Surface and Electronic Structure Study of Substrate-dependent Pyrite Thin Films

Talk Outline

- **Stoichiometry and sodium study of pyrite thin films: Quick Review**
- Surface structure of pyrite thin films
- Electronic structure of pyrite thin films

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August 25, 2011

UCI center for solar energy
SCHOOL OF PHYSICAL SCIENCES

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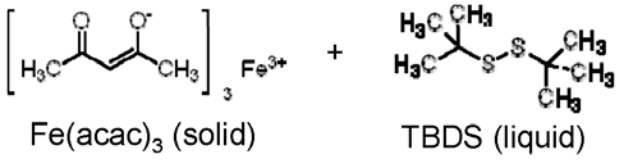
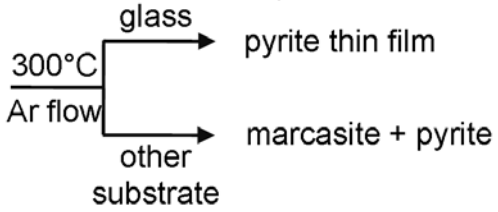
Pyrite Thin Films Grown by MOCVD

- Substrates: Si, Glass
- Ar Carrier Gas or Ar/H_2 Mixtures
- Temperature: 300~350°C
- Precursors:



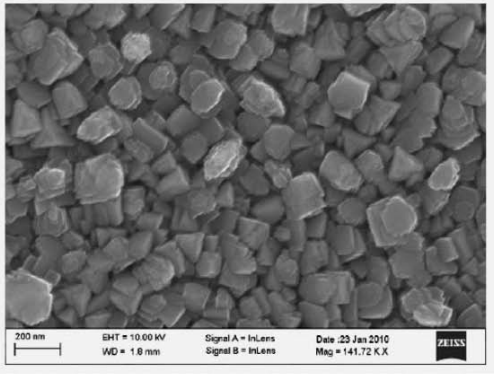


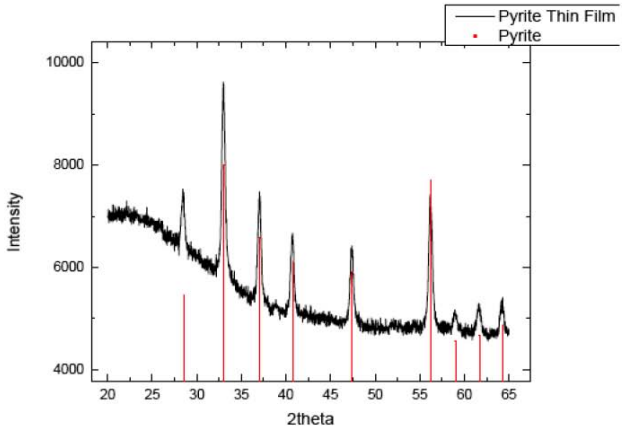
- Annealing in Elemental Sulfur above 450°C

Built by Nicholas Berry

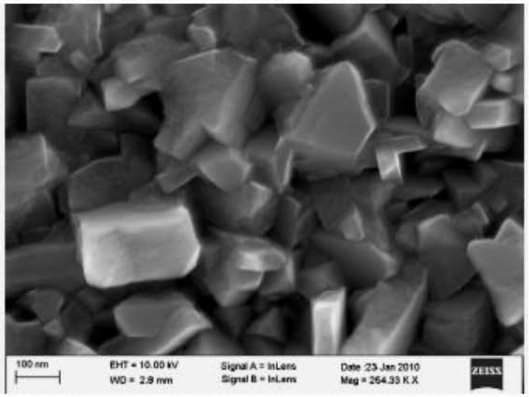
Why Glass works?!

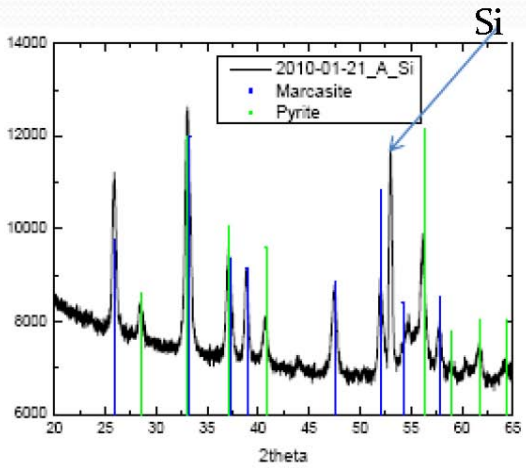
• Pyrite on glass





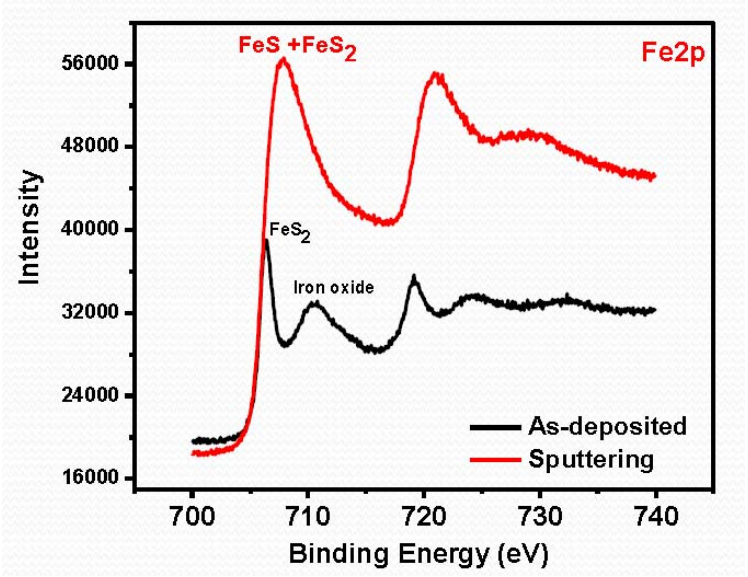
• Pyrite on Si

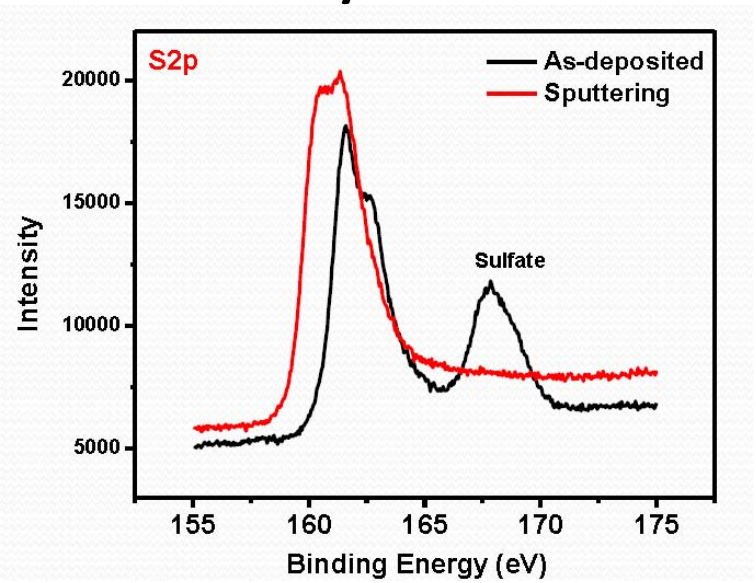


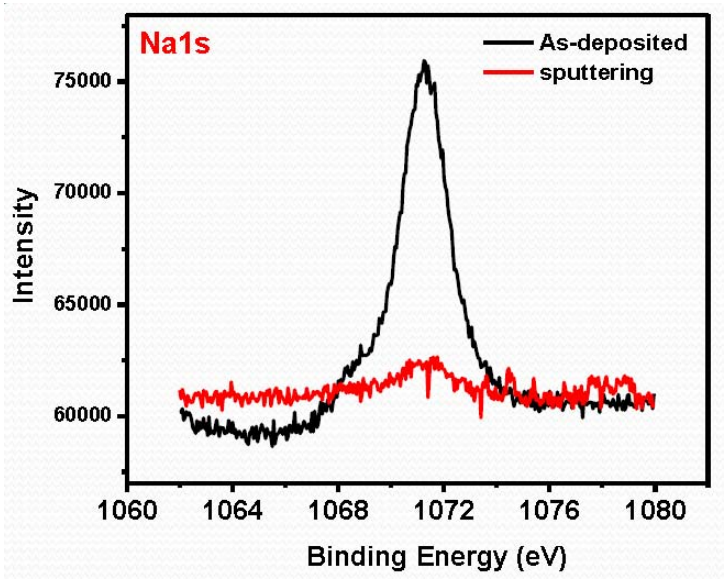


Law Research Group

Sodium on the Surface of Pyrite on Glass





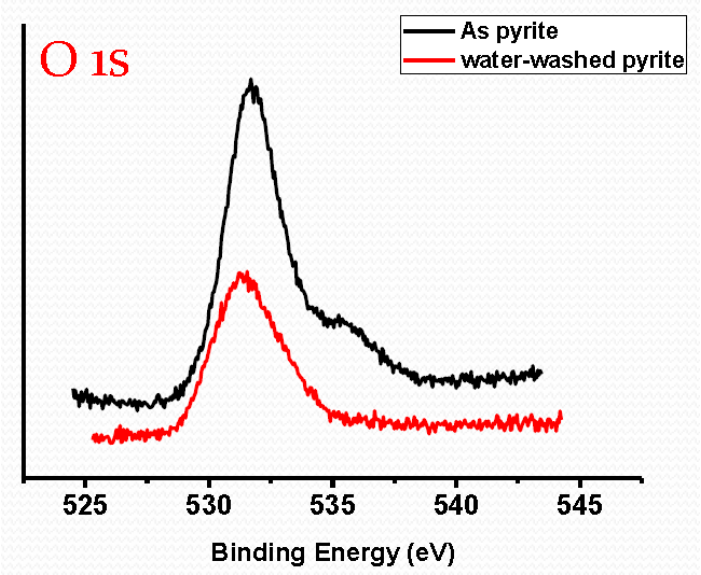


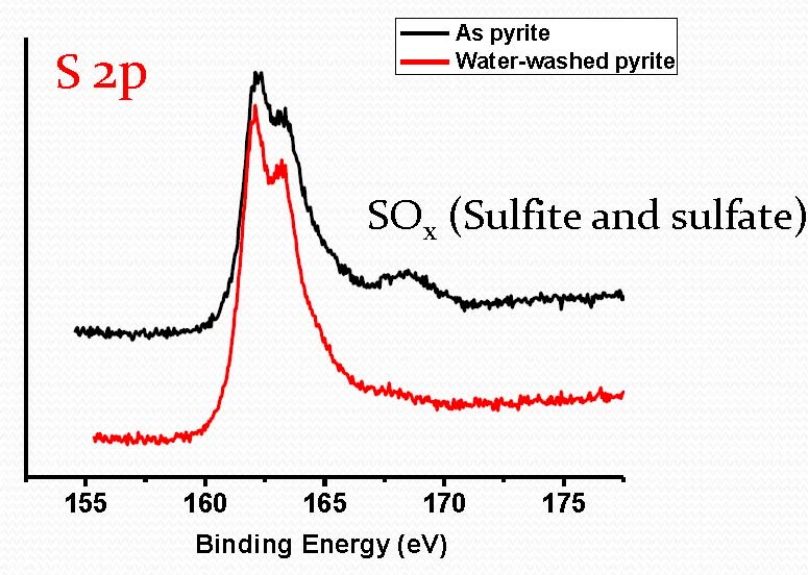
- **Na only exists on the surface**
(Na is removed by Ar Sputtering)

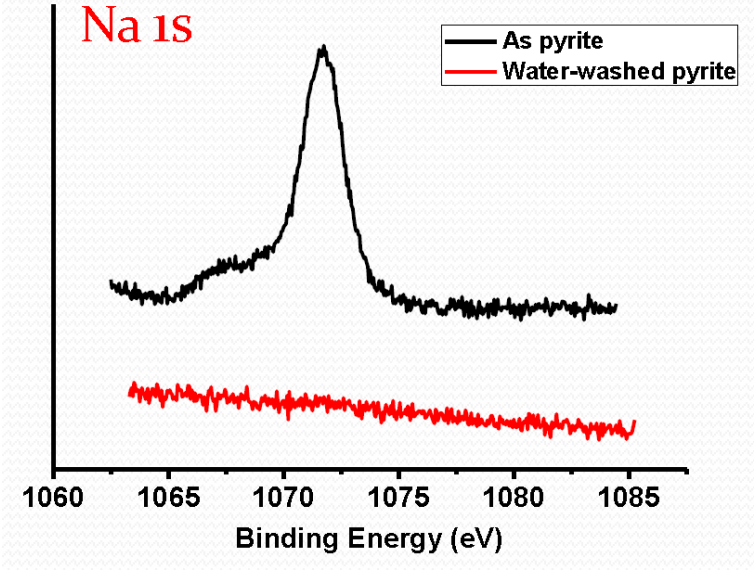
- **Sulfur preferential sputtering**
(shown by the broadening of Fe-2p and S-2p peaks)

Where does Na come from?

