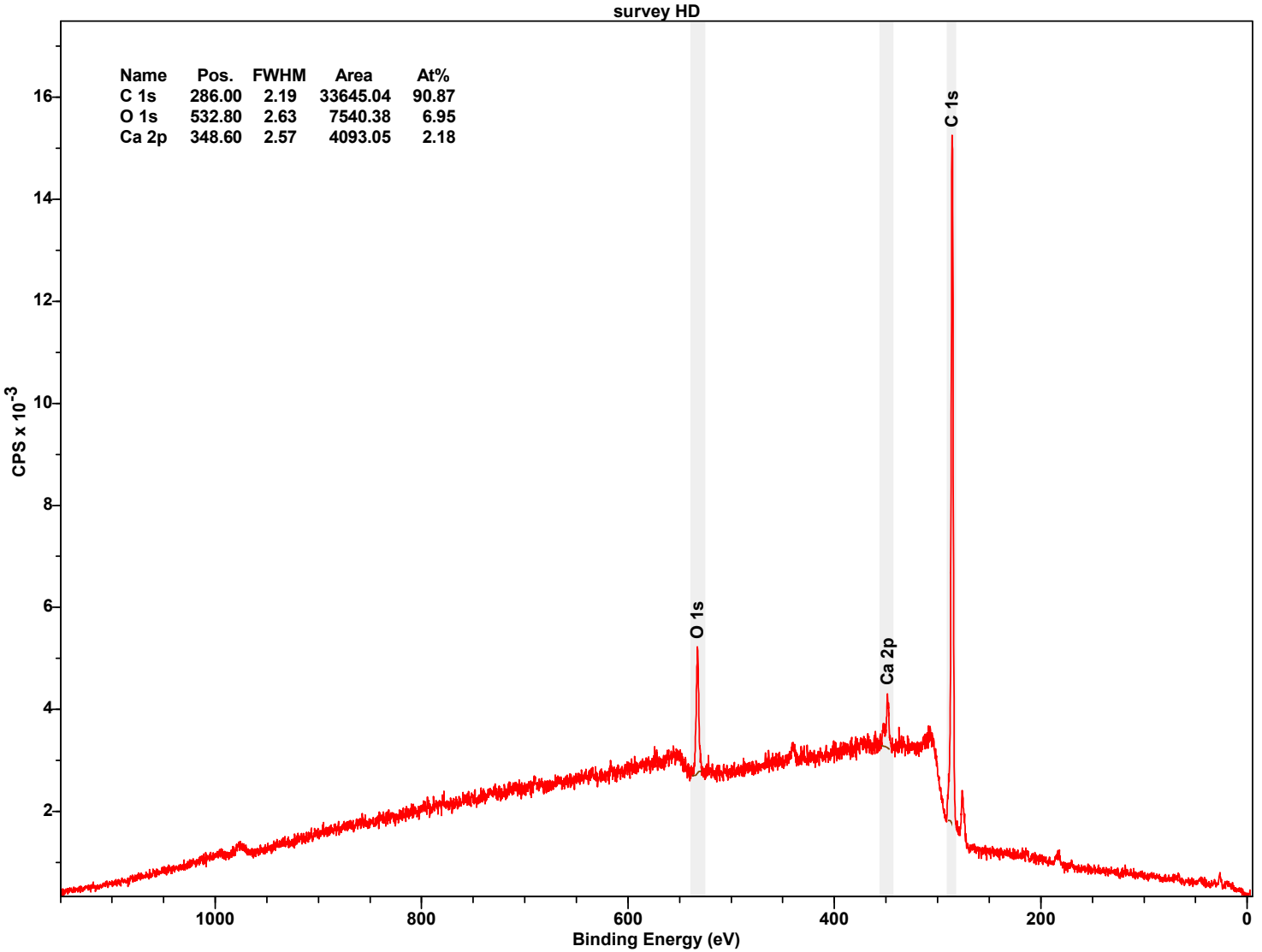
Environmental XPS





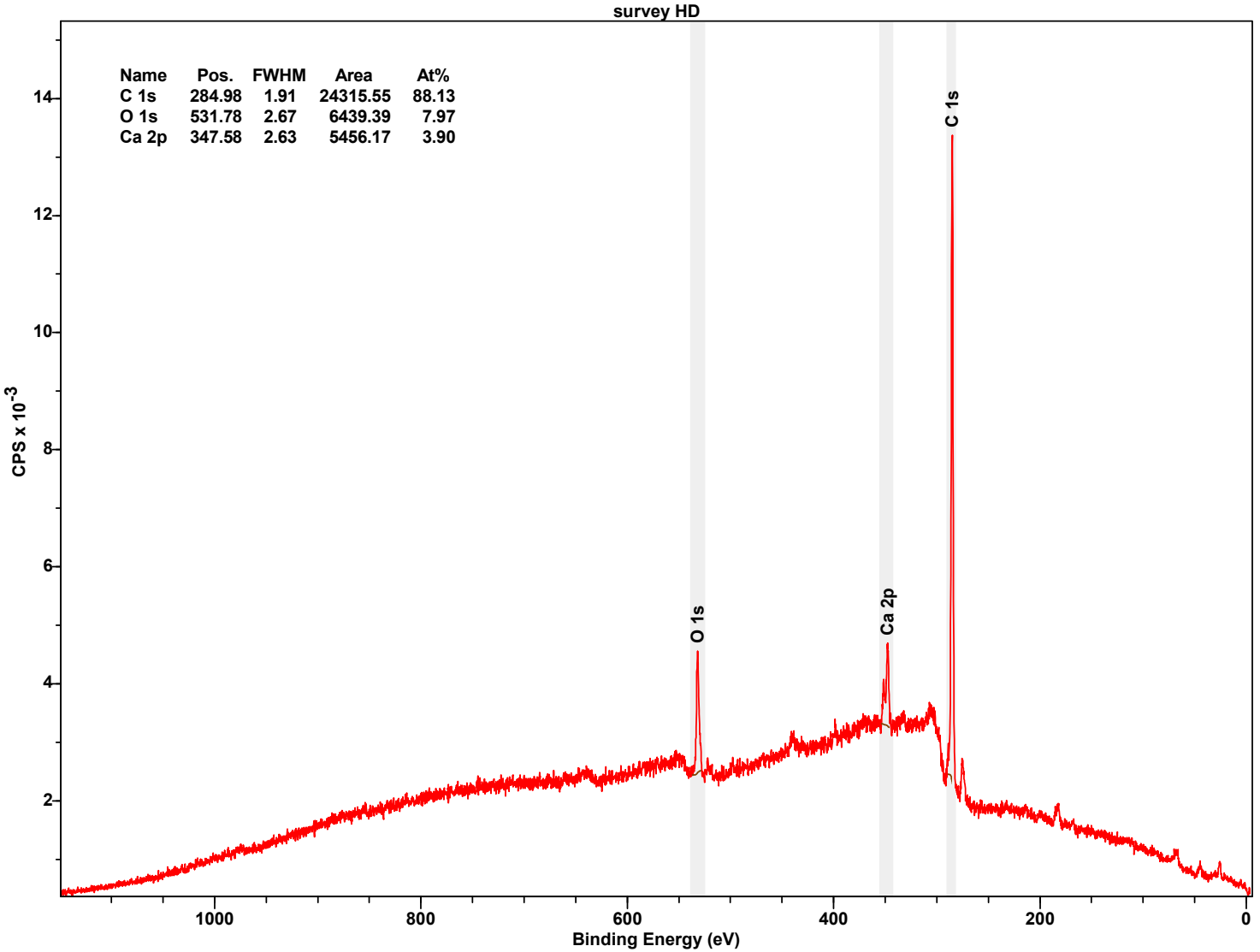
Sample surface chemistry as received

- Almost completely covered by carbon (91%)
- 7% surface oxygen
- Calcium detected
- Zr and Ni not detected (<<1%)

