Tailoring Electrical Contact Resistivity at Metal-Thermoelectric Interfaces Using a Molecular Nanolayer

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Nanomolecular monolayers (NML)

- **Self assembly**
- **Diffusion barriers in Cu- based systems[1]**

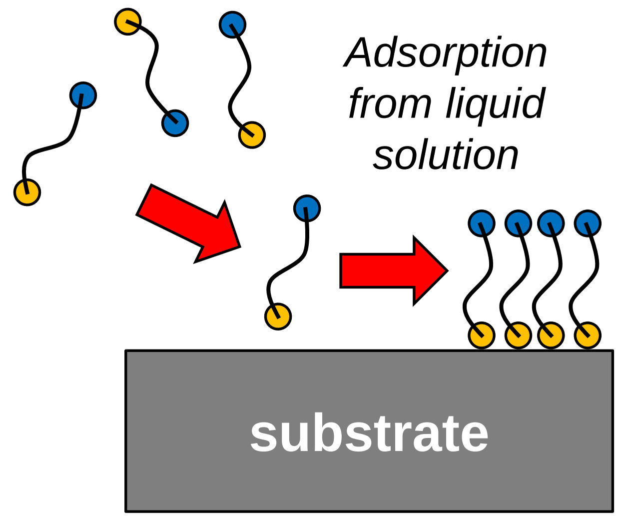
  [1] *P. G Ganesan et al., Appl. Phys. Lett., (2004)*

- **Improve thermal conductivity[2] and mechanical strength[3] of Cu-SiO_2 interfaces**

  [2] *P. O'Brien et al., Nat Mat. (2012)*
  [3] *D.D. Gandhi et al., Nature (2007)*

- **Organosilanes found to improve Au/Ni-Bi_2Te_3 interface resistivity[4]**

  [4] *S.P. Feng et al., PCCP (2013)*



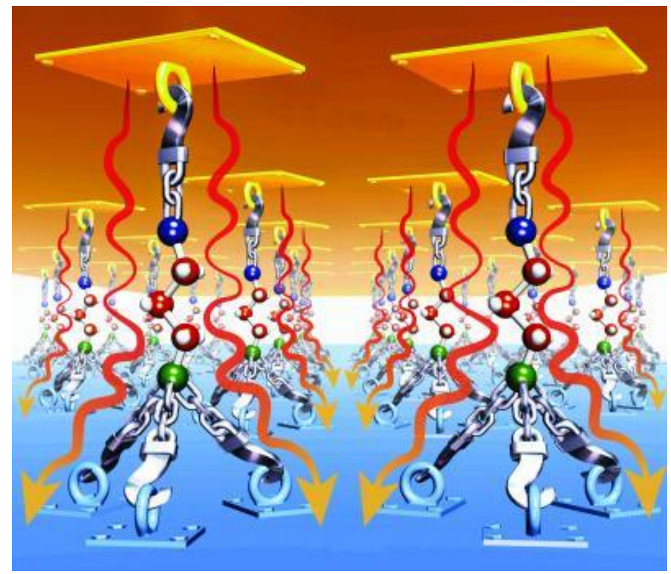
APPROACH:
Double Sulfur-terminated NML

1,8-octanedithiol (ODT)

S-Metal bonds known to form[1,2,3]

S-Bi, S-Te bonds known to form as well[5]