Water Effect of Pyrite on Glass



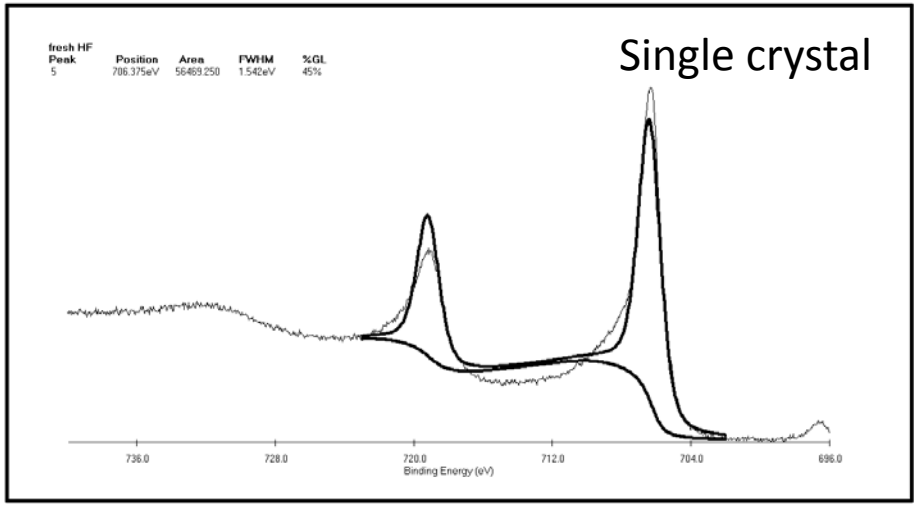


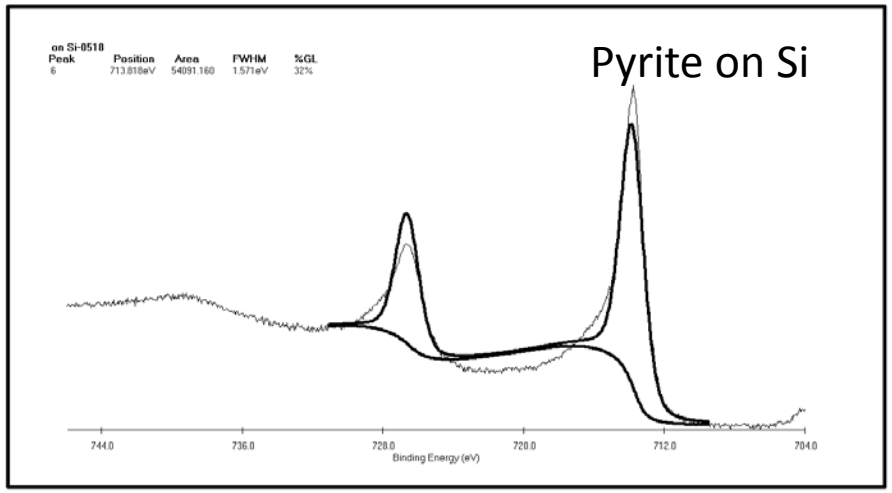


Water remove Na
from the surface of pyrite on glass

Na-1s fitting

Stoichiometry of Pyrite Thin Films





Sample	Area(%)			stoichiometry
	Fe-2p	S-2p	S/Fe	
Fresh HF single crystal (From Moriz samples)	56469	27076	0.48	**2**
pyrite on Si-05182011	54091	26625	0.49	**2.04**

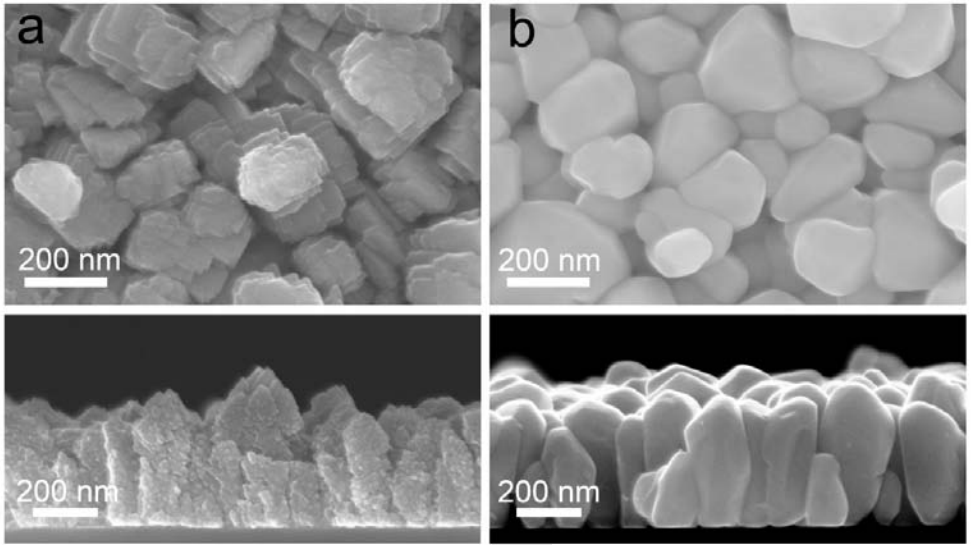
Atomic Sensitivity Factor: 4.17
(Lab XPS, Irvine)

Polished pyrite single crystal
with HF cleaning
or HF:AA:HNO3 (1:1:2) cleaning
Raw Data

Moritz, Law Research Group

Pyrite on Glass with and w/o Annealing

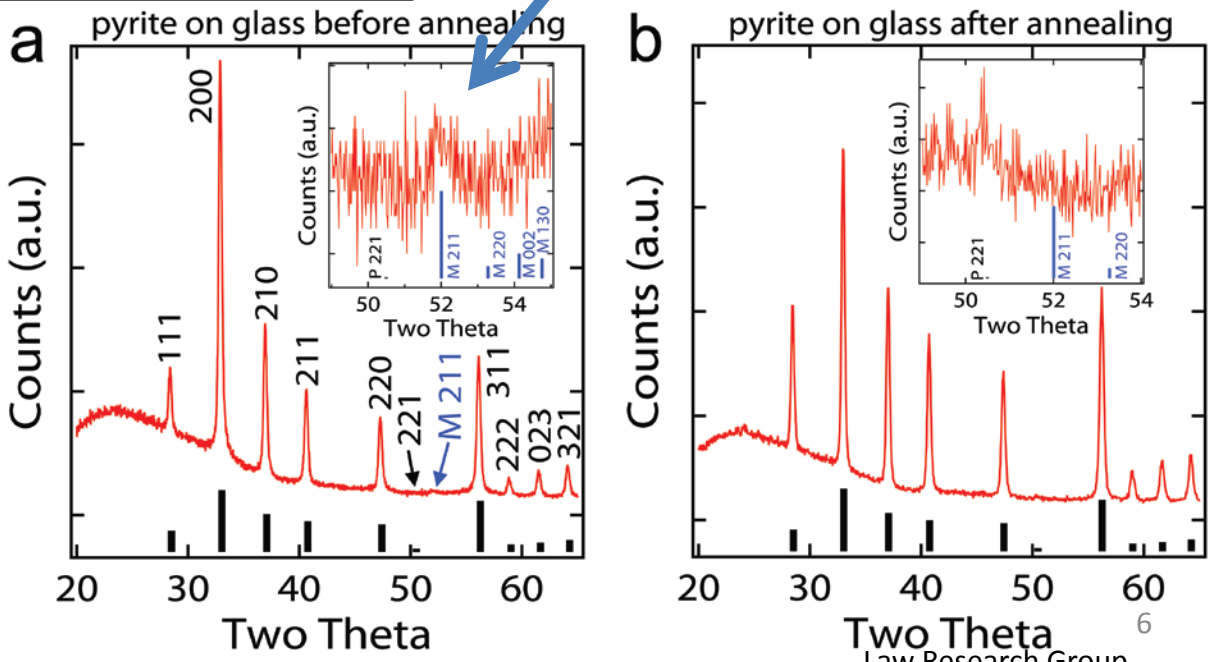
Pyrite on Glass- Before and After Annealing



Band Gap
Pyrite**: 0.95 eV** indirect transition
Pyrite: **1.03 eV** for direct transition
Marcasite **0.34eV**

Marcasite

XRD+XPS
High quality pyrite thin films



Surface Study of Pyrite Thin Films with Different Chemical Treatments

Talk Outline

- Stoichiometry and sodium study of pyrite thin films
- **Surface structure of pyrite thin films**
- Electronic structure of pyrite thin films

Photoelectric Current Reducing

Impurities?!

Defects?!

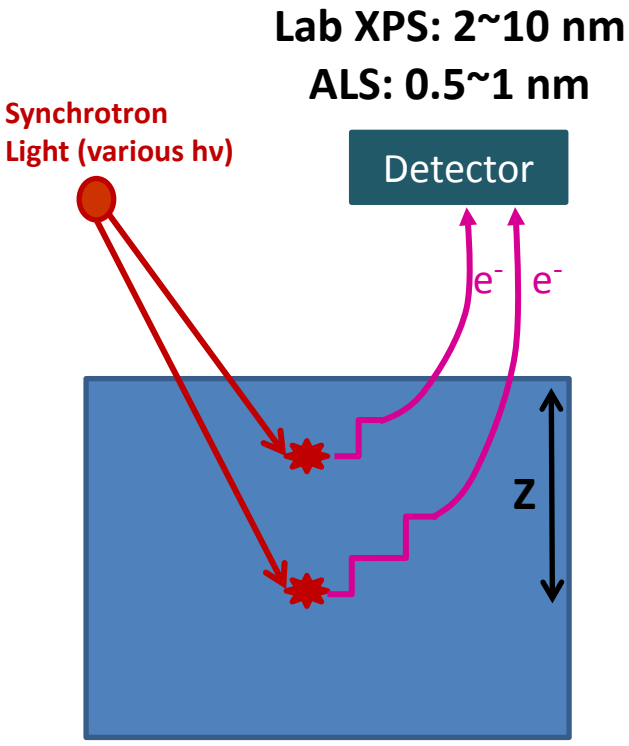
Distortion Effect?!