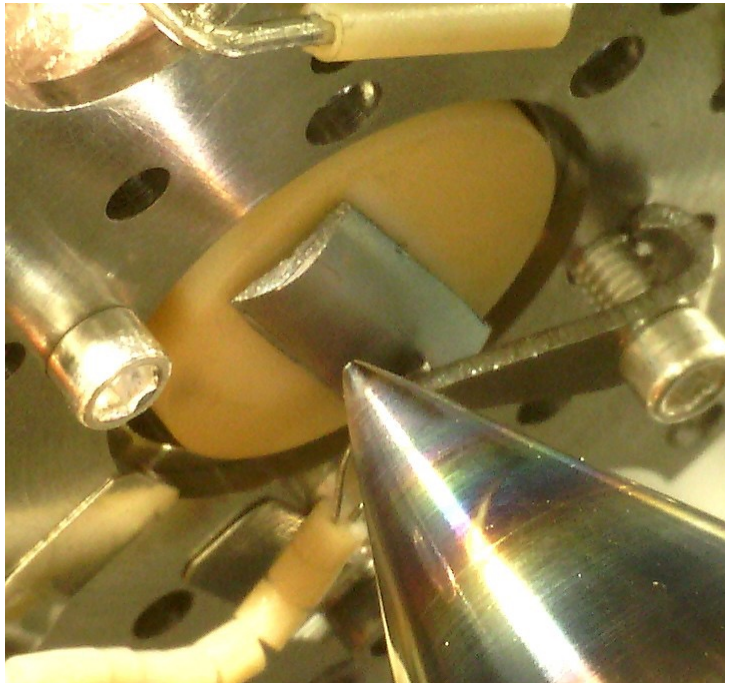


Sample surface: T= 220 C, P= 300mtorr of H_2

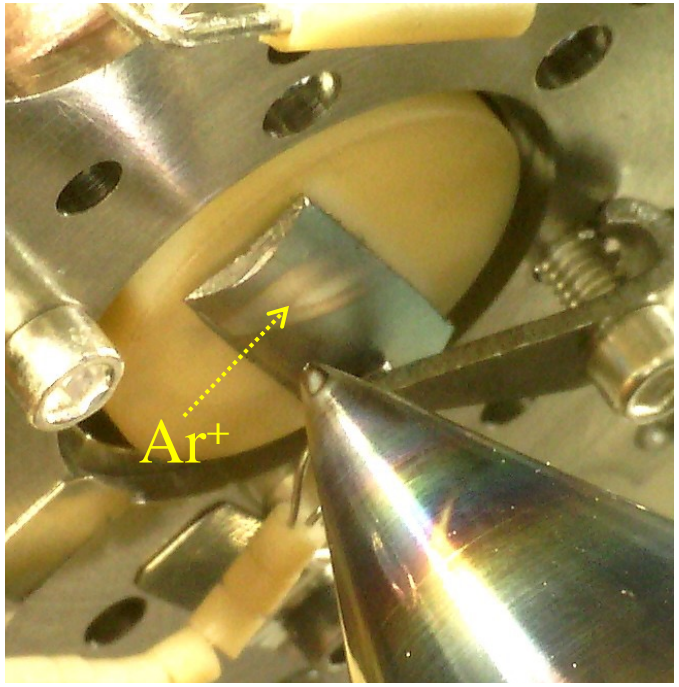
- No substantial changes under hydrogen environment
- Carbon is unreactive to hydrogen at 220 C



