XPS analysis of pyrite thin films

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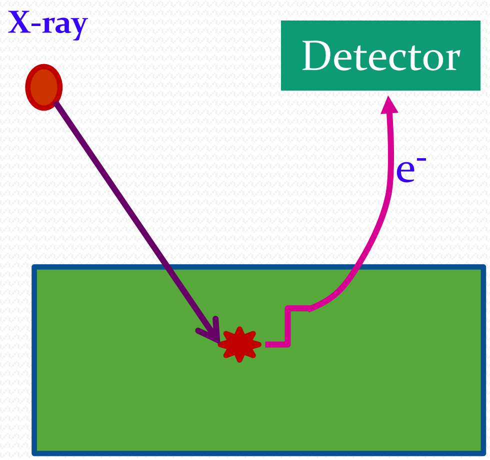
Outline

- **Introduction of XPS**
- **Pyrite thin films on the glass**
  - Na migration to the surface
  - Ar sputtering effect
- **Pyrite thin films on the quartz**
  - Removal of oxidation layers on the surface
  - Time-dependent oxidation study
- **Pyrite thin films on the Si substrate**
  - Synchrotron radiation (Advance Light Source in Berkeley National Labs)
  - Surface chemical states of pyrite thin films on the Si substrate

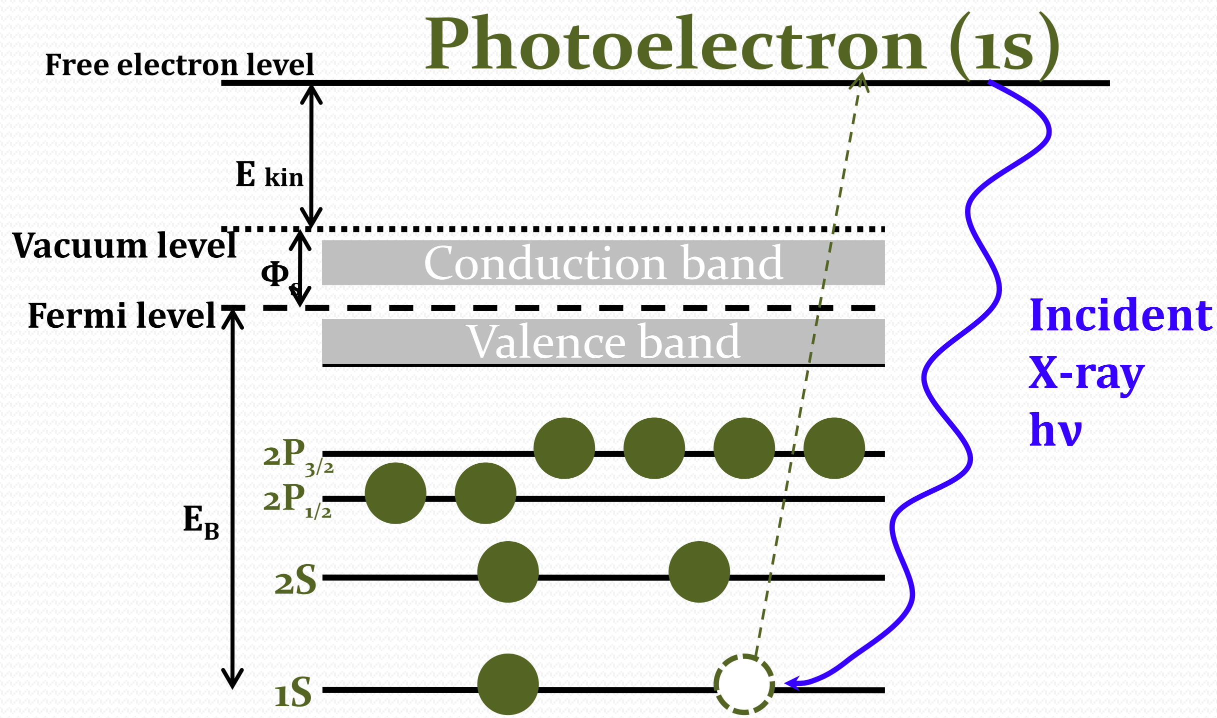
The principle of X-ray photoelectron spectroscopy (XPS)

Photoelectron effect



Ultra-high vacuum (<10^{-9} torr) is required.