Crystal Phase?!

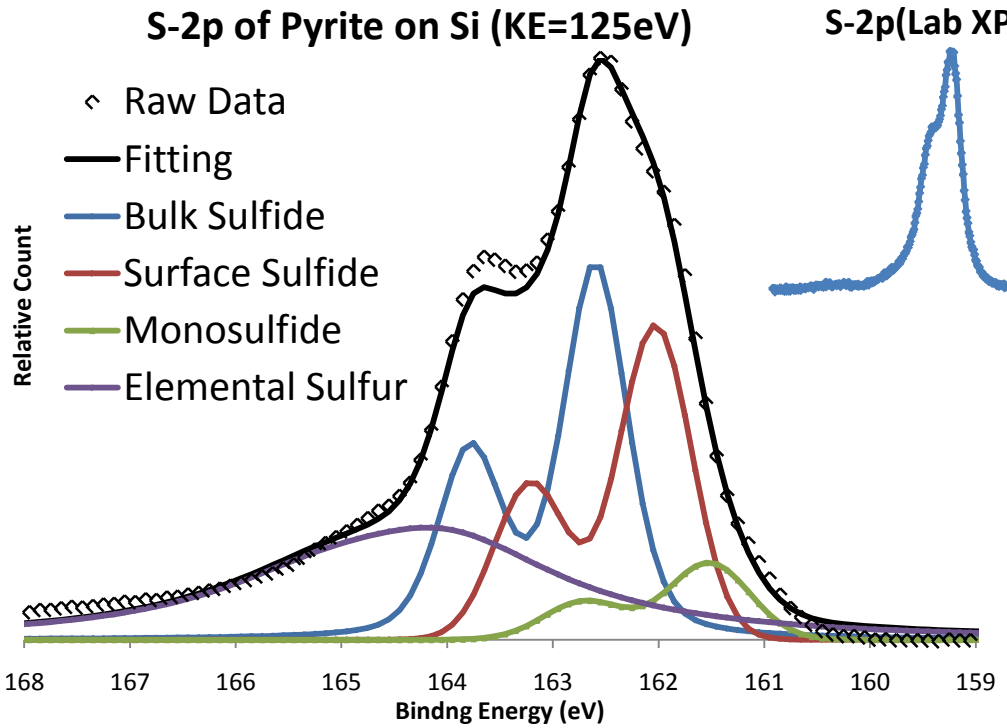
Synchrotron Light Source: continuous tunable

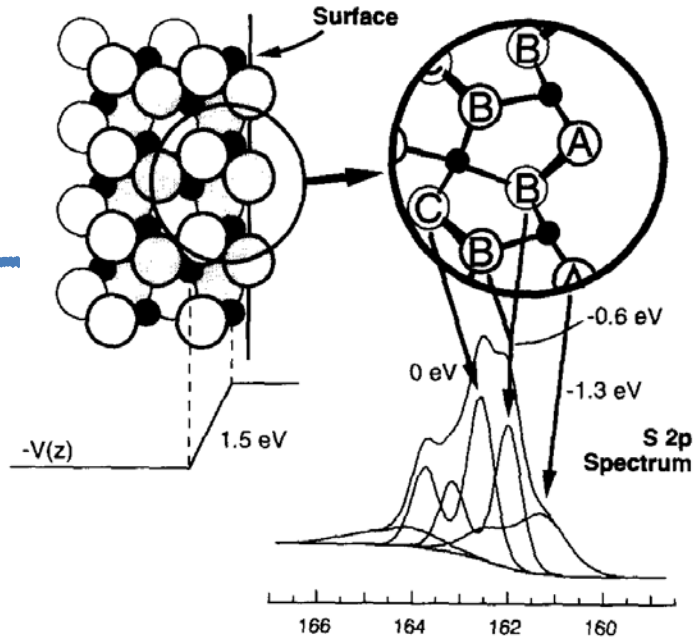
Substrate-Dependent Pyrite Thin Films

- Pyrite on Si with Elemental Sulfur Annealing
- Pyrite on Glass without Annealing
- Pyrite on Glass with Elemental Sulfur Annealing



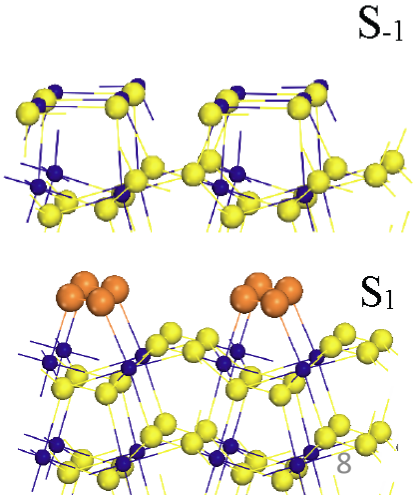
Surface Structure of Pyrite Thin Films



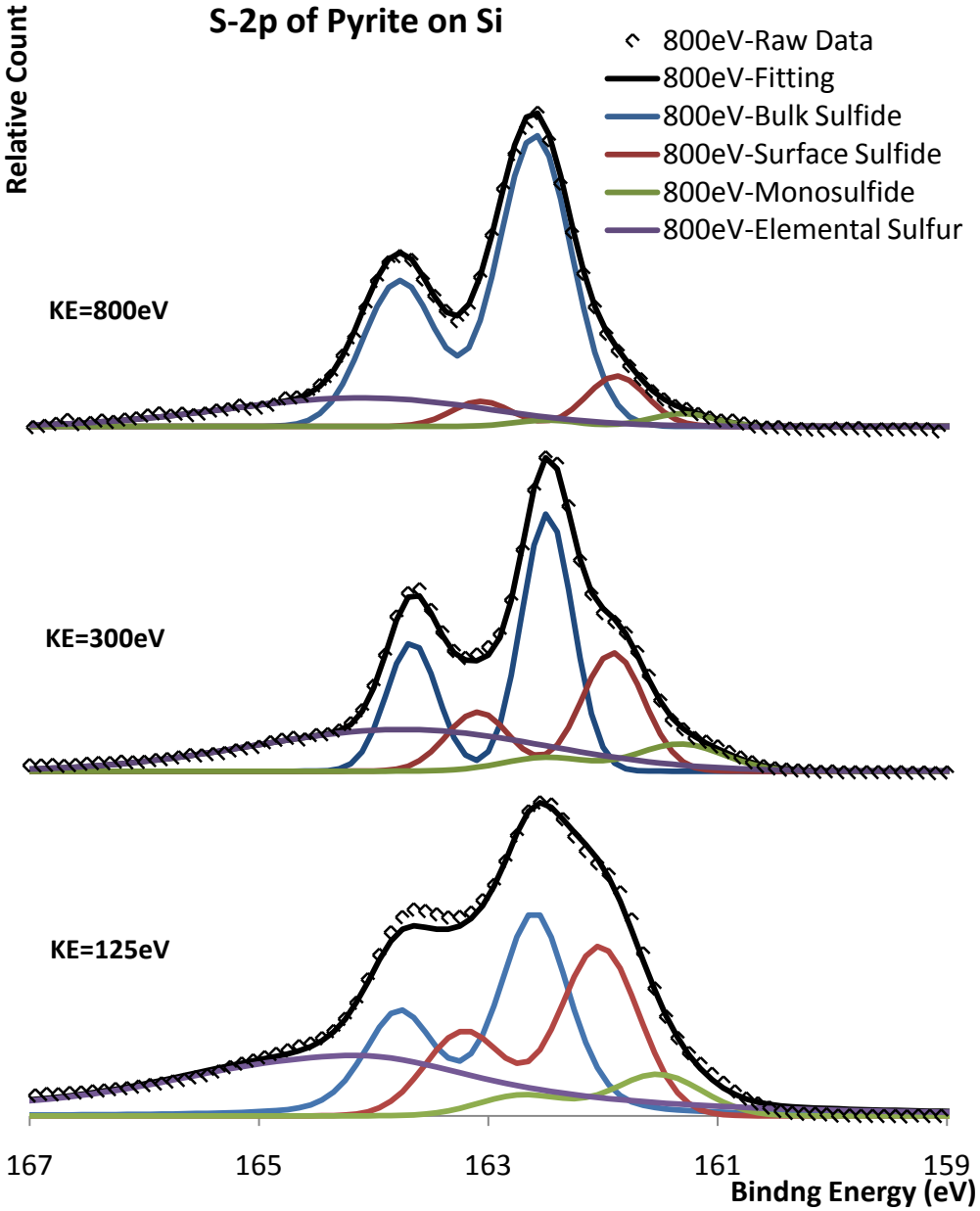


M. Bronold et al. *Surf. Sci. Lett.* 314 (1994), pp. L931–L936

Collected Kinetic Energy (eV)	S 2p	BE (eV)	Area(%)	Note
125 (~5Å)	Bulk Sulfide	162.62	26.0	FeS_2 (FCC)
	Surface Sulfide	162.01	25.9	Edge, loss one S
	Monosulfide	161.26	11.5	S^{2-}
	Elemental Sulfur	164.14	36.6	
Binding Energy Calibrated by Au 4f				



Depth Profile of Pyrite on Silicon



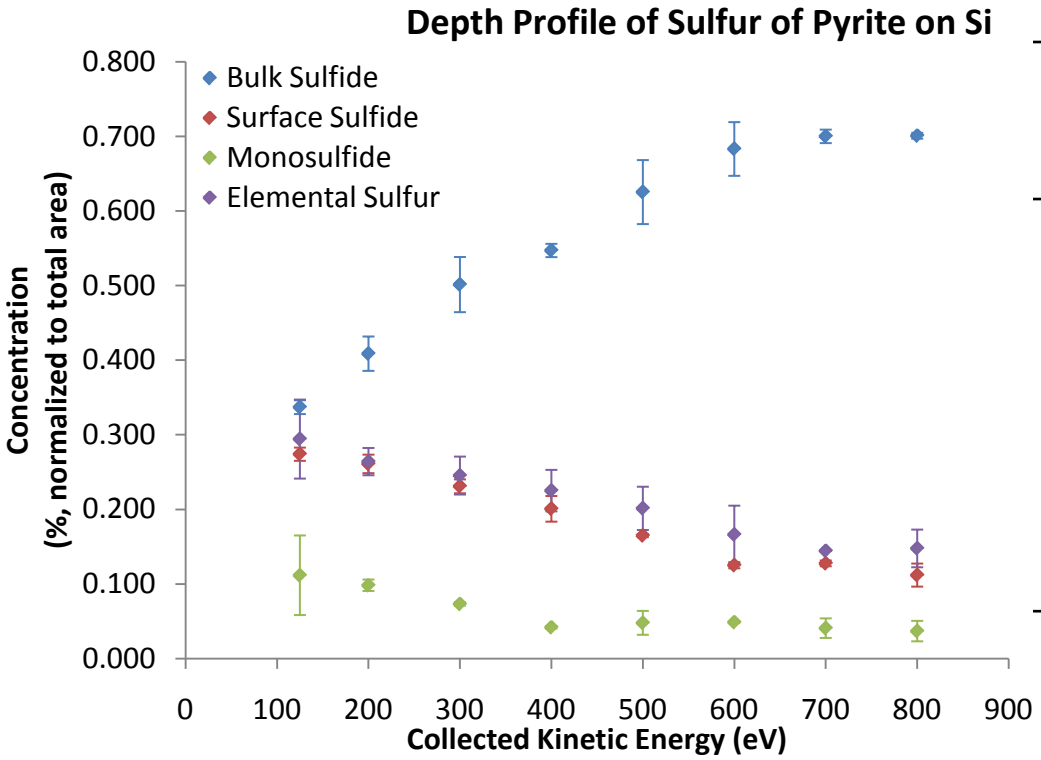
Collected Kinetic Energy (eV)	S 2p		
		BE (eV)	Area(%)
800 (~14Å)	Bulk Sulfide	162.59	70.1
	Surface Sulfide	161.83	11.2
	Monosulfide	161.16	3.7
	Elemental Sulfur	163.80	14.8
300 (~7Å)	Bulk Sulfide	162.49	50.1
	Surface Sulfide	161.91	23.1
	Monosulfide	161.32	7.3
	Elemental Sulfur	163.42	24.5
125 (~5Å)	Bulk Sulfide	162.60	33.7
	Surface Sulfide	162.03	27.4
	Monosulfide	161.52	11.2
	Elemental Sulfur	163.98	29.4