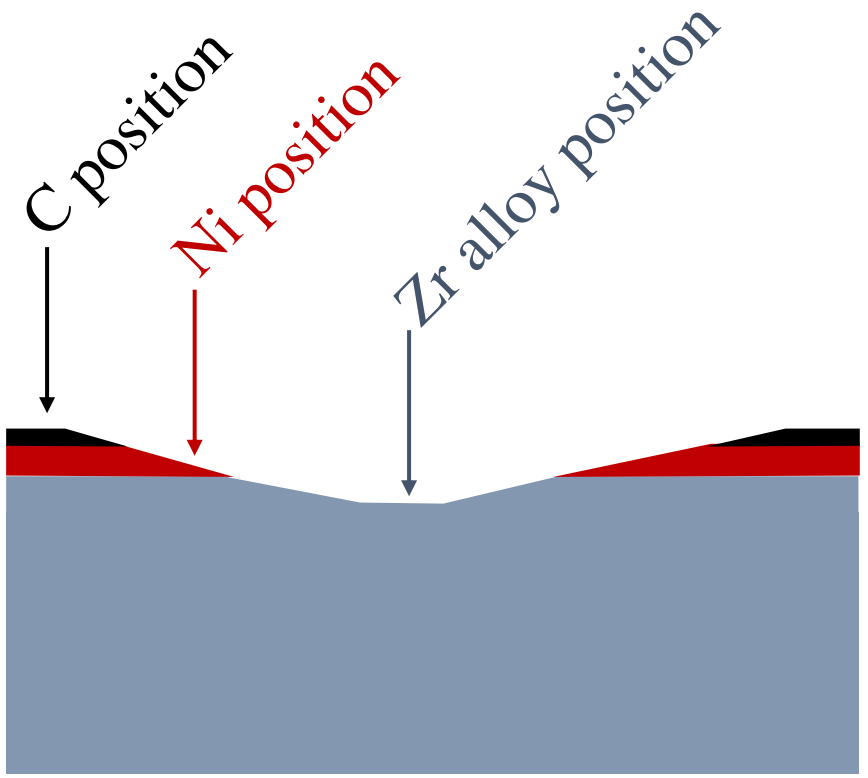
We sputtered the surface with Ar+ ions to remove surface carbon



Before sputtering



After Ar^+ sputtering
(3 kV, 30 mA)