[5] R.J. *Mehta et al., Nat. Mat (2012)*

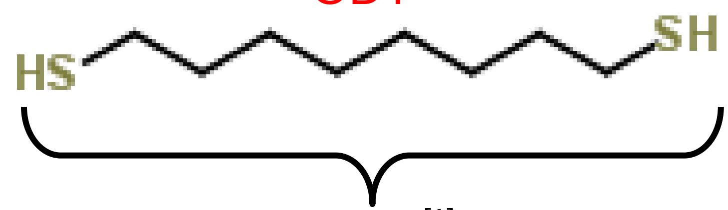


NML-Functionalized Bi_2Te_3

FUNCTIONALIZATION PROCEDURE

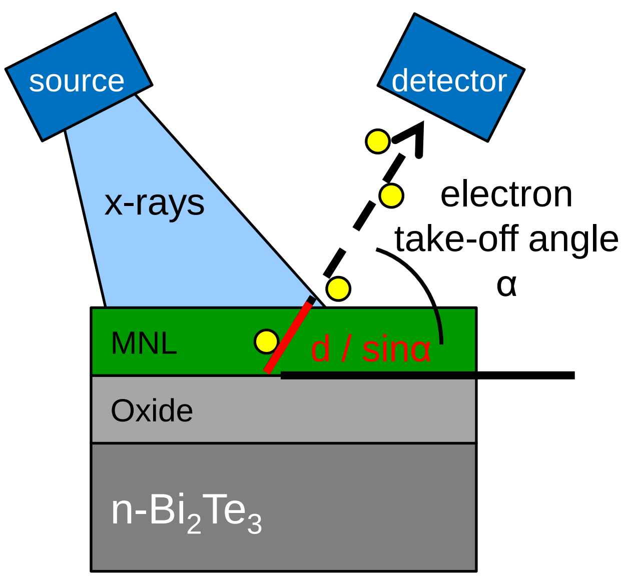
- 5 mM ODT in ethanol prepared
- n-Bi_2Te_3 samples polished with 1200 grit SiC
- Samples immersed in solution for 60 min
  - Low humidity glovebox
- Sonicate in ethanol to remove physisorbed species

GOAL:
Achieve a single edge-standing layer of ODT

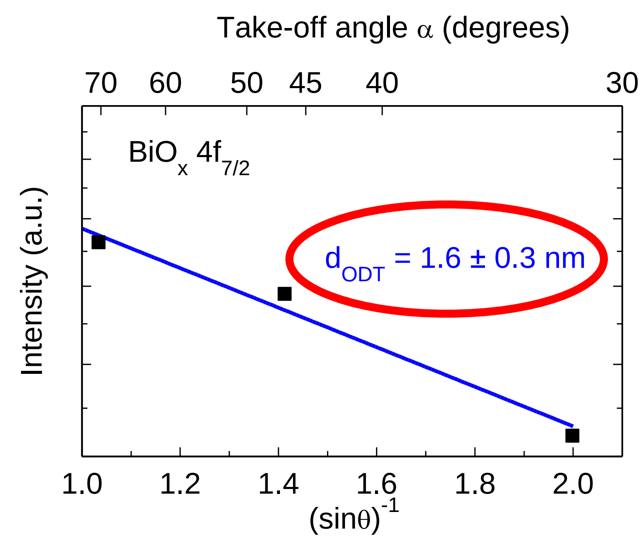


1.5 nm[1]

[1] Jun et al., Langmuir (2006)