Binding Energy Calibrated by Au 4f

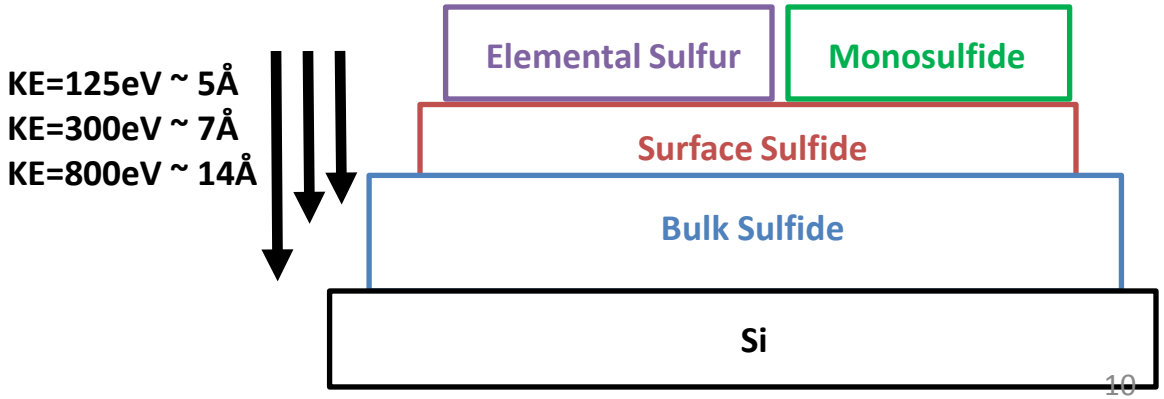
Electron Inelastic Mean Free Path

Lab XPS: 2 nm
ALS: 0.5~1.4 nm

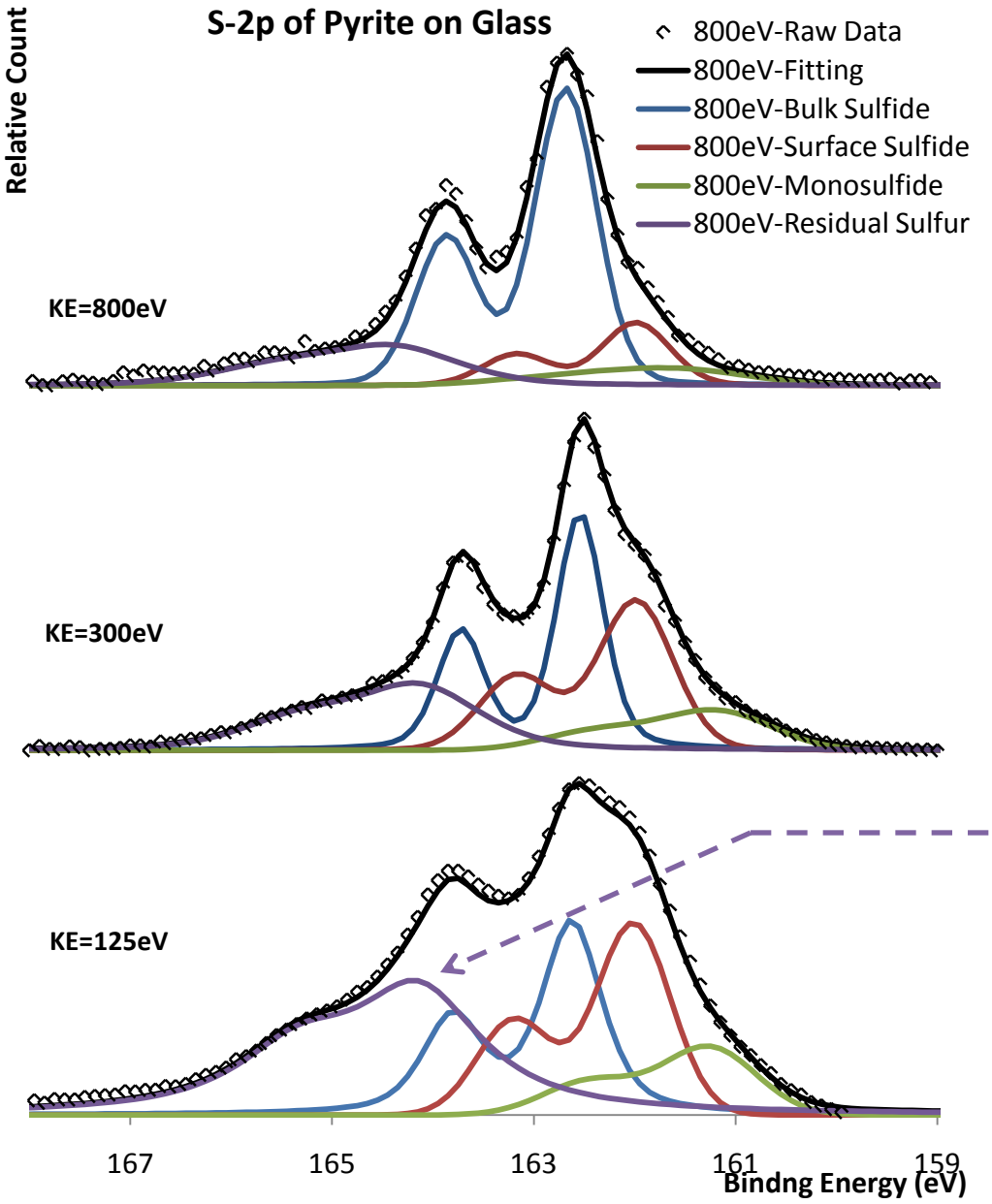
Depth Profile of Pyrite on Silicon



Collected Kinetic Energy (eV)	Concentration (%)			
	Bulk Sulfide	Surface Sulfide	Monosulfide	Elemental Sulfur
800	70.1	11.2	3.7	14.8
700	70.0	12.8	4.1	14.4
600	68.3	12.5	4.9	16.6
500	62.5	16.5	4.8	20.1
400	54.7	20.1	4.2	22.5
300	50.1	23.1	7.3	24.5
200	40.9	26.1	9.8	26.4
125	33.7	27.4	11.2	29.4



Depth Profile of Pyrite on Glass

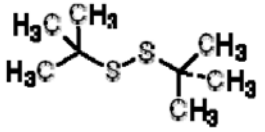


Collected Kinetic Energy (eV)	S 2p		
		BE (eV)	Area(%)
800	Bulk Sulfide	162.68	62.0
	Surface Sulfide	161.99	14.2
	Monosulfide	161.56	7.0
	Residual Sulfur	164.38	16.8
300	Bulk Sulfide	162.54	34.7
	Surface Sulfide	161.99	31.2
	Monosulfide	161.18	11.5
	Residual Sulfur	164.13	22.7
125	Bulk Sulfide	162.62	26.0
	Surface Sulfide	162.01	25.9
	Monosulfide	161.26	11.5
	Residual Sulfur	164.14	36.6
Binding Energy Calibrated by Au 4f			

Higher Binding Energy Species:

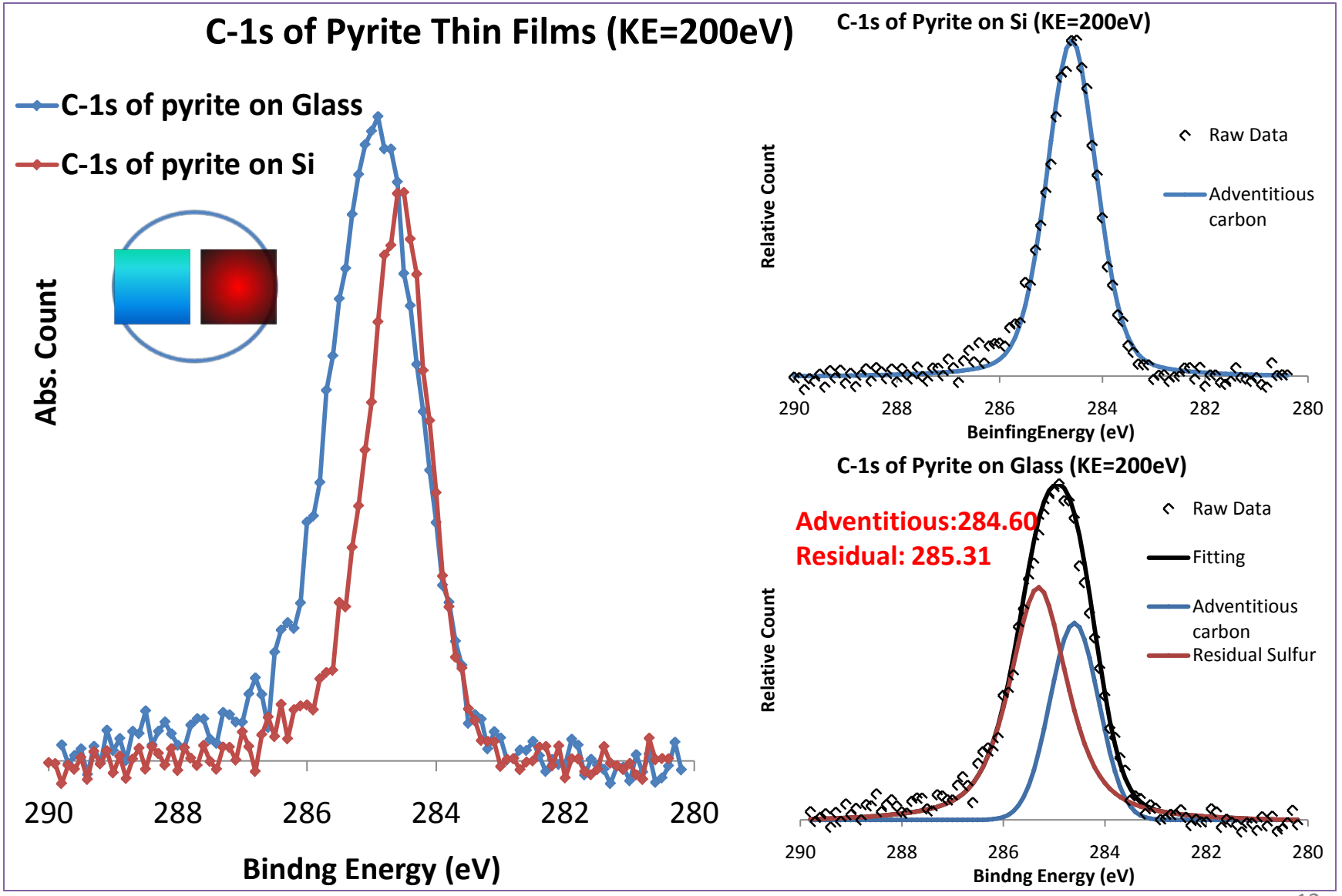
Residual Sulfur?!