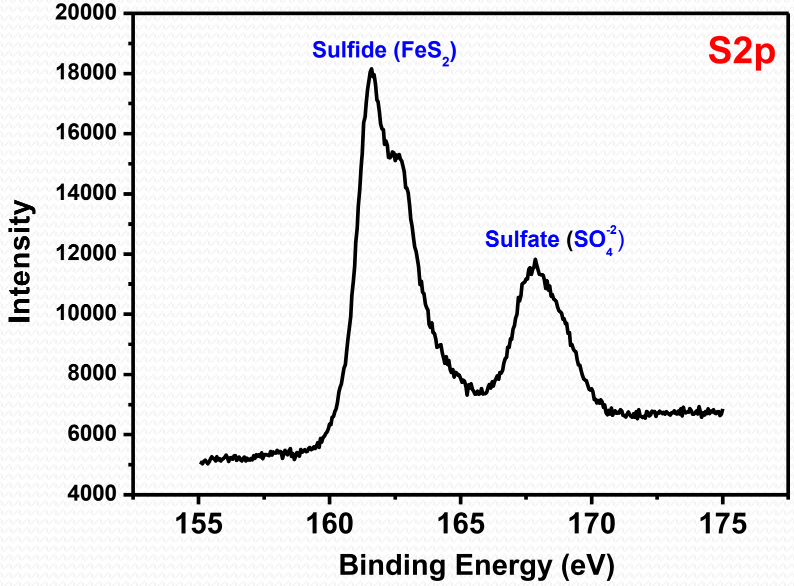
XPS energy level diagram

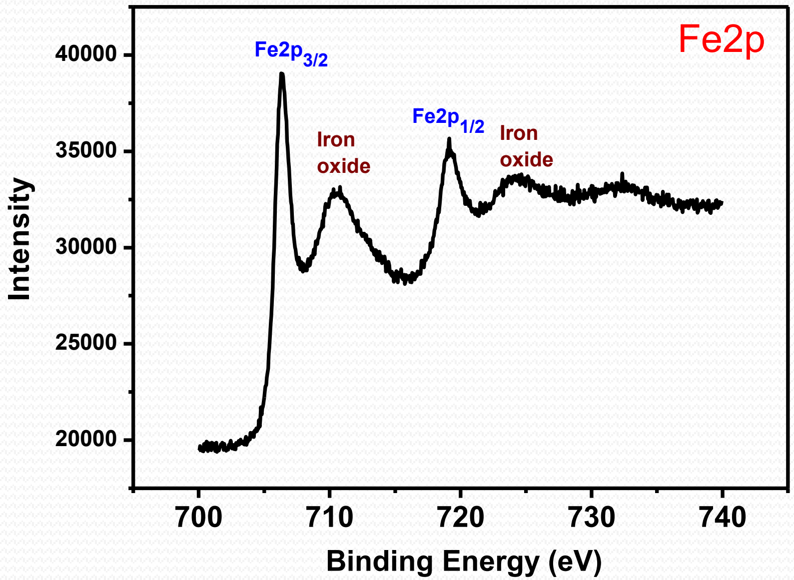


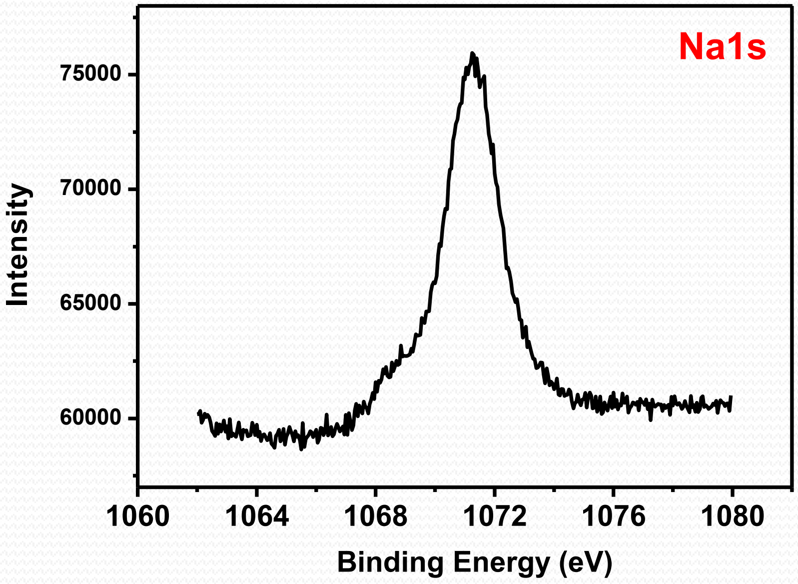
$$E_{kin} = h\nu - E_B - \Phi_s$$

E_{kin} : The kinetic energy of ejected photoelectrons; E_B : Binding Energy
$h\nu$: The energy of the incident X-ray photons. Φ_s : Work function term (almost constant)

Pyrite thin films on the glass

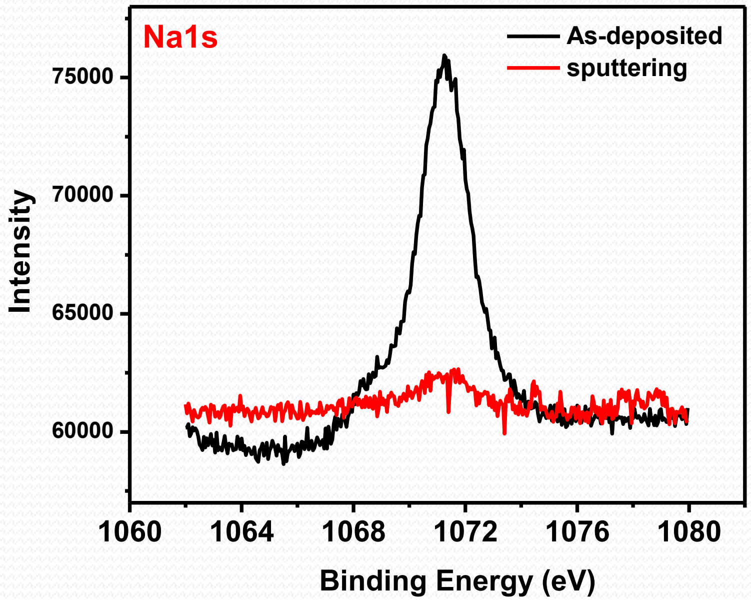


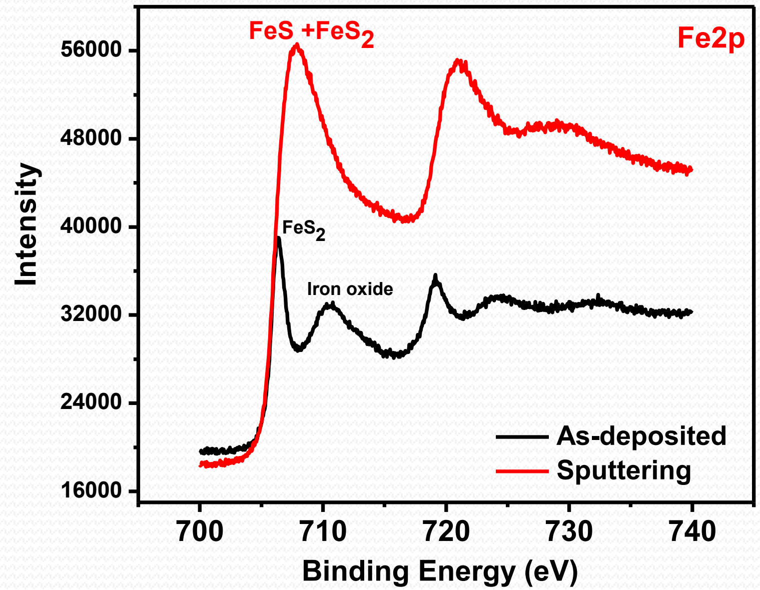


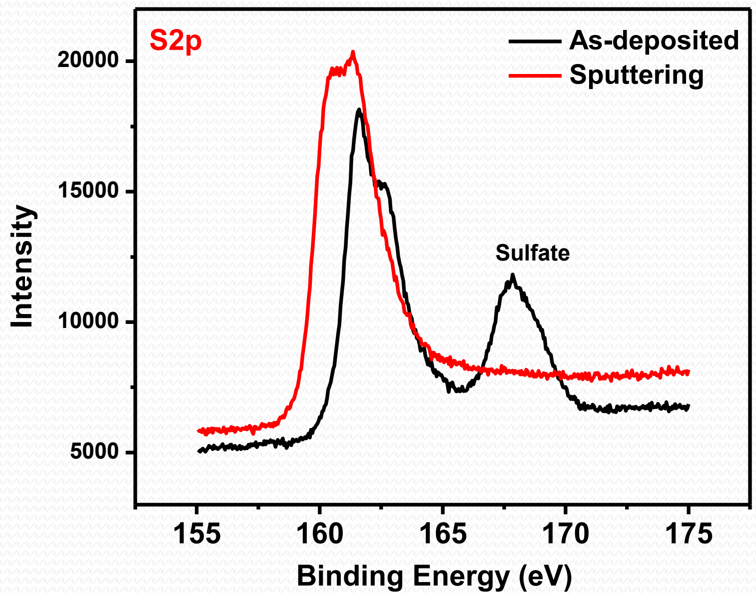


- The pyrite has been **oxidized**.
- **Na exists** on the surface of the pyrite thin film.