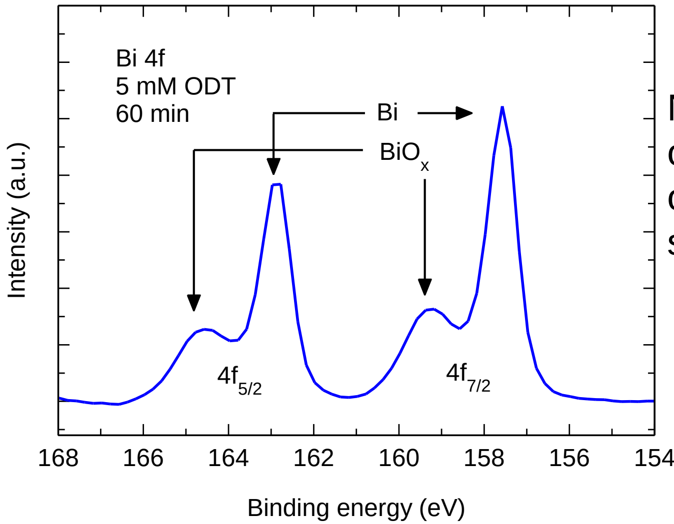


Variable take-off angle XPS measures MONOLAYER of ODT

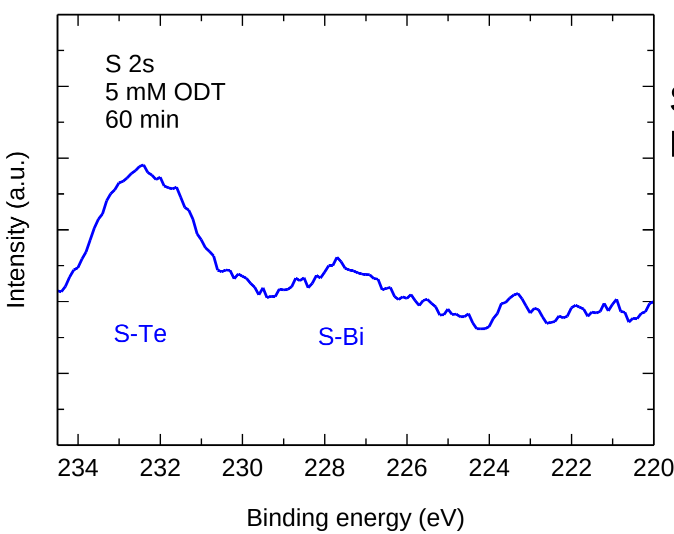


$$\ln \boldsymbol{I} = -\frac{\mathbf{1}}{\sin \alpha} \frac{\boldsymbol{d_{MNL}}}{\boldsymbol{\lambda_{MNL}}} + \boldsymbol{k}$$

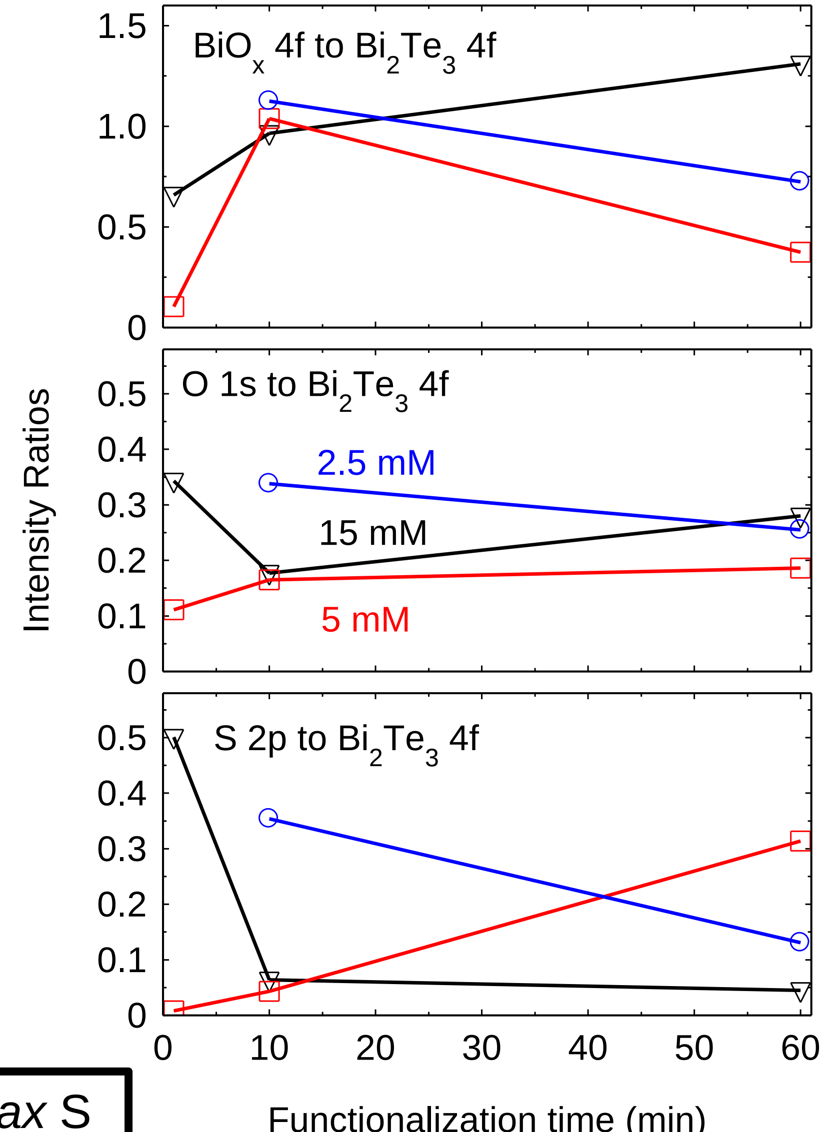
NML Characterization on Bi_2Te_3 Surfaces



Nanoscale oxide formation on Bi_2Te_3 surface.