Elemental Sulfur?!

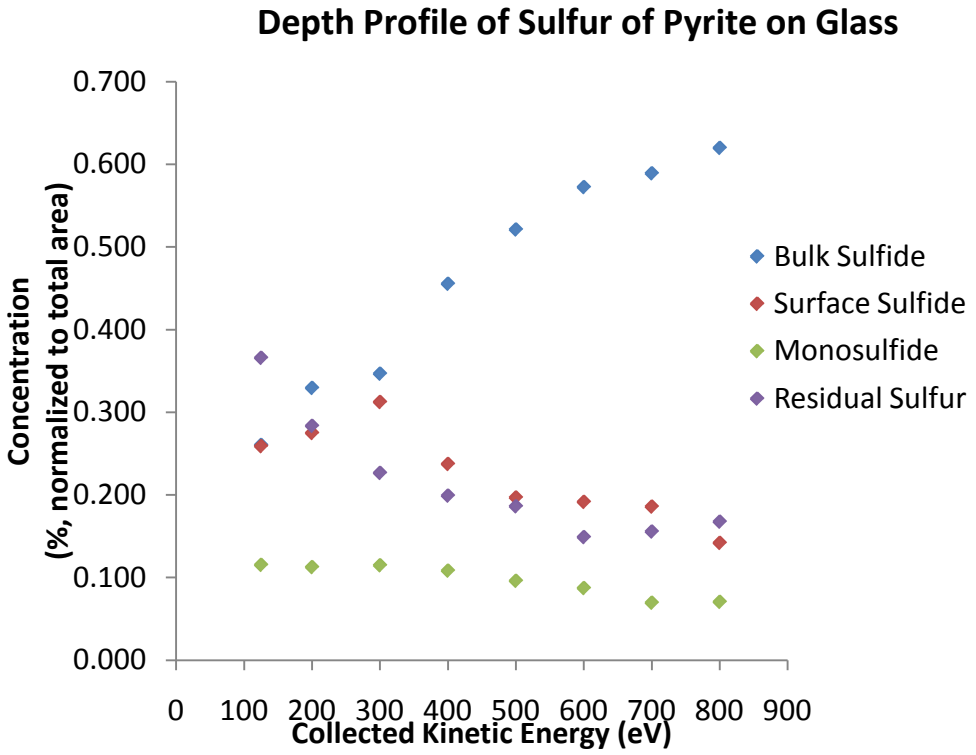


TBDS (liquid)

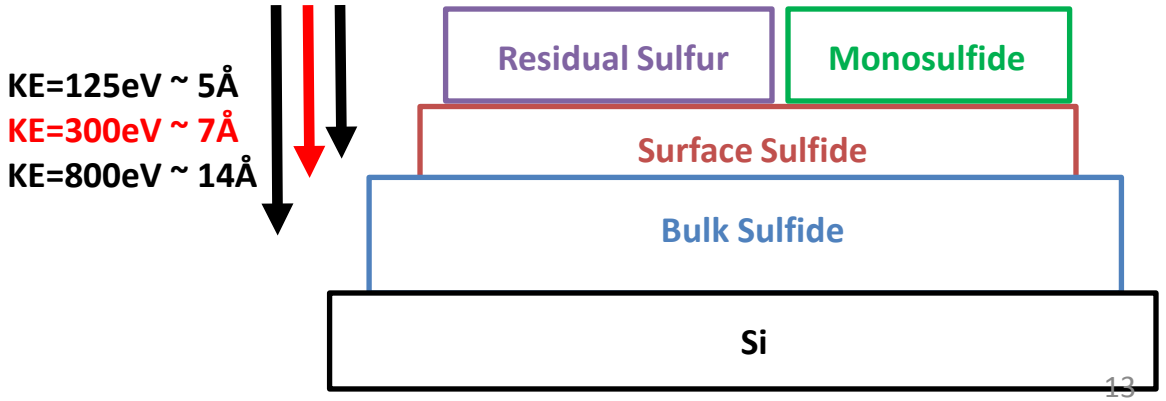
C-1s Spectra of Pyrite on Si and Glass



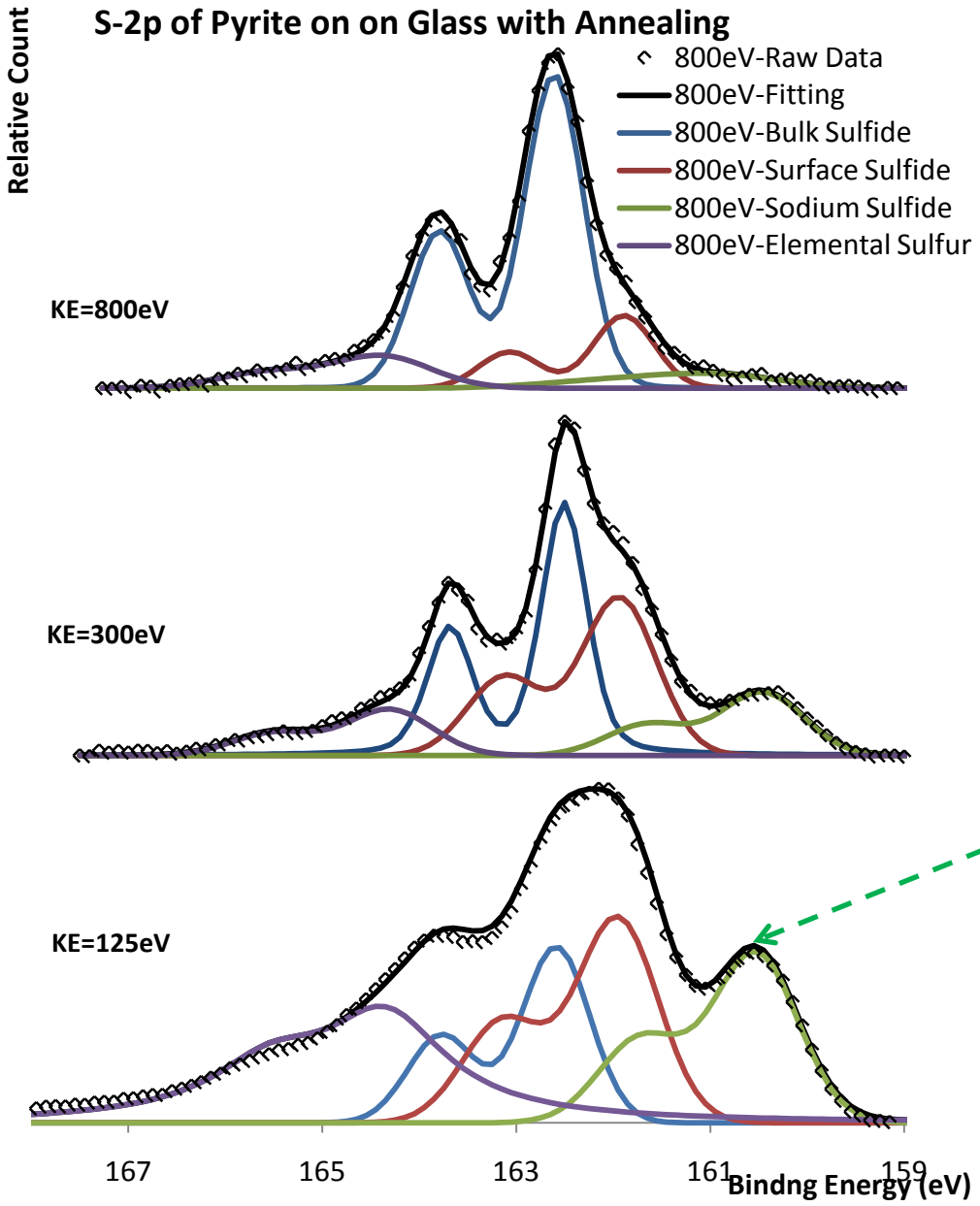
Depth Profile of Pyrite on Glass



Collected Kinetic Energy (eV)	Concentration (%)			
	Bulk Sulfide	Surface Sulfide	Monosulfide	Residual Sulfur
800	62.0	14.2	7.0	16.8
700	58.9	18.6	6.9	15.6
600	57.2	19.2	8.7	14.9
500	52.1	19.7	9.6	18.6
400	45.5	23.7	10.8	19.9
300	34.7	**31.2**	11.5	22.7
200	32.9	27.5	11.2	28.3
125	26.0	25.9	11.5	36.6



Depth Profile of Pyrite on Glass w/ Annealing

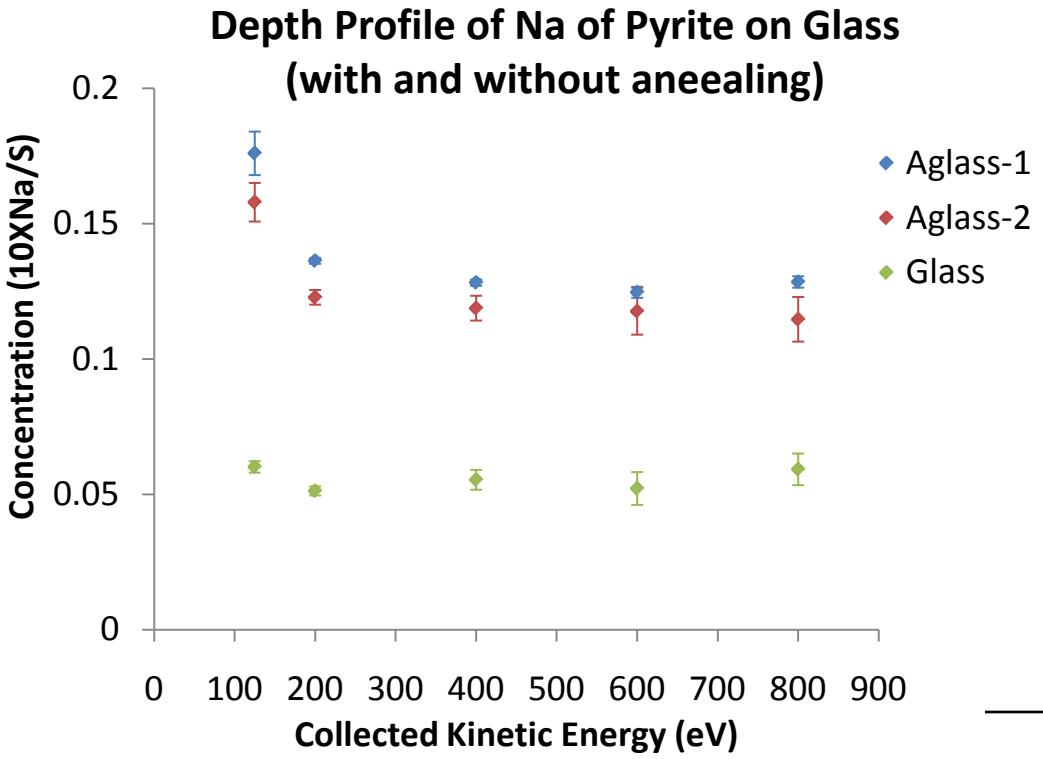


Collected Kinetic Energy (eV)	S 2p		
		BE (eV)	Area(%)
800	Bulk Sulfide	162.60	67.4
	Surface Sulfide	161.86	17.0
	Sodium Sulfide	160.94	4.9
	Elemental Sulfur	164.44	10.7
300	Bulk Sulfide	162.51	35.5
	Surface Sulfide	161.96	36.7
	Sodium Sulfide	160.46	15.2
	Elemental Sulfur	164.32	12.6
125	Bulk Sulfide	162.59	18.6
	Surface Sulfide	161.96	29.9
	Sodium Sulfide	160.53	23.5
	Elemental Sulfur	164.35	28.0
Binding Energy Calibrated by Au 4f			

Lower Binding Energy Species:
Sodium Sulfide 160.53eV ?!
Monosulfide 161.50eV ?!