As-deposited VS Sputtered

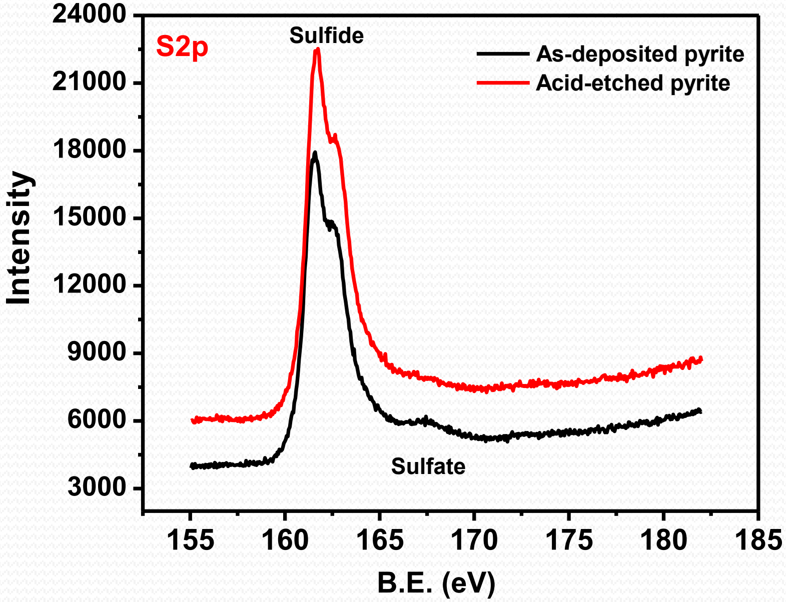


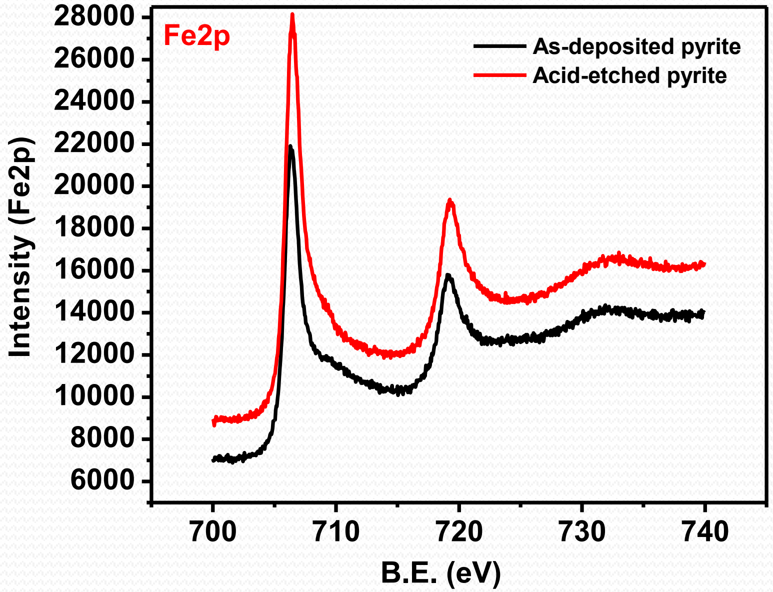


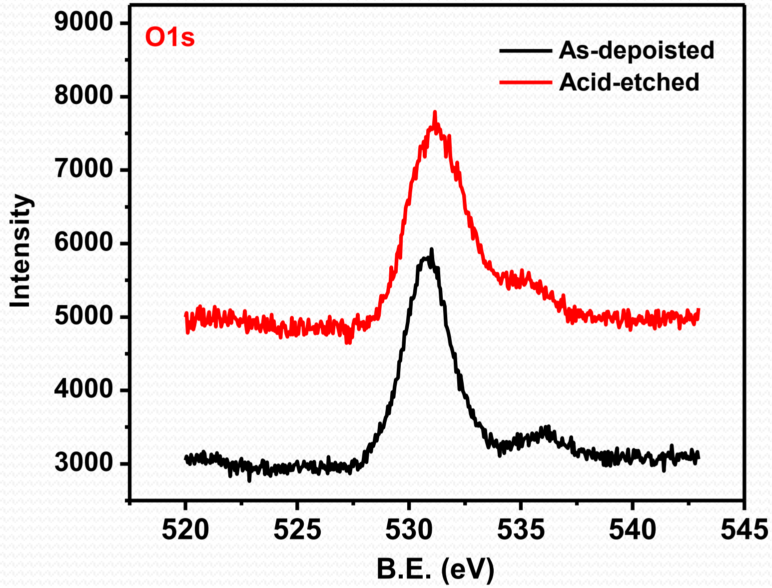


- **Sputtering condition:** 5*10-5 torr Ar, 2 KV (beam energy), 20mA (emission current), 5 mins.
- **Na is removed** by Ar sputtering which indicates Na only exists on the surface.
- **The broadening** of Fe 2p and S2p peaks after Ar sputtering is attributed to **sulfur preferential sputtering.**