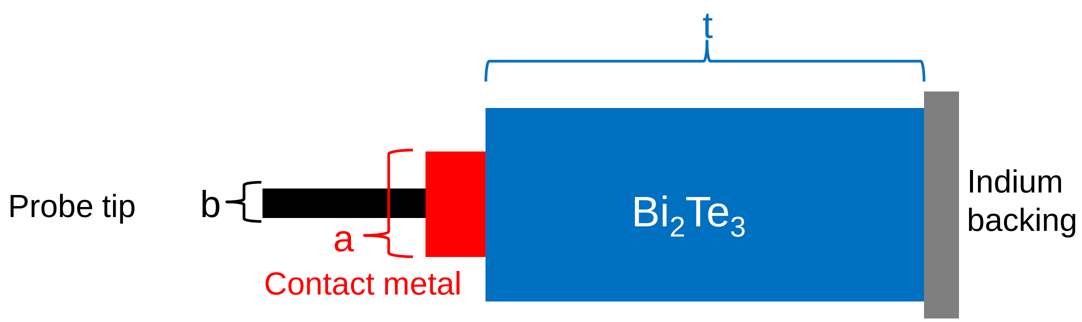
Sulfur bonding with Bi_2Te_3 surface

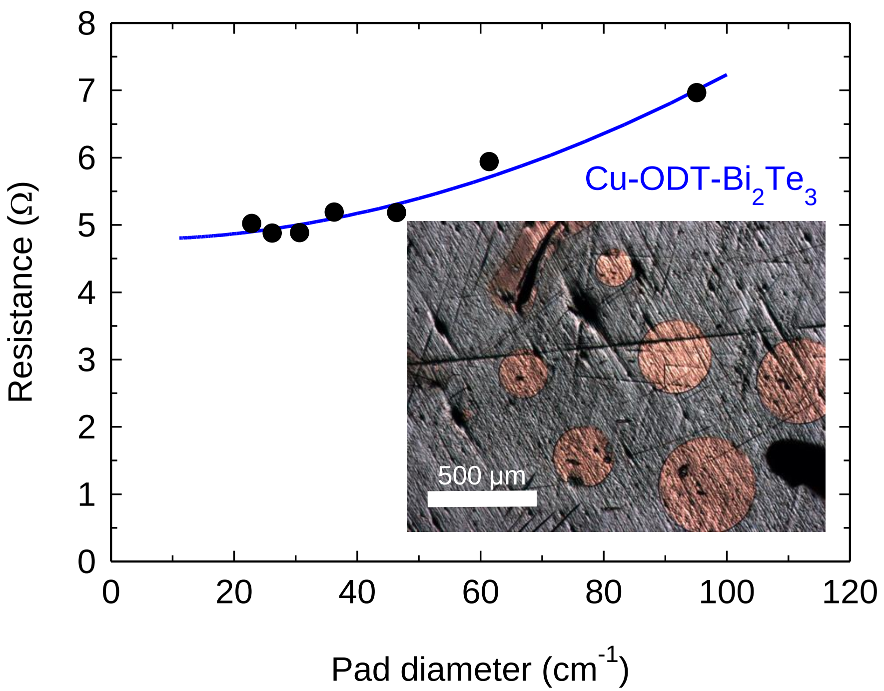


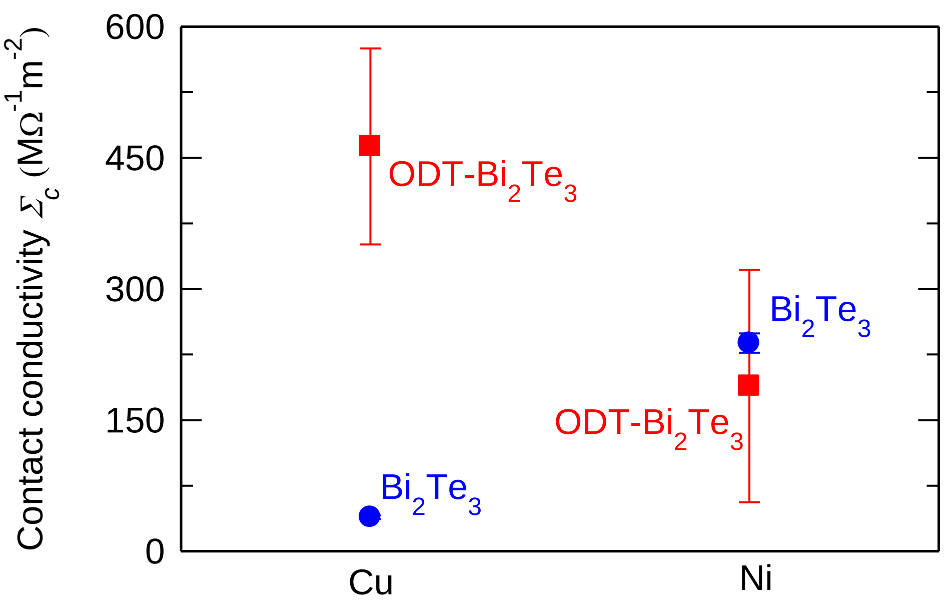
Min BiO_x, O & *Max* S for 5 mM, 60 min

Contact conductivity, Σ_c via Cox & Strack method

