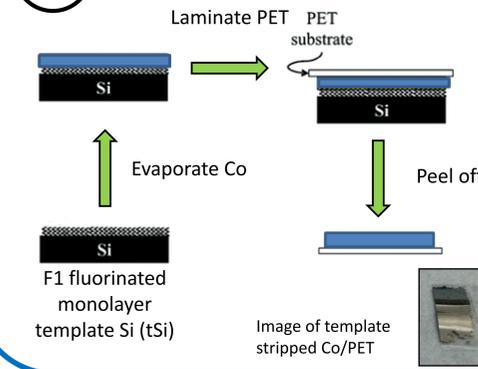


Introduction

- Cobalt containing materials used in: magnetic recording/storage, catalysis, batteries
 - Co: ferromagnetic metal with high Curie temperature, high saturation magnetization
 - Molecular layer formation on Co not well known
 - Co surface is complicated -- oxide formation, many oxide forms
 - One option: electrochemically prepare oxide-free ferromagnetic surface for molecular self-assembly (SAM)^{1,2}
- Organic materials important for next generation electronic devices
 - Organic materials in light emitting diodes, solar cells, displays
 - Phosphonic acids self-assembled onto (La,Sr)MnO₂ served as tunneling barrier^{3,4}
 - Molecule-metal electrode interface crucial for organic spintronics
- Critical metrology: characterization and control of the interface formation between organic materials and the ferromagnetic electrode

[1] S. Devillers et al., *Langmuir* **27**, 14849 – 14860 (2011).; [2] P. G. Hoertz et al., *J. Am. Chem. Soc.* **130**, 9763 – 9772 (2008).; [3] S. Tatay et al., *ACS Nano* **6**, 8753 – 8757 (2012).; [4] M. Galbiati et al., *Adv. Mater.* **24**, 6429 – 6432 (2012).

1



Template-stripped Cobalt Surfaces

2

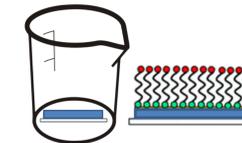
Monolayer Formation on Co

“Fruit fly” molecules:

Octadecanethiol (ODT)

Mercaptohexadecanoic acid (MHA)

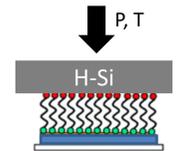
1 mmol/L in ethanol, overnight



3

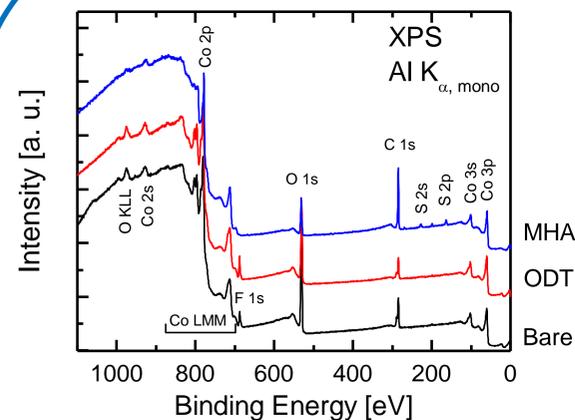
Molecular Junction Formation

- For electrical measurements
- Lamination onto H-Si (n-type, $\rho = 0.001 \Omega \cdot \text{cm}$)

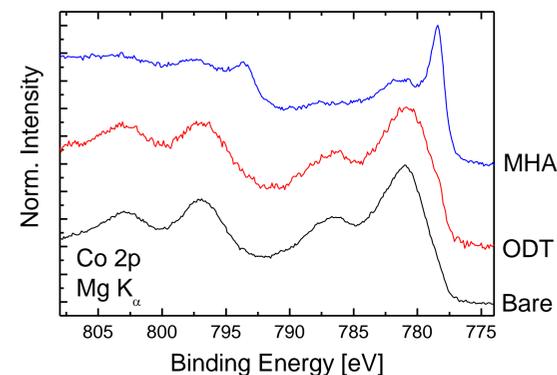
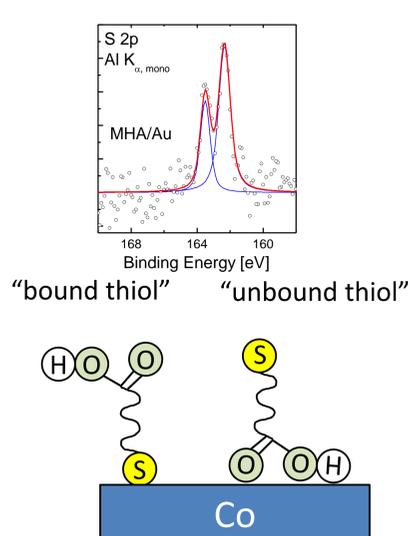
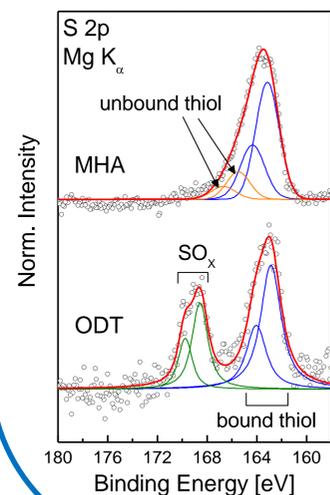