Pyrite thin films on the quartz



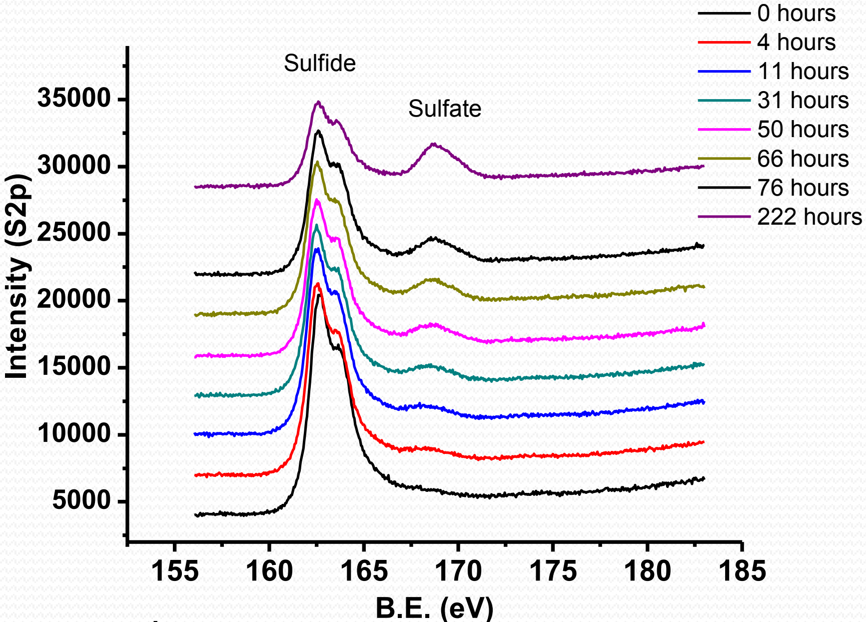


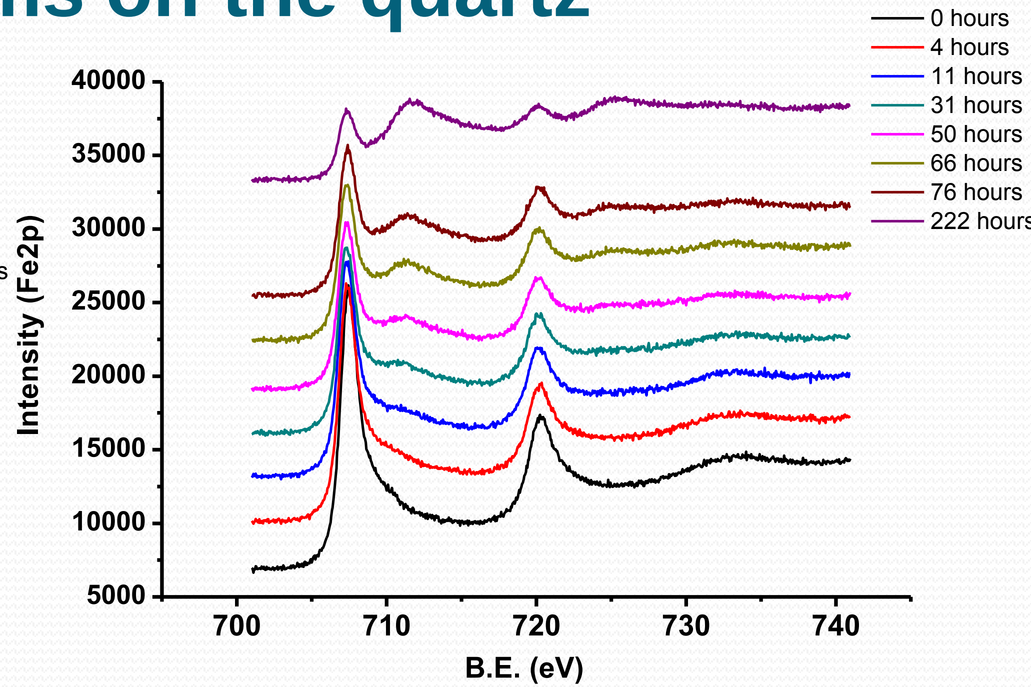


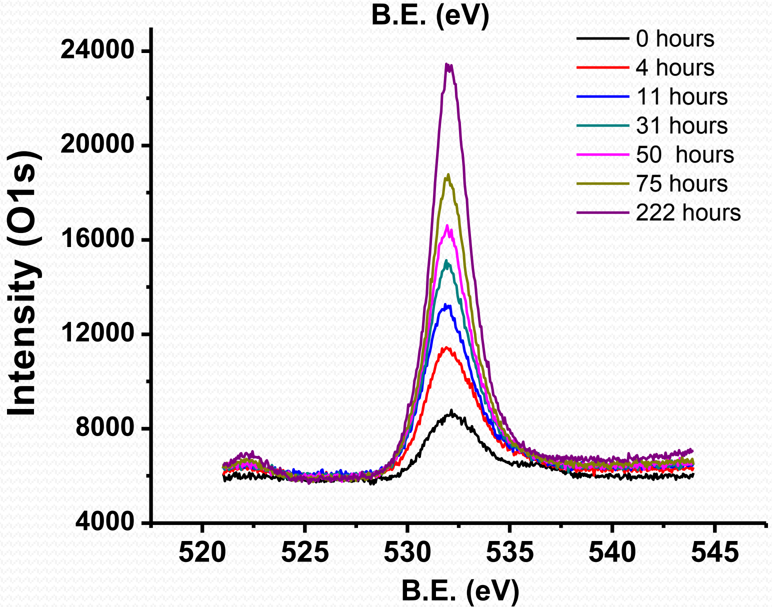
- The composition of mixed acid used for removing the oxide layer is: **0.1% HF, 0.1% Acetic acid, and 0.1% Nitric acid**

- The oxide layer can be **removed** by this mixed acid.

Time-dependent oxidation study of acid-etched pyrite thin films on the quartz

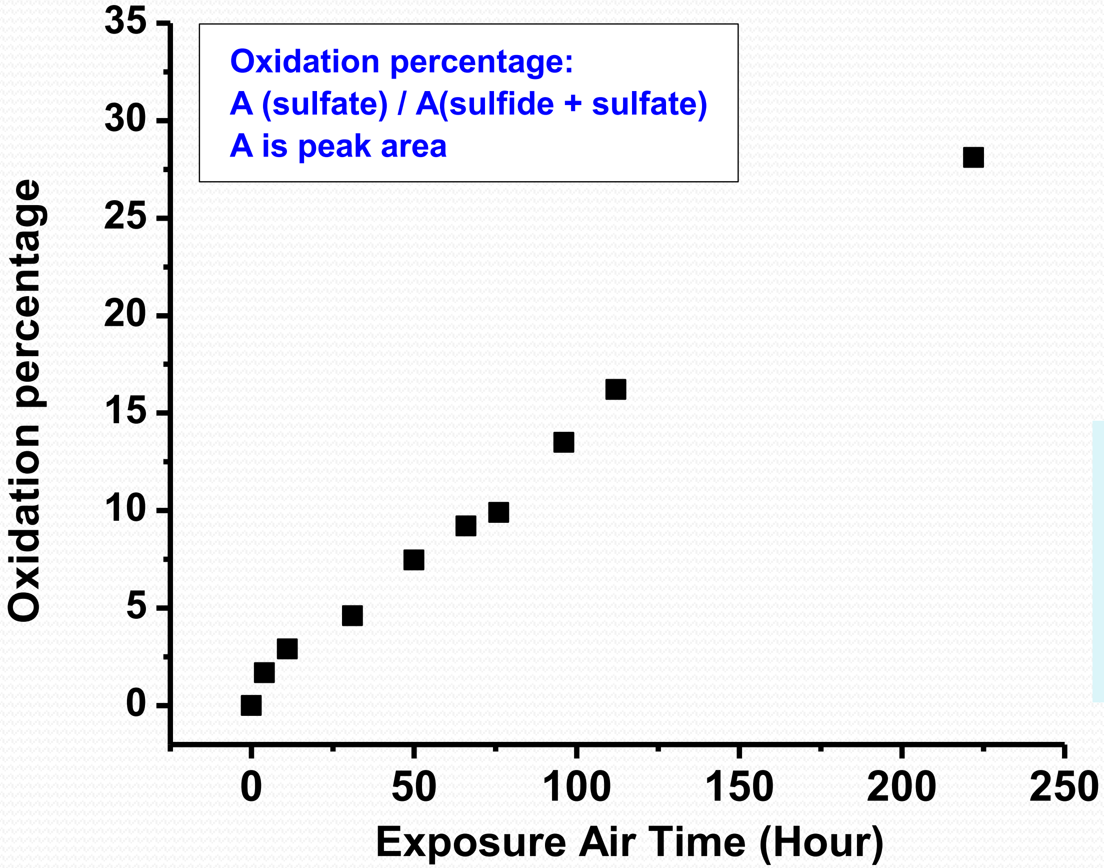






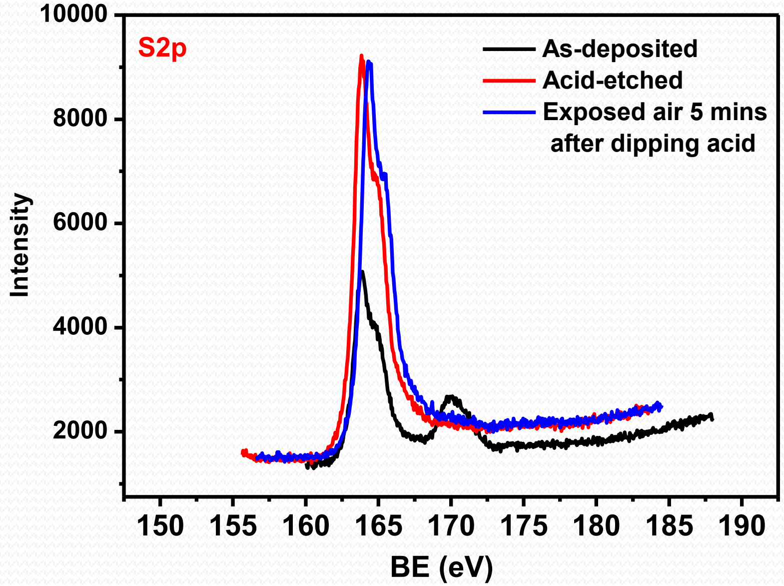
- **The oxide layer grows with respect to exposure air time.**