Sample side view after Ar^+ sputtering

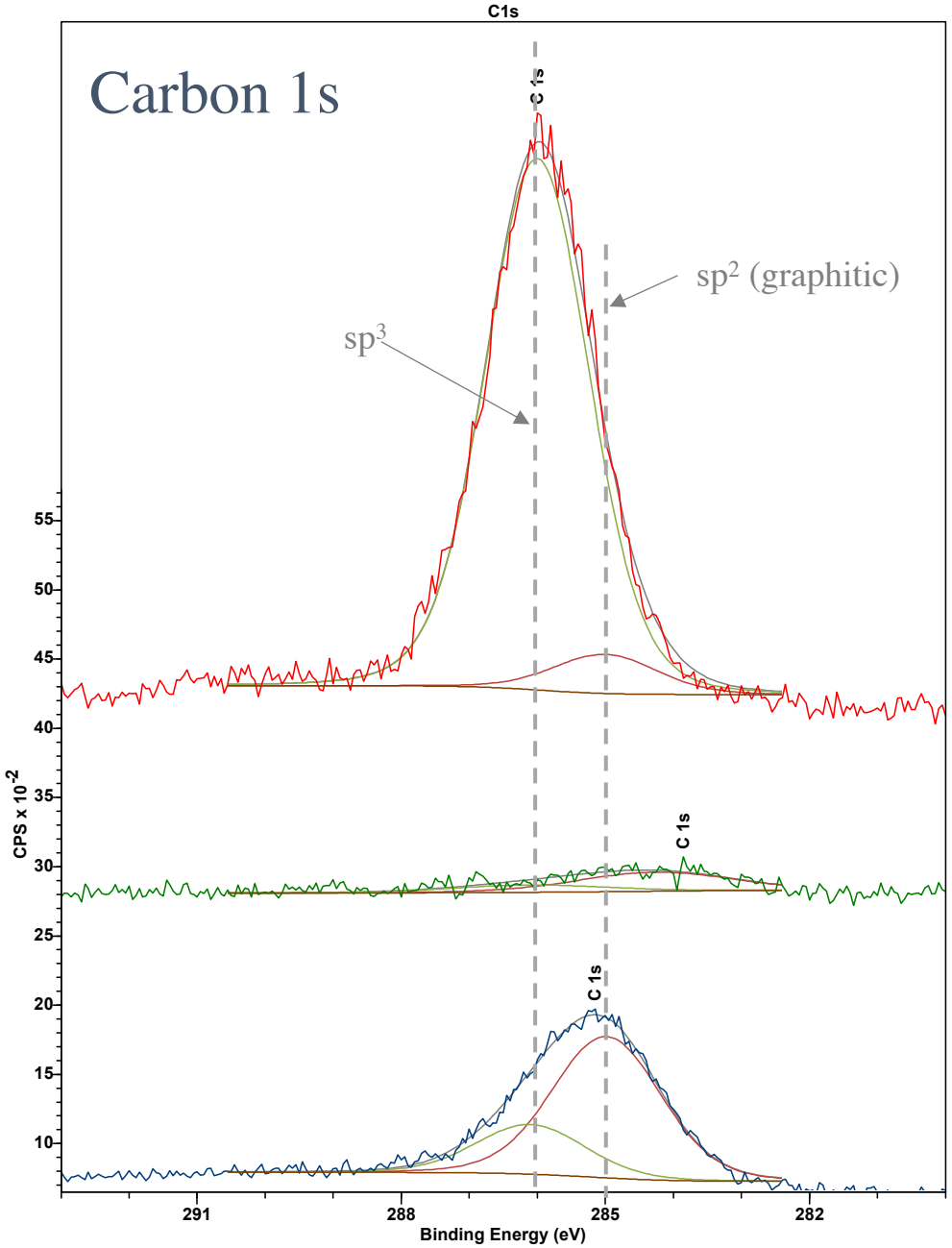
Evolution of Carbon

1. Ar^+ sputtering removes most of the carbon

2. Carbon slowly (days) segregates to the surface after sputter cleaning.

3. The Ni coating must have considerable amount of dissolved carbon in the near-surface region. Nickel can dissolve and store carbon in the bulk if exposed to carbon at high T.

4. Even a very small amount of carbon impurity in the bulk of Ni can result in high C surface coverages after segregation. A clean nickel surface becomes unstable if there is bulk carbon.