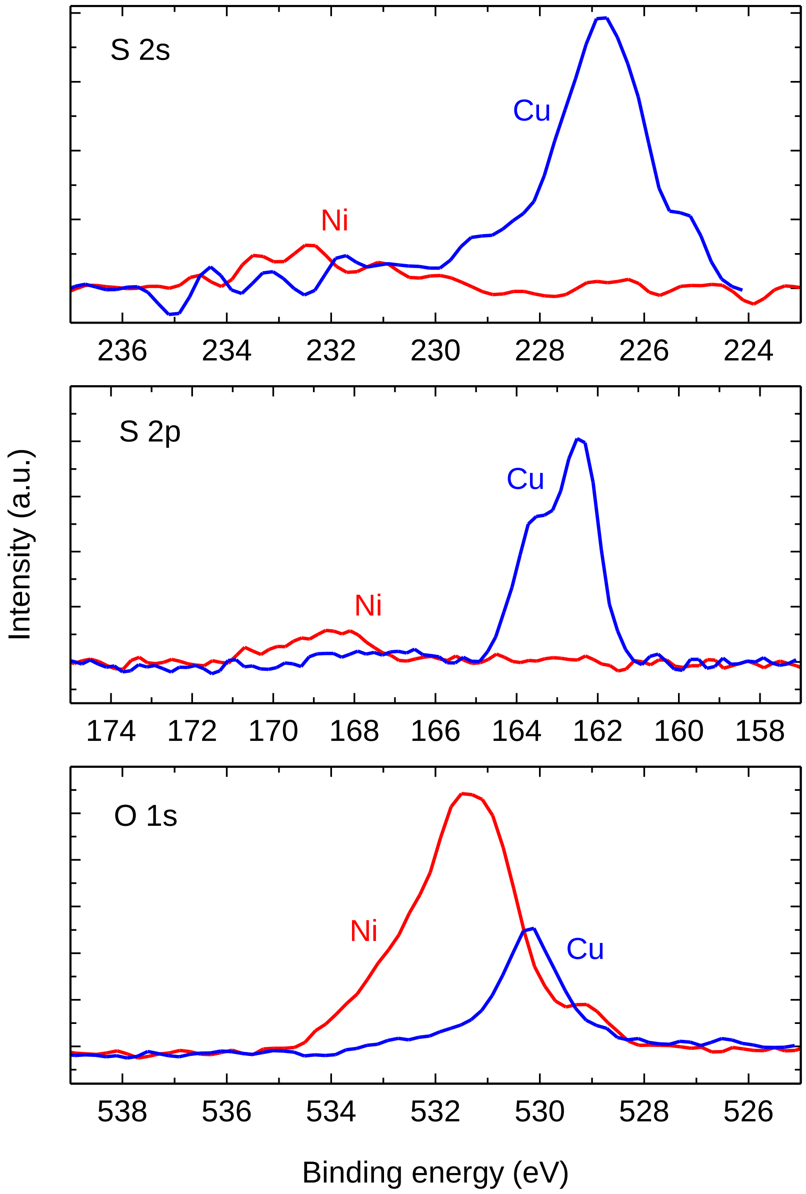
$$R_t = \left[\frac{R_{sm}}{2\pi}\ln\frac{a}{b} - \frac{R_{sm}}{4\pi}\left(1-\frac{b^2}{a^2}\right)\right] + \left[\frac{4R_c}{\pi}\frac{1}{a^2} + \frac{\rho}{\pi a}\tan^{-1}\left(\frac{4t}{a}\right)\right] + R_o$$