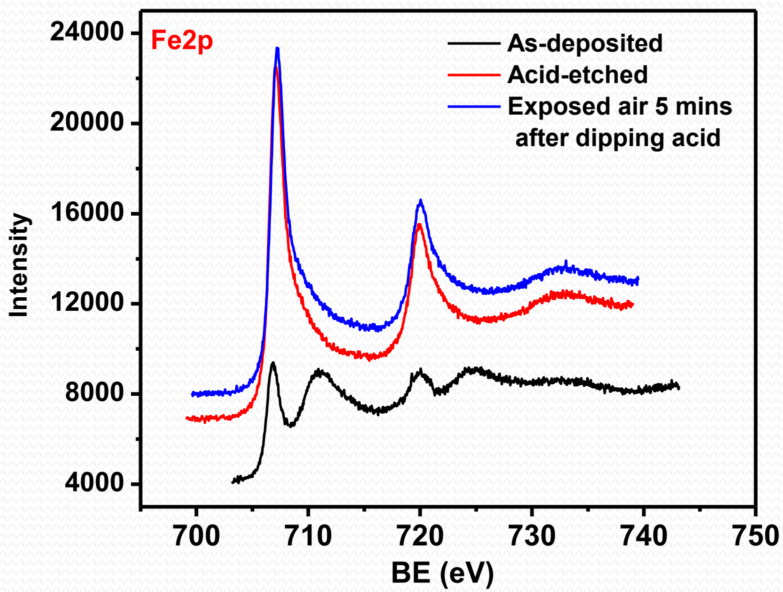
Time-dependent oxidation study of acid-etched pyrite thin films on quartz

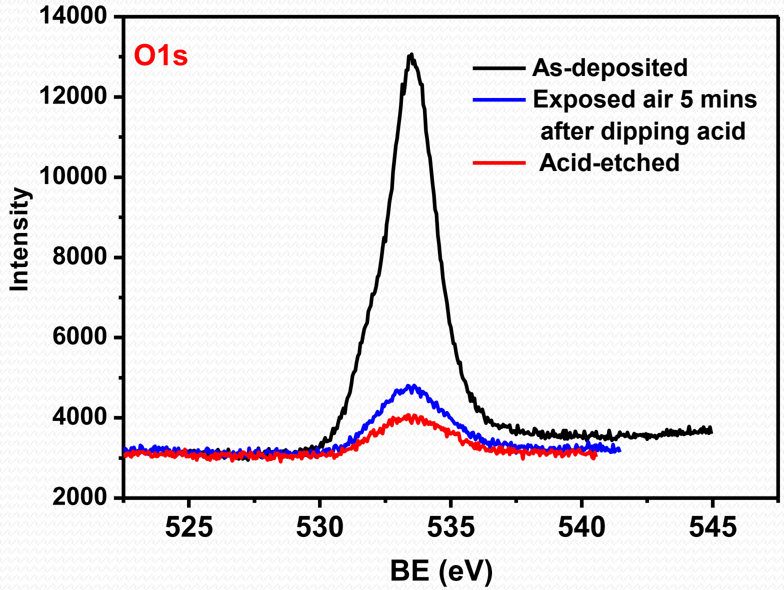


•This oxidation study is still in progress, since the oxide layer is NOT saturated.

Pyrite thin films on the Si (in Irvine)





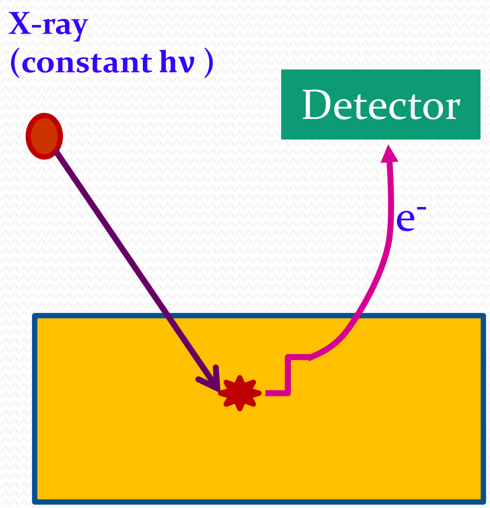


- After dipping the acid solution, the oxide layer was removed.

- The acid-etched pyrite keeps unoxidized after exposing to air 5 mins.

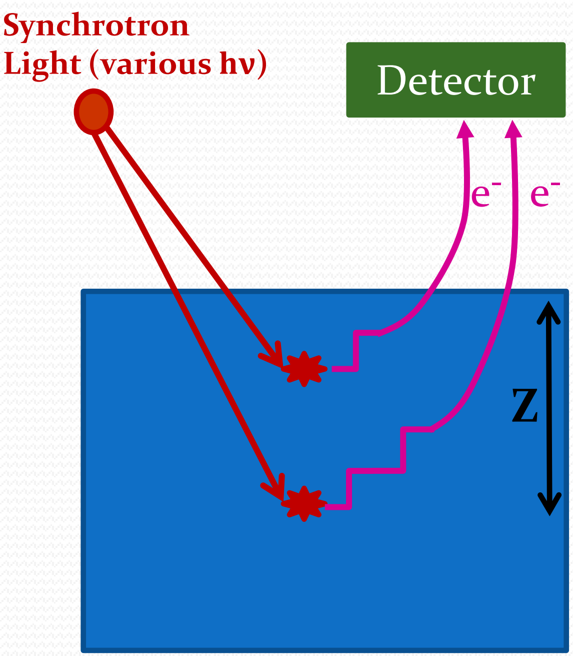
Depth profile experiment and inelastic mean free path (IMFP)