As received

91% of surface

Immediately after Sputtering

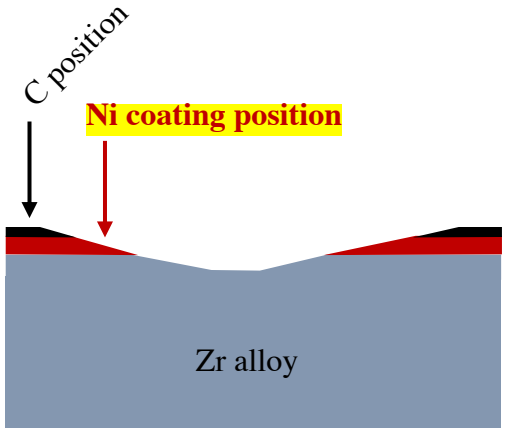
6 % of surface

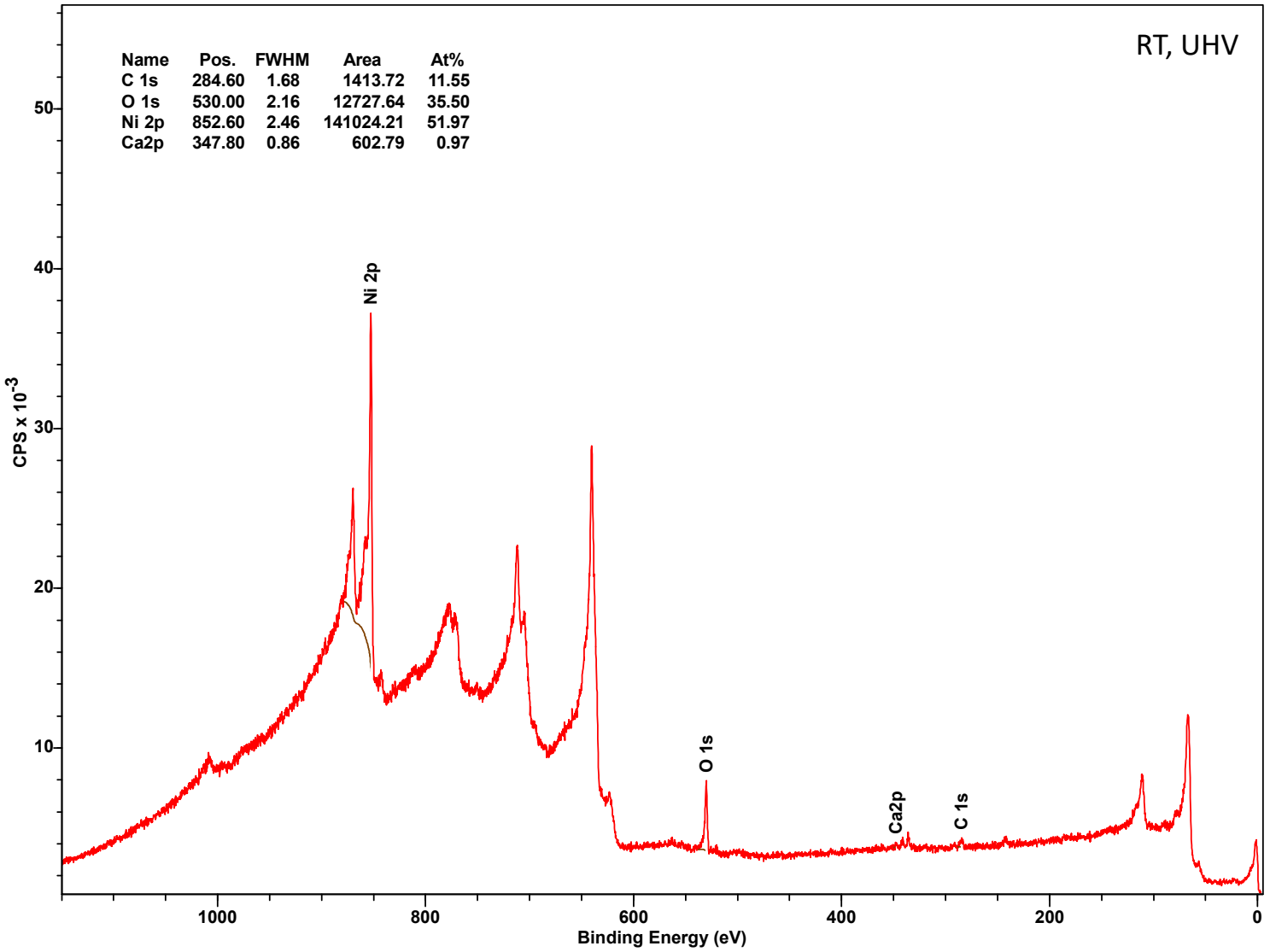
A few days after sputtering

51% of surface

Sample after sputtering: Ni coating position