M. Coll et al., *JACS* **131**, 12451-12457 (2009).

Chemical Structure on Cobalt

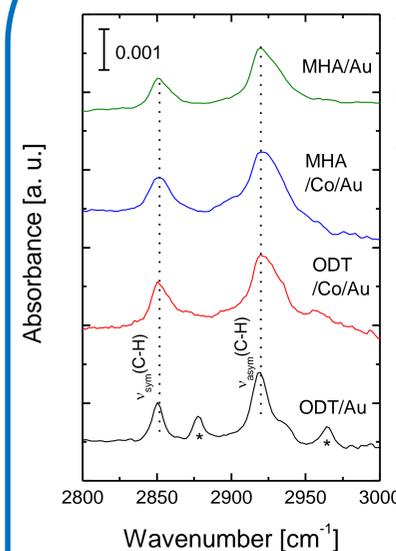


- X-ray Photoelectron Spectroscopy (XPS): surface- and chemically-sensitive technique to probe composition
- Bare: as-stripped Co/PET
 - Some oxidation: O 1s and Co 2p multiplet peaks
 - Oxidation during evaporation ($P \sim 10^{-6}$ Torr) or after stripping
 - F 1s and C 1s → from F1 molecule
 - Some F1 molecule transferred from tSi to Co/PET, giving rise to the voids in the AFM image
- ODT and MHA on Co
 - S atoms confirm molecular layer on Co
 - For ODT: S atoms are either bound to Co or oxidized
 - For MHA: S atoms are either bound or unbound → lack of selectivity
 - Packing density: 2 - 4 molecules per nm² (using Co 3s attenuation). On Au: 5 - 6 molecules per nm²

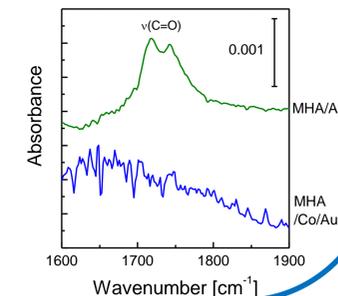


- Co chemical structure
 - Likely oxidized as Co₃O₄
 - ODT/Co not change Co environment
 - MHA/Co → narrow peak Co 2p_{3/2} and low E_B → reduced Co (metallic)

Molecular Structure on Cobalt

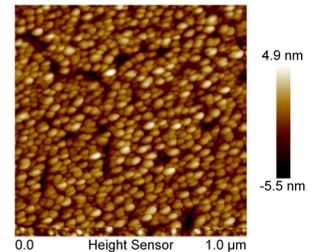


- P-polarized Reflection-Absorption Infrared Spectroscopy (p-RAIRS) to probe molecular layer
- Co/Au/PET structure to enhance reflection
- Molecular structure of SAMs on Co vs. Au
 - ν_{asym} and ν_{sym} C-H seen on all
 - Similar frequency and peak heights → similar molecular packing density
 - For ODT, C-H stretch of terminal CH₃ (marked as *) not discernible on Co → CH₃ tilt different on Co
 - For MHA, C=O stretch not seen → indicates tilt could be different and/or -COOH group docks to Co

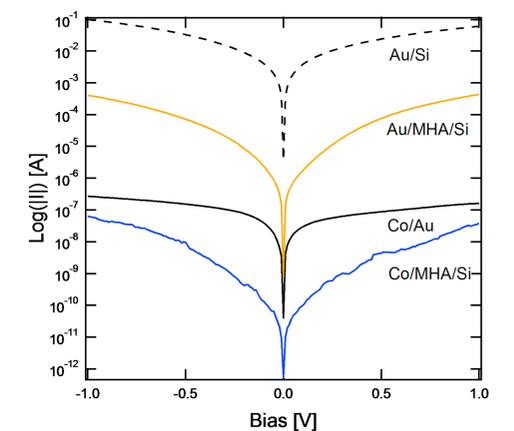


Cobalt Topography

- Atomic force microscopy → surface topography
 - Some gaps (dark spots) on surface
 - RMS roughness: 1.3 nm
 - Likely uneven stripping from tSi
 - Co adhesion onto tSi too large → some F1 molecules on Co/PET and some Co left on F1/Si



Molecular Electronic Junctions



- MHA molecular layer active within junction → current attenuated
- Co/Au control: likely CoSi₂ formed at interface
- MHA/Co and MHA/Au should have comparable current
 - Oxidized Co contribution?

Conclusions

- AFM and XPS are vital tools to investigate and monitor changes to Co surface
- XPS and p-RAIRS are important to probe molecular layer
- These tools combined reveal organic-ferromagnetic metal interface
- Template-stripped Co as a way to prepare consistent Co surfaces
- Ability to attach some simple molecules onto cobalt, but lack selectivity