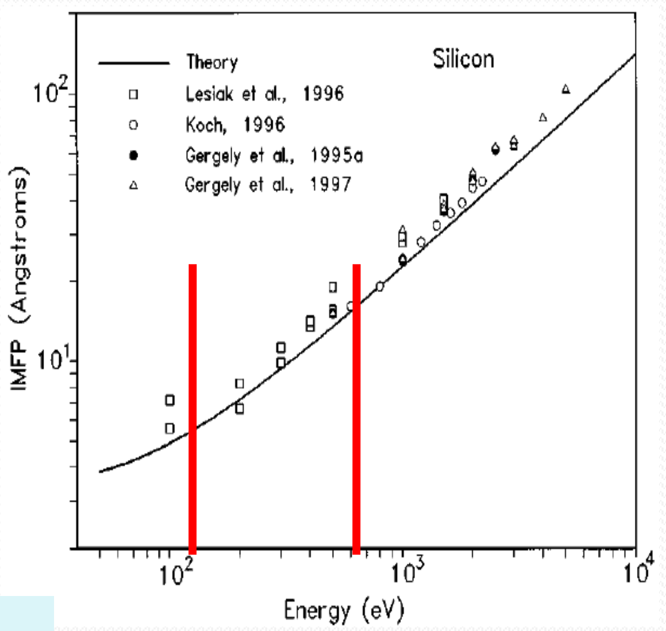
Photoelectron effect



$$E_{kin} = h\nu - E_B - \Phi_s$$

Depth profile experiment

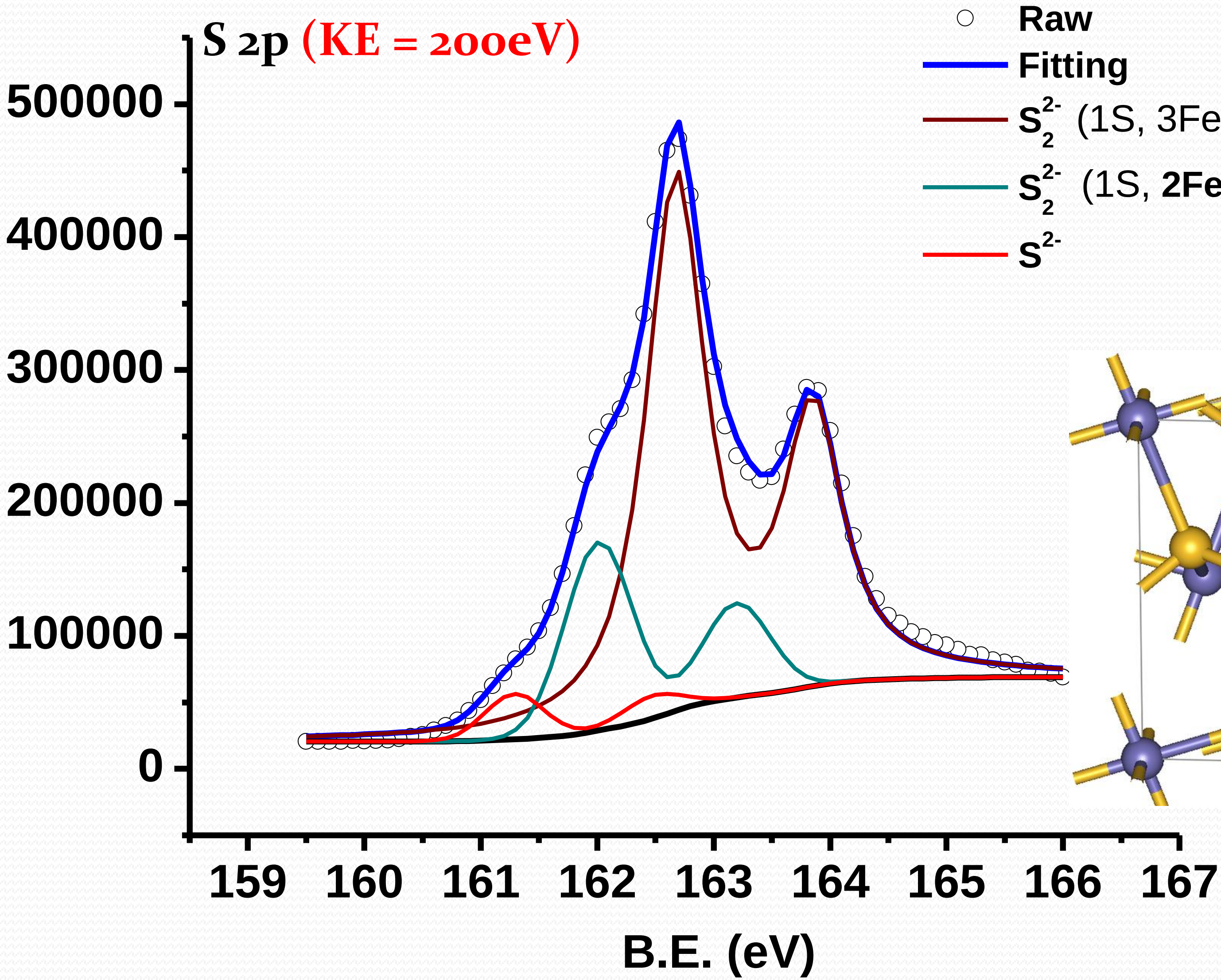


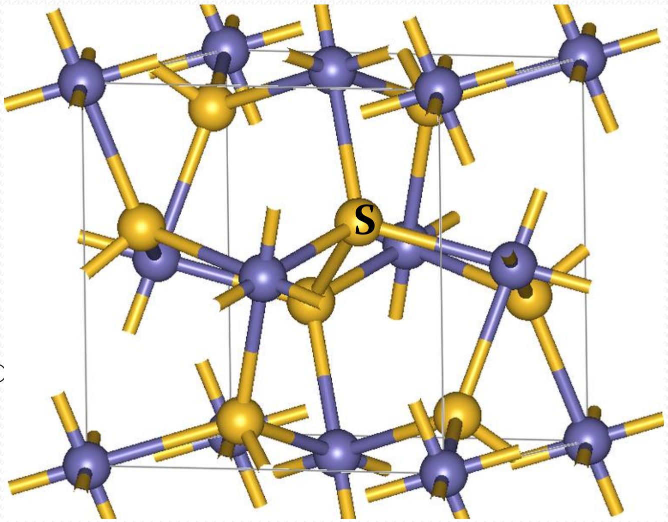


Photoelectrons with different kinetic energies come from different depth of the sample.

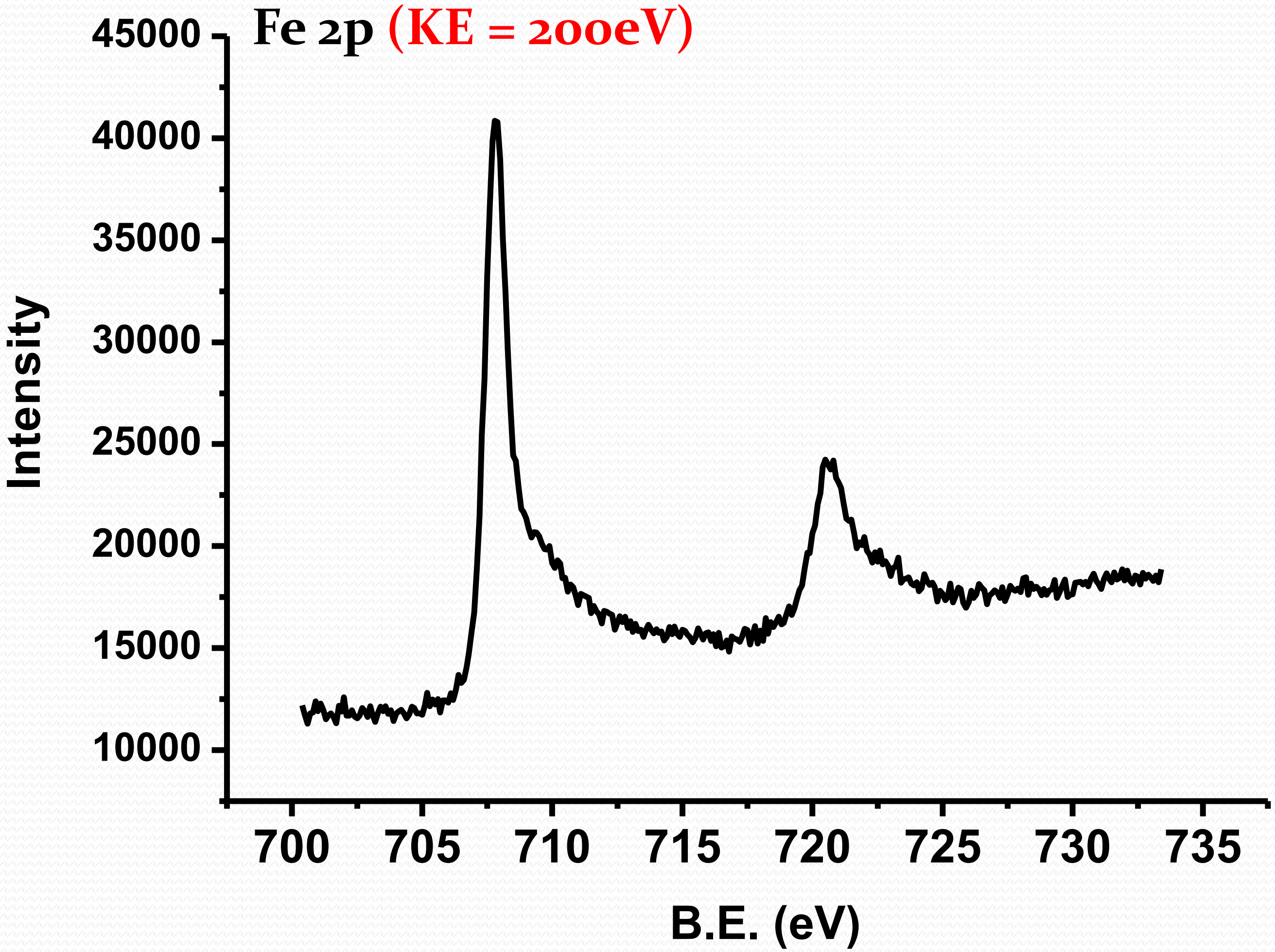
J. Phys. Chem. Ref. Data, Vol. 28, No. 1, 1999