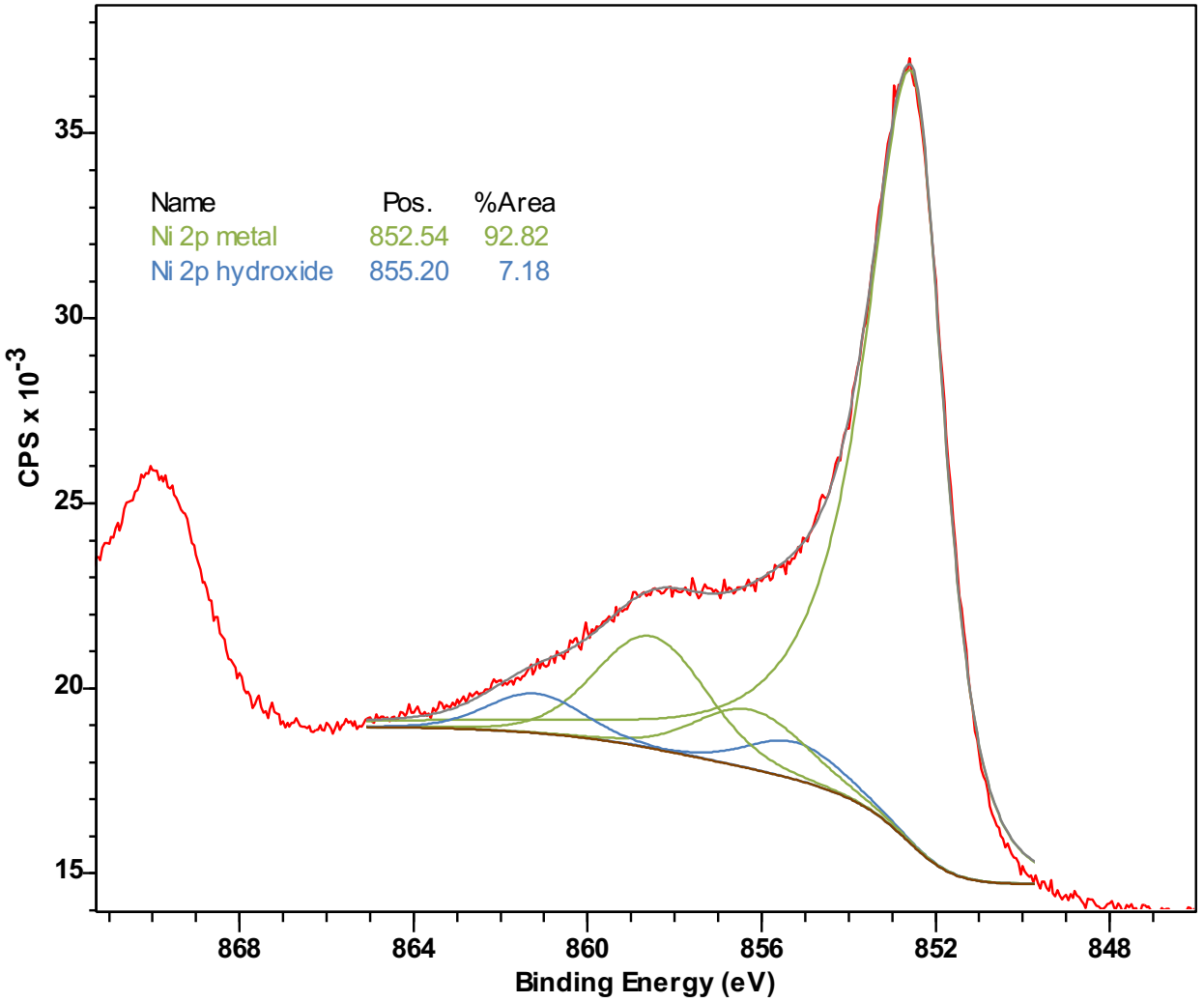
- Nickel: 52 %
  - 92.8% Ni metal
  - 7.2% $Ni(OH)_2$
- Oxygen: 35.5%
- Carbon: 11.5%
- Calcium contamination detected (1%)
- Oxygen probably bonded to carbon and $Ni(OH)_2$