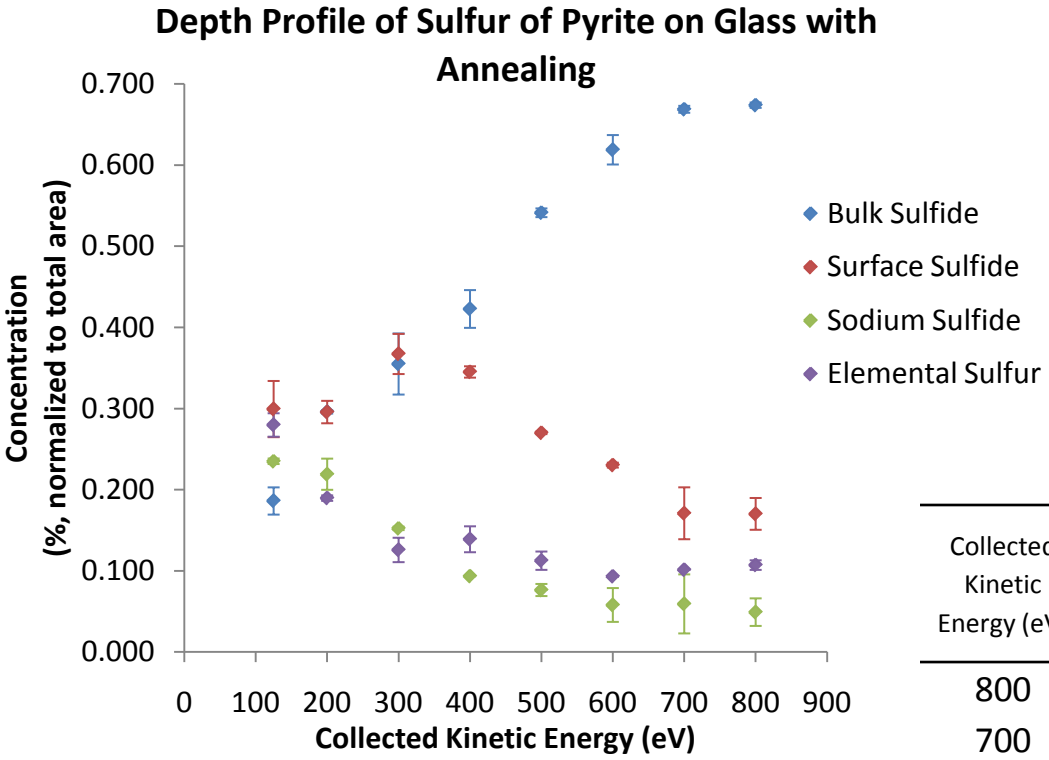
Lab XPS: 2 nm
ALS: 0.5~1.4 nm

Depth Profile of Pyrite on Glass w/ Annealing



Collected Kinetic Energy (eV)	Concentration (Na 2s/ S 2p) AGlass-1 (X10)	AGlass-2 (X10)	Glass (X10)
800	0.128	0.115	0.059
600	0.125	0.118	0.052
400	0.128	0.119	0.055
200	0.136	0.123	0.051
125	**0.176**	**0.158**	**0.060**

Depth Profile of Pyrite on Glass w/ Annealing



Collected Kinetic Energy (eV)	Concentration (%)			
	Bulk Sulfide	Surface Sulfide	Sodium Sulfide	Elemental Sulfur
800	67.4	17.0	4.9	10.7
700	66.9	17.1	5.9	10.1
600	61.9	23.0	5.8	9.3
500	54.1	27.0	7.6	11.2
400	42.3	34.5	9.3	13.9
300	35.5	**36.7**	15.2	12.6
200	29.6	29.6	21.9	19.0
125	18.6	29.9	23.5	28.0

Surface Study of Pyrite Thin Films with Different Chemical Treatments

Talk Outline

- Stoichiometry and sodium study of pyrite thin films
- **Surface structure of pyrite thin films**
- Electronic structure of pyrite thin films

Lab XPS: 2~10 nm
ALS: 0.5~1 nm

Short Summary

- Surface chemical composition and stoichiometry (Lab XPS)
- Sulfur defects and the elemental composition depth profiles (ALS)

Electronic Structure Study of Pyrite Thin Films

Talk Outline

- Stoichiometry and sodium study of pyrite thin films
- Surface structure of pyrite thin films
- **Electronic structure of pyrite thin films**

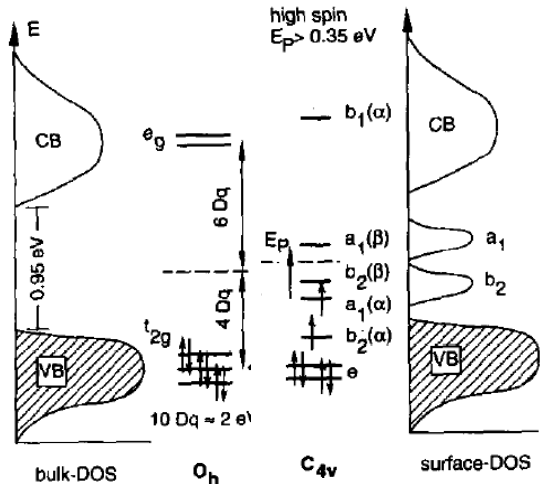
Photoelectric Current Reducing

Impurities?!

Defects?!

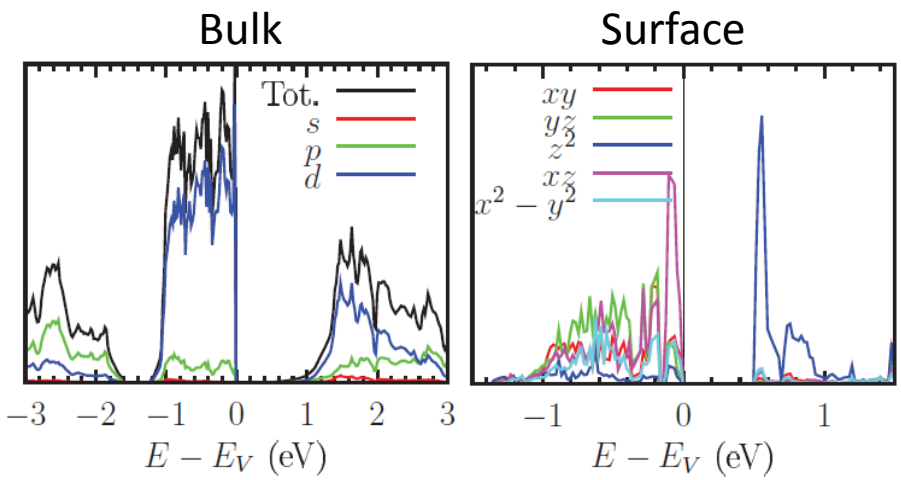
Distortion Effect?!

Crystal Phase?!

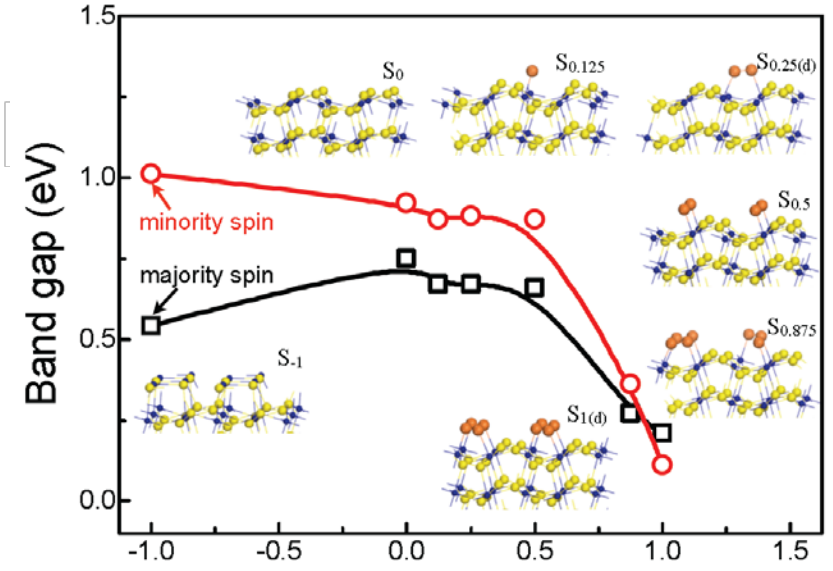


M. Bronold et al. *Surf. Sci. Lett.* 314 (1994), pp. L931–L936

CB tail: 0.4 eV above the VB edge

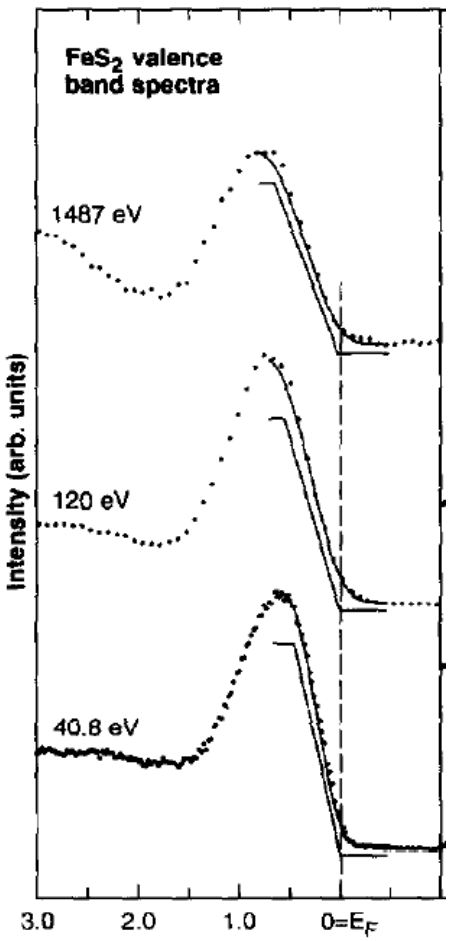


MIT group, Physical Review B 83, 235311 (2011)



Yanning Zhang, Ruqian Wu

Band Gap Estimation of Pyrite on Thin Films



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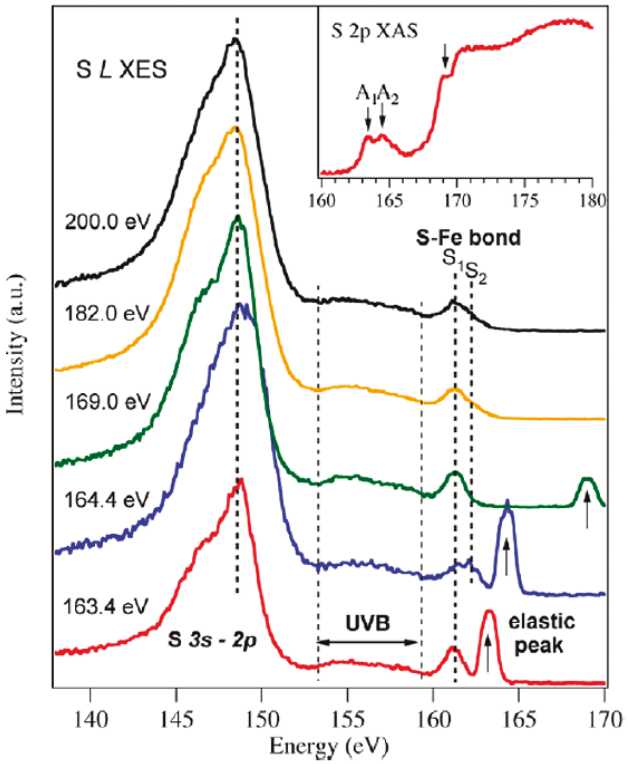