Acid-etched pyrite thin films on Si (in Berkeley)

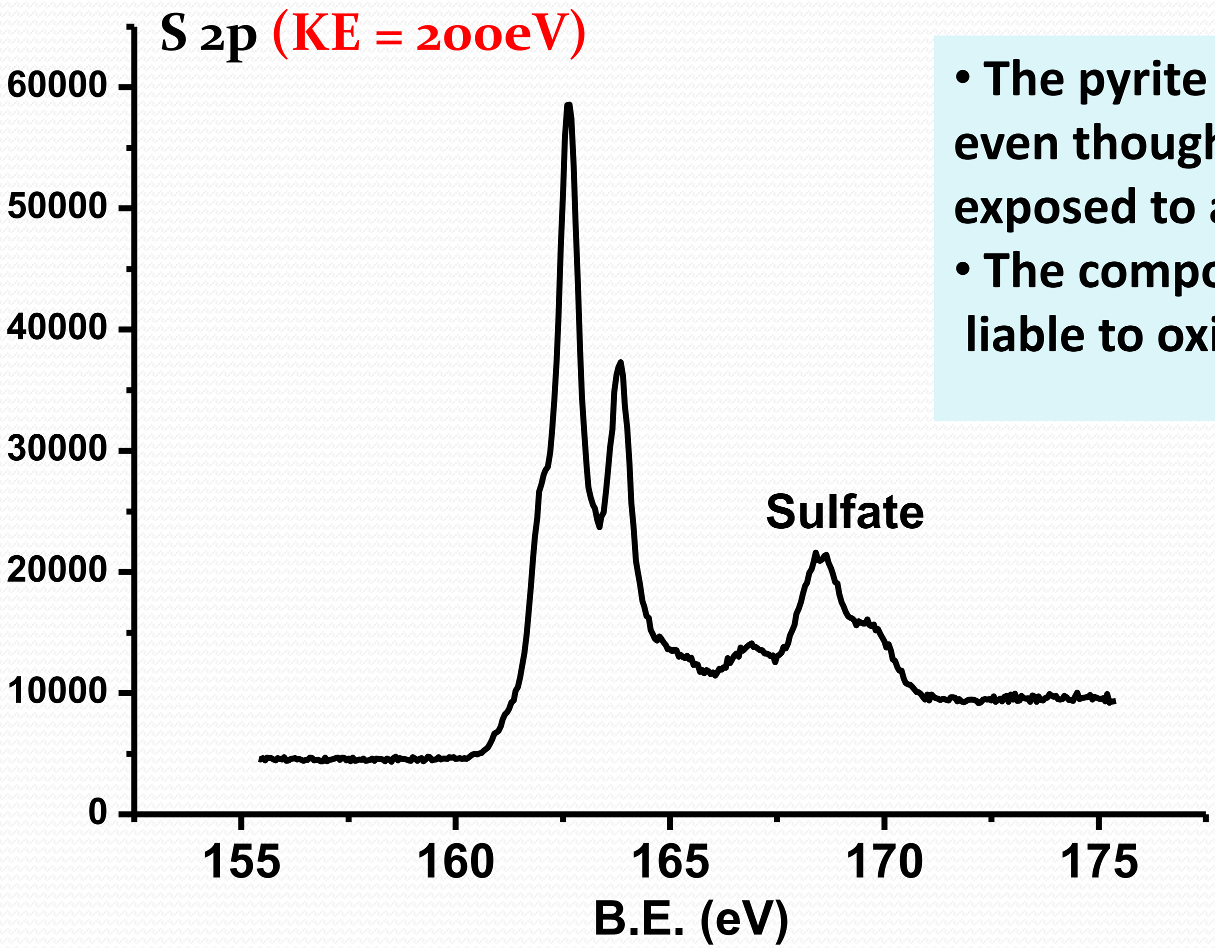




Acid-etched pyrite thin films on Si (in Berkeley)