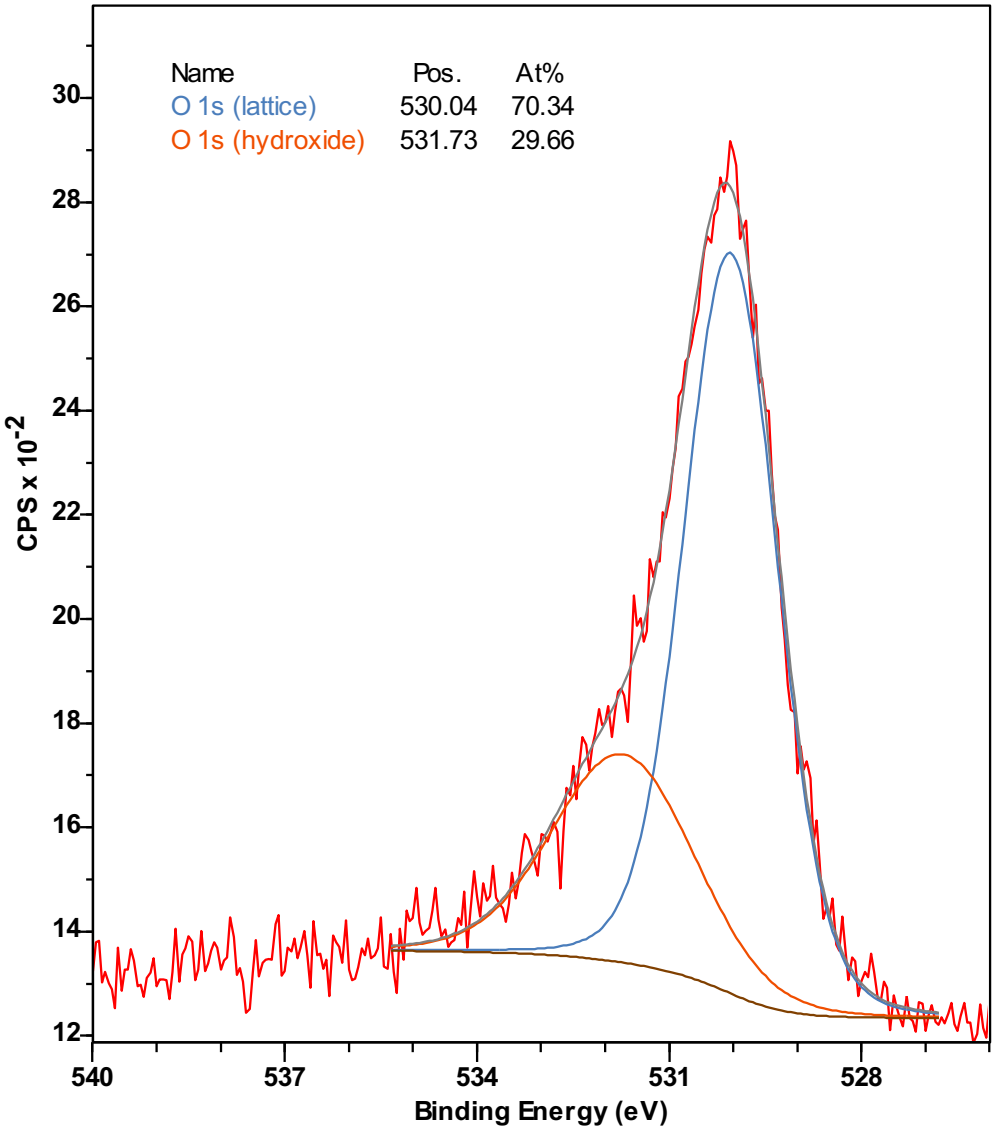


Ni Coating XPS

Ni 2p

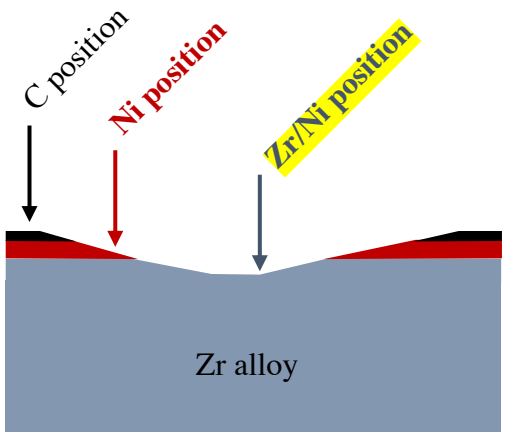


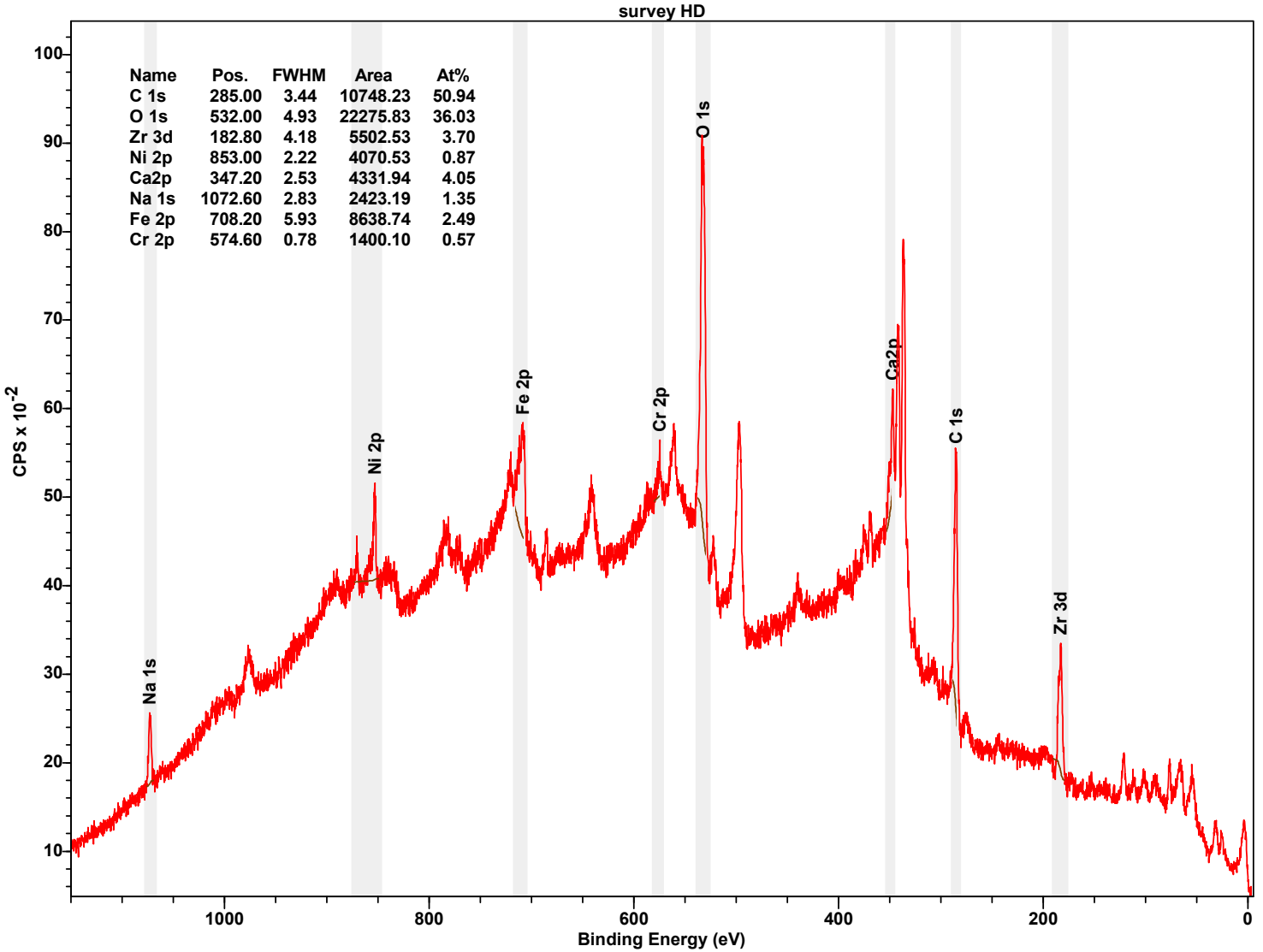
O1s



Zr position
RT, UHV

- Multitude of impurity elements:
  - Carbon (50%)
  - Calcium (4%)
  - Sodium (0.5%)
  - Oxygen remains at ~36%