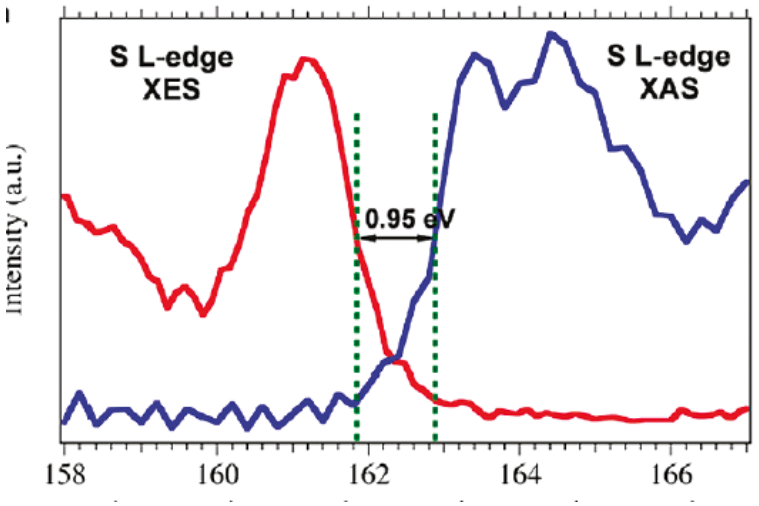

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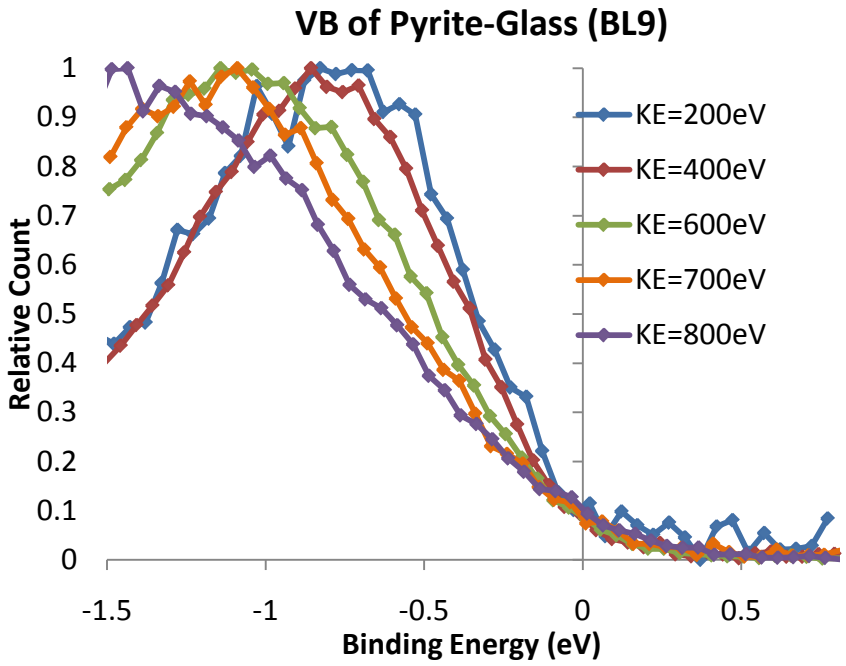
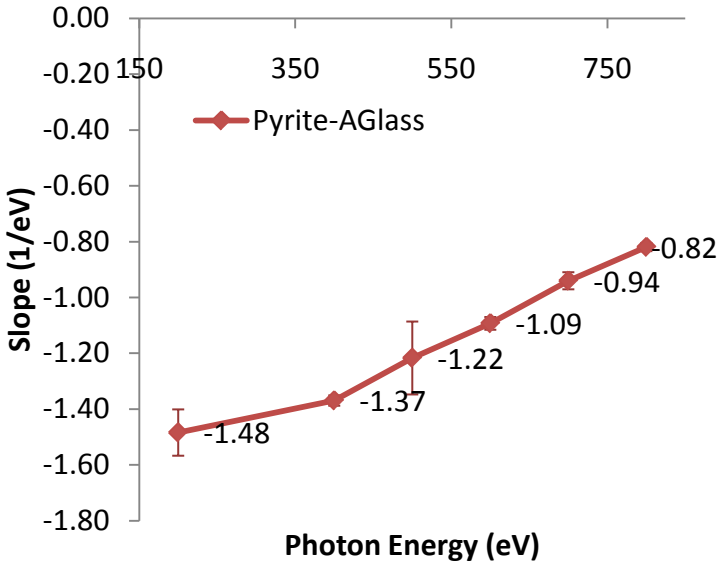
- VB only
- XAS + XES
  (S L-edge Spectrum only)

- VB only
- **XAS with XPS + VB**
  (both Fe and S L-edge Spectra)

Density of State of Valence Band





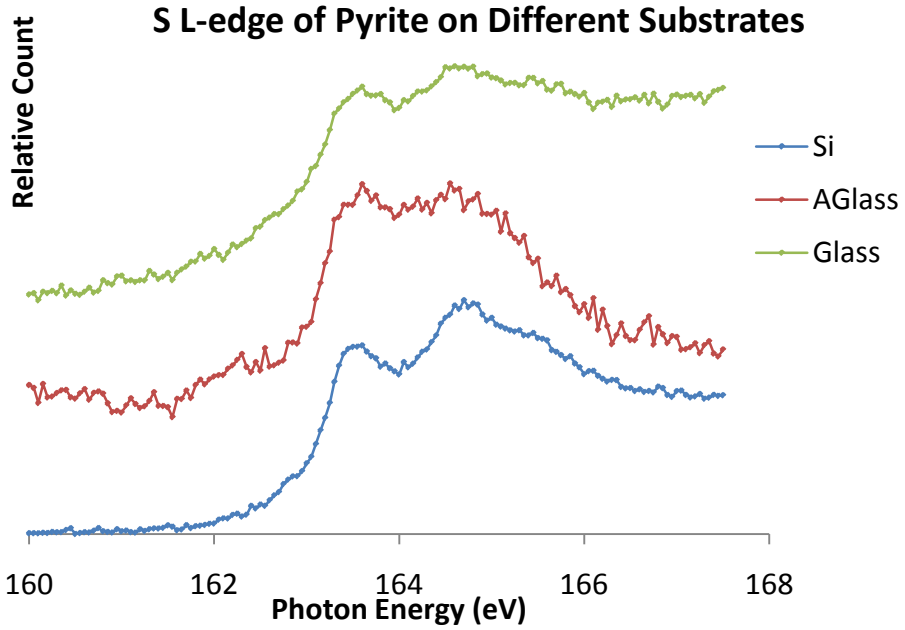
Bulk Band Gap
0.95 eV indirect transition
1.03 eV for direct transition

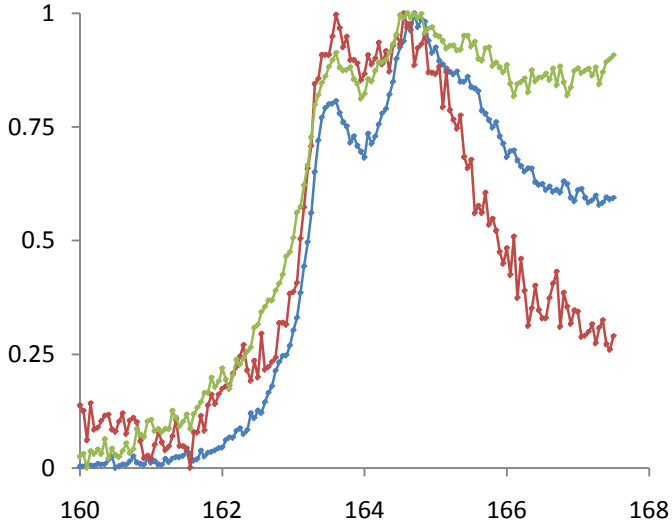
Surface Band Gap
0.3~0.5 eV

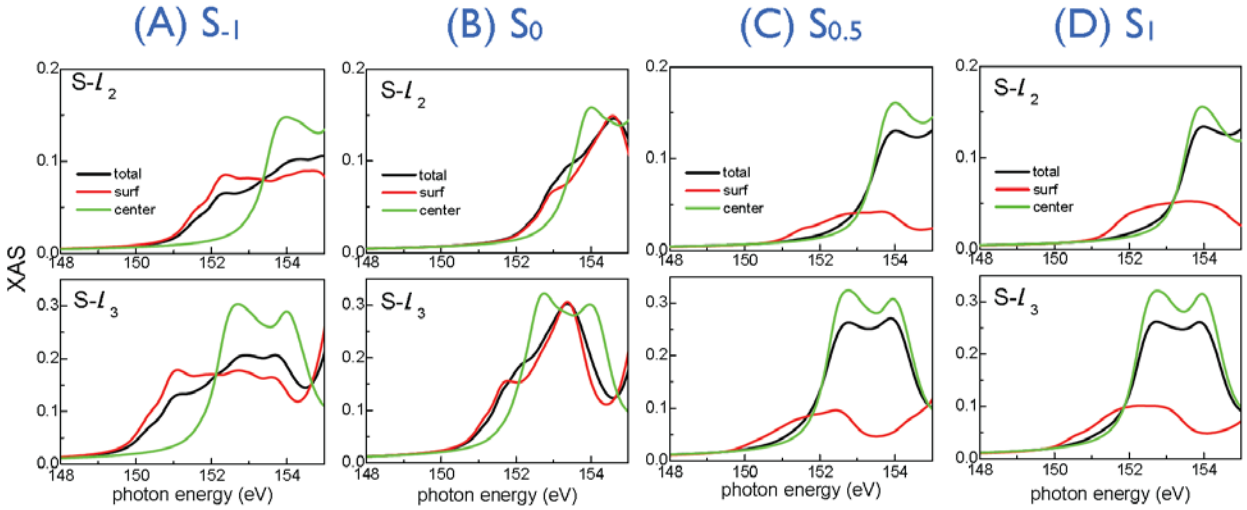
Substrates:
Si, Glass, Glass with annealing

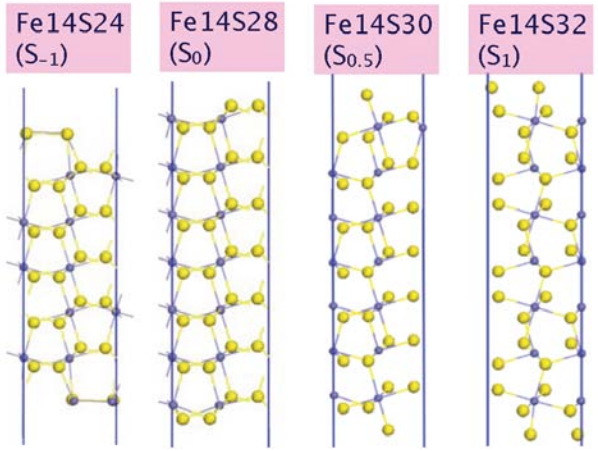
Collected Kinetic Energy (eV)	Slope (1/eV) AGlass-AVG	Silicon	Glass
200	-1.48		
240			
400	-1.37	-1.49	-1.55
500	-1.22	-1.44	-1.34
600	-1.09	-1.18	-1.17
700	-0.94	-0.86	-0.74
800	-0.82		