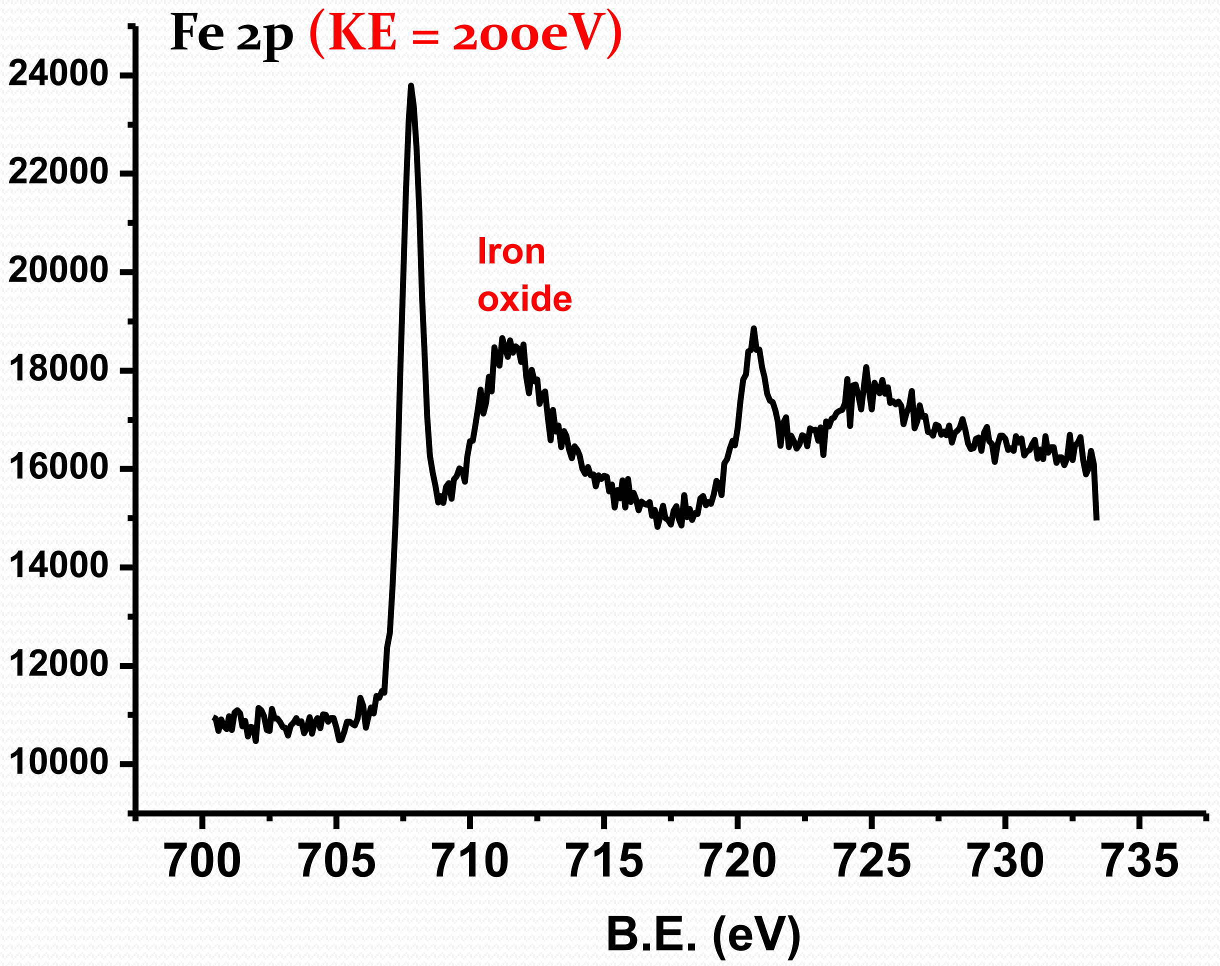


Acid-etched pyrite thin films on Si after exposing to air 4 hours (in Berkeley)

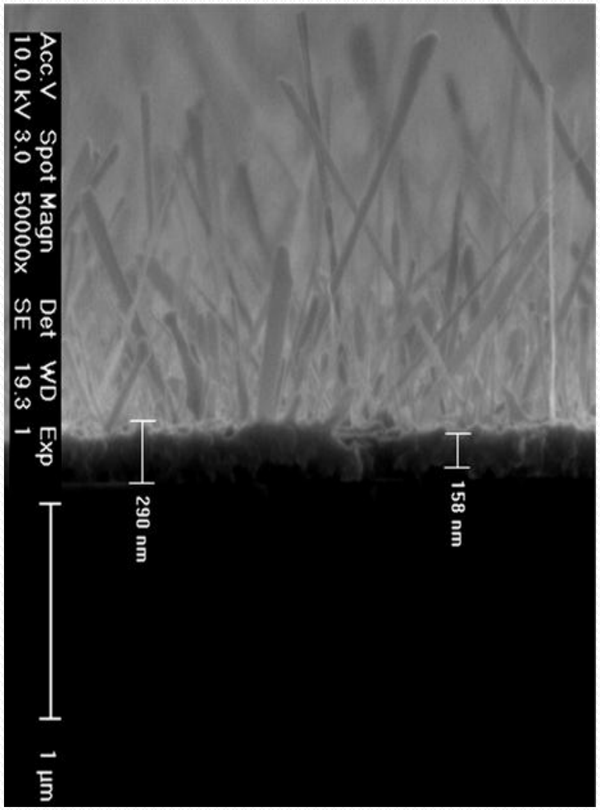


- The pyrite has been oxidized even though it only has been exposed to air for 4 hours.
- The component, S^{-2}, is the most liable to oxidize.

Acid-etched pyrite thin films on Si after exposing to air 4 hours (in Berkeley)

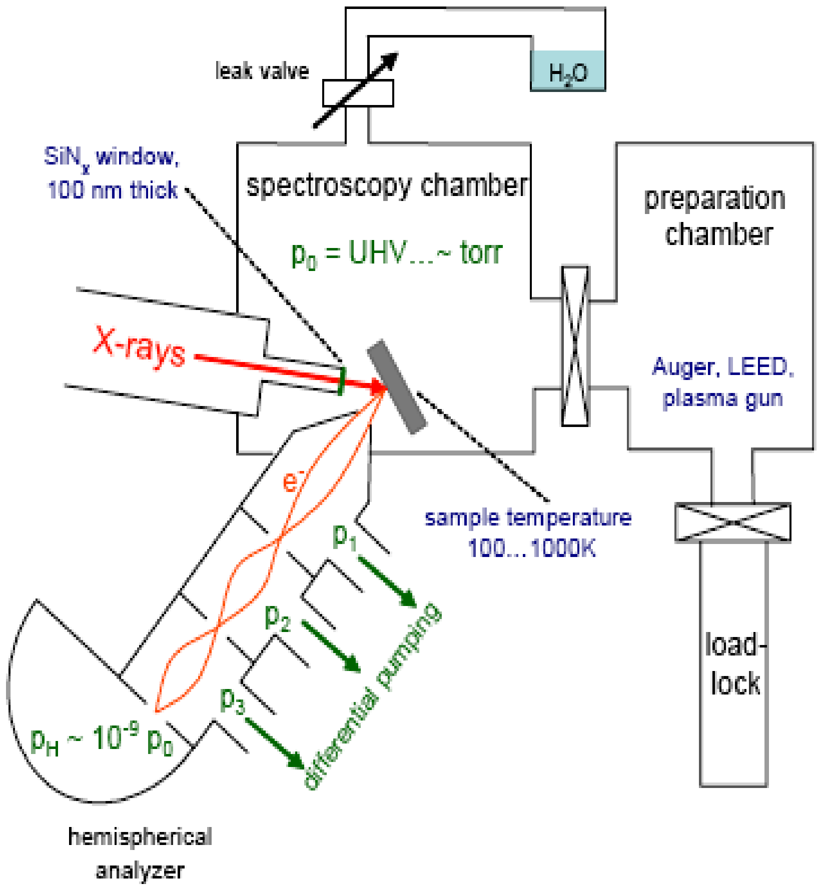


Pyrite thin films on the Si substrate



The pyrite nanowires were formed on Si substrate instead of forming pyrite thin films.

Setup of Ambient Pressure XPS



Adjustable experimental conditions:

- **Adding H_2O vapor up to a few torr.**
- **Lower down temperature (~-20 degrees) for the sample (change humidity)**
- **Rise up temperature (~1000 degrees) for the sample.**

Bluhm et al, *Journal of Electron Spectroscopy and Related Phenomena* ***2006, 150, 86***

Salmeron et al, *Surface Science Reports* ***2008, 63, 169.***

Conclusion

- Pyrite thin films on the glass
  - **Na migrates to the surface of the pyrite thin films on the glass.**

  - **Ar sputtering is NOT a good way to remove the oxide layer due to sulfur preferential sputtering.**

- Pyrite thin films on the quartz
  - **The oxidation layers on the surface can be removed by the mixed acid but we still don't know when the oxide layer will be saturated.**

- Pyrite thin films on the Si substrate
  - **Using Synchrotron radiation, three sulfur surface chemical states can been revealed and the component, S^{-2}, is the most liable to oxidize.**

Acknowledgements

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- **Funding Sources**