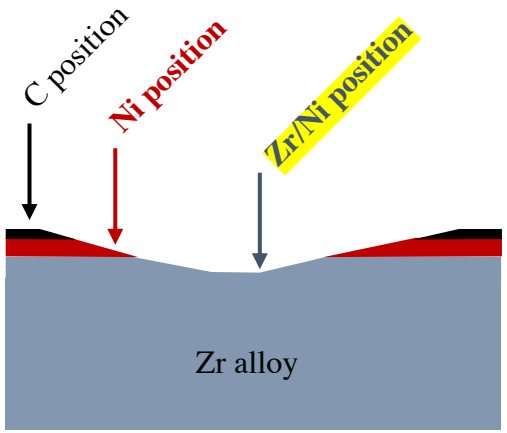


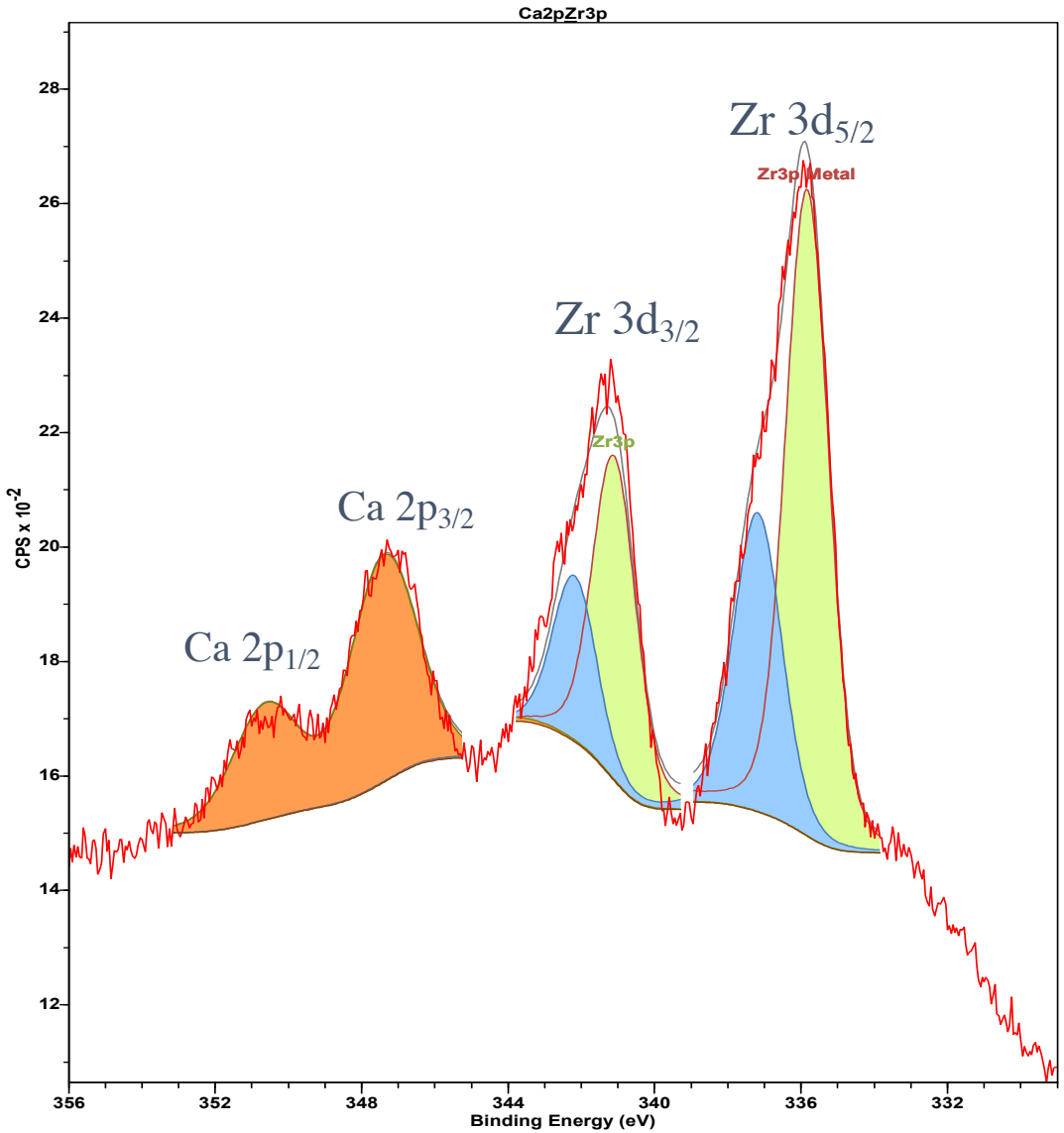
SNL/CA

Sample after sputtering: Zr/Ni position RT, UHV

Zr 3d, Ca 2p detailed peaks:

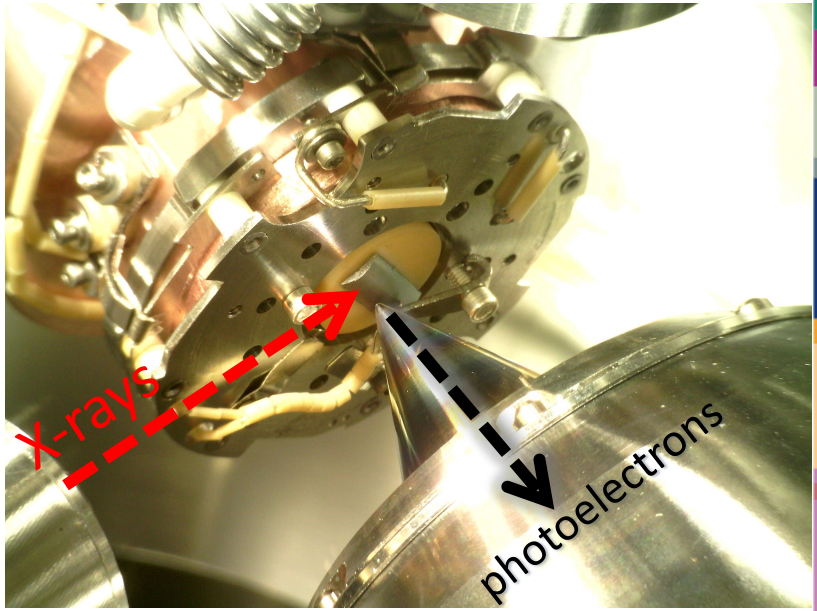
- Zr:
  - 66% Zr metal/alloy
  - 33% ZrO_2
- Ca: 100% $CaCO_3$





Summary of the project so far

1. Severe surface carbon contamination coats the surface. The carbon is much thicker than the penetration of XPS (3-8 nm).
2. 300 mTorr of hydrogen at 220 C did not affect this surface, suggesting that the surface has been effectively passivated by carbon.
3. Sputtering with Ar^+ allowed us to access the Ni coating layer and monitor its surface chemical state.
4. Bulk impurities like C, Ca, Na, and oxides are present after sputtering cleaning, suggesting bulk contamination.



Next steps:

- Monitor the chemical interaction of hydrogen on the exposed Ni surface at temperatures between 200-500 C.

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Thank you