Density of State of Conduction Band









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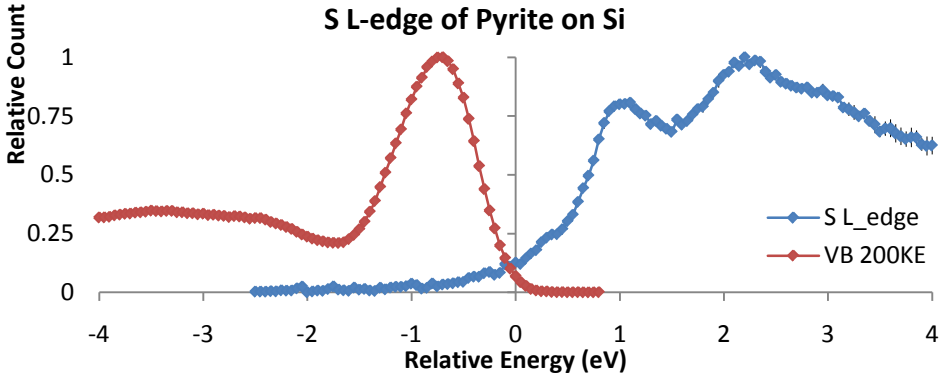
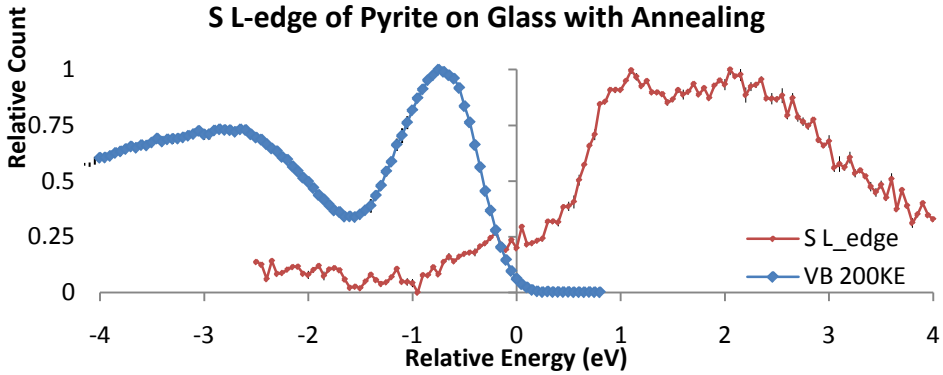
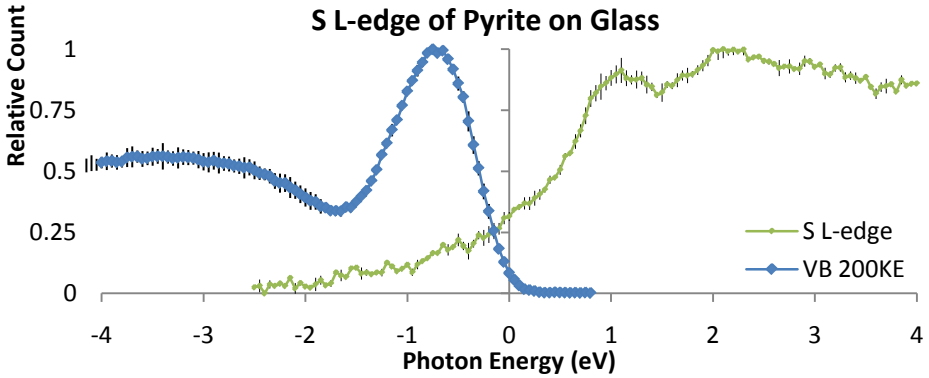
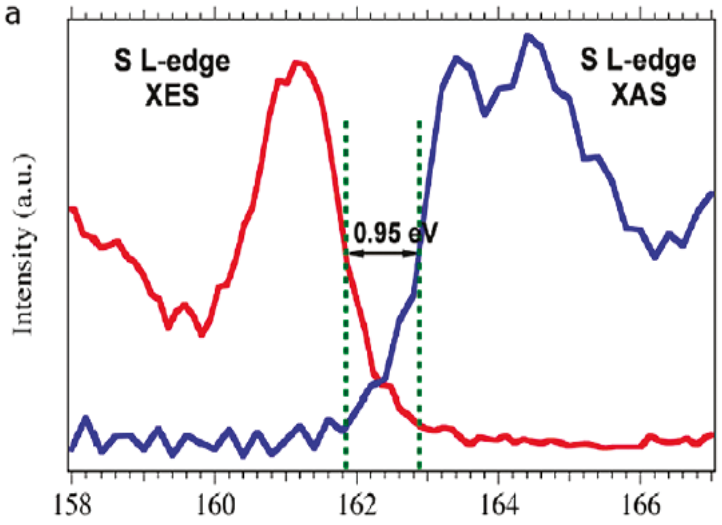
Band Gap Estimation of Pyrite on Thin Films







Band Gap Estimations	Pyrite Thin Films		
	Silicon	AGlass	Glass
$\Delta_{\text{half-half}}$ S-Ledge+VB	1.10	0.86	0.90
Δ VB only	0.90	0.95	0.90



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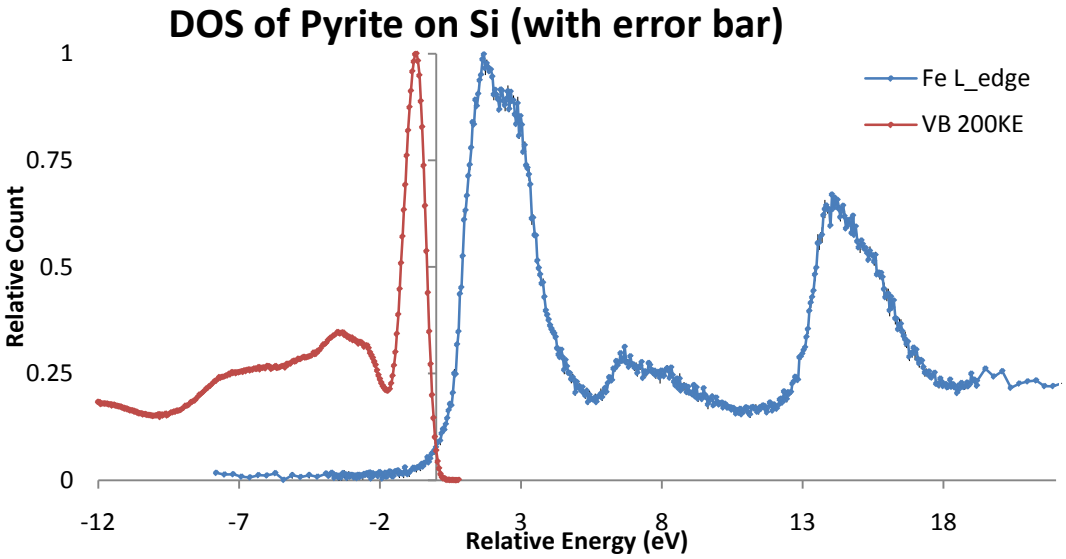
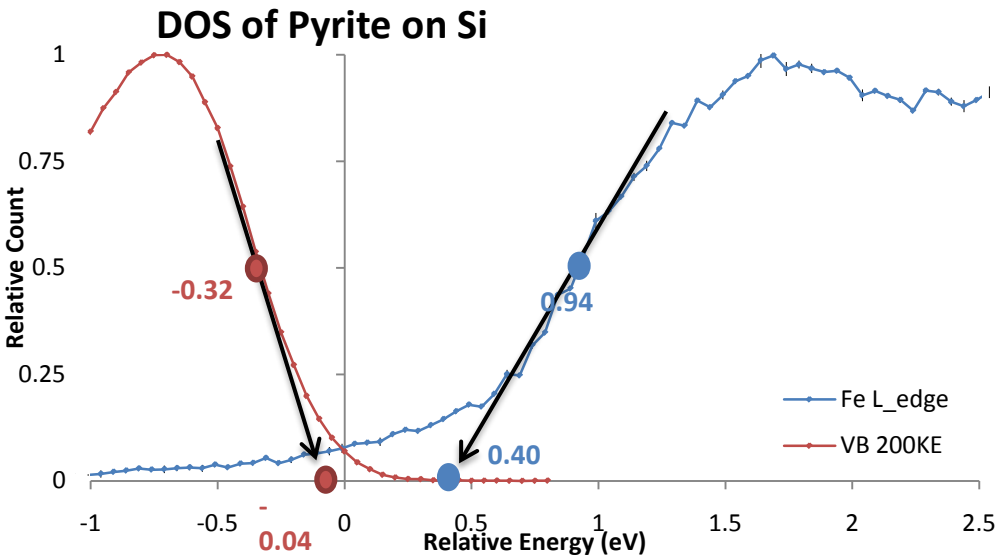
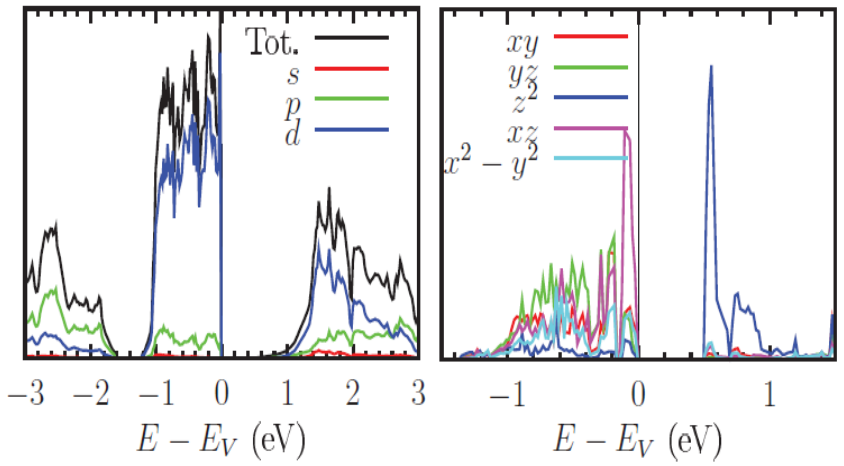
Band Gap Estimation of Pyrite on Thin Films





Band Gap Estimations	Pyrite Thin Films		
	Silicon	AGlass	Glass
$\Delta_{half\text{-}half}$ S-Ledge+VB	1.10	0.86	0.90
Δ VB only	0.90	0.95	0.90
$\Delta_{zero\text{-}zero}$ Fe L-edge+VB	0.44	0.44	0.31



MIT group, Physical Review B 83, 235311 (2011)

Summary

Surface and Electronic structures of substrate-dependent pyrite thin films grown by MOCVD

- Surface chemical composition and stoichiometry
- Sulfur defects and the elemental composition depth profiles
- Density of state of valence and conduction bands
- Band gap estimations

1. Surface Structure and Depth Profile Study of Pyrite Thin Films Grown by MOCVD
2. Depth Profile of Valence Photoemission and X-ray Absorption Study of Substrate-Dependent Pyrite Thin Films

Acknowledgements

Hemminger Group, UC Irvine

Prof. Matt Law, Prof. Ruqian Wu, Dr. Yanning Zhang, Nicholas Berry, Moritz Limpinsel, Beamline Scientist: Hendrik Bluhm (BL11), Zhi Liu (BL9)