Bonding characteristics of S-Cu & S-Ni

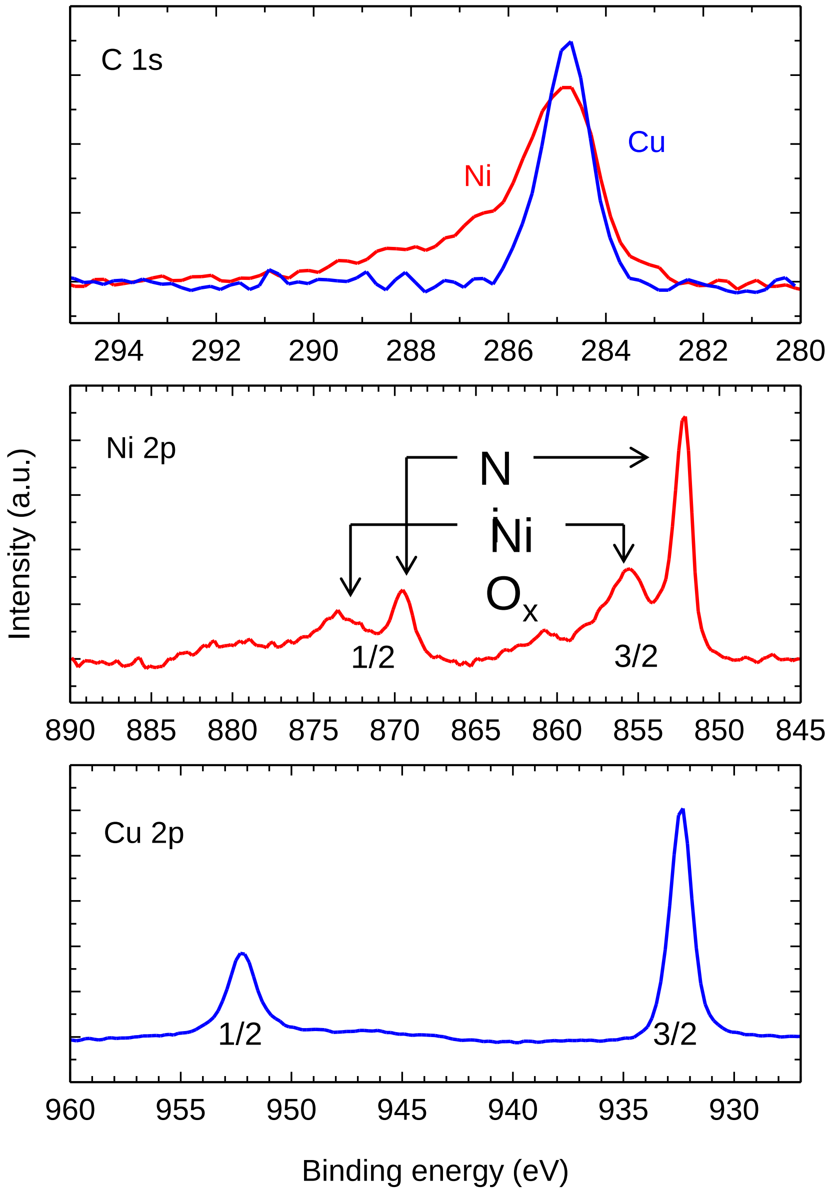


EXPERIMENT:

- Cu, Ni pellets immersed in 5 mM solution of *1-Octanethiol* for 1 hour, rinsed & sonicated in ethanol
- XPS characterization immediately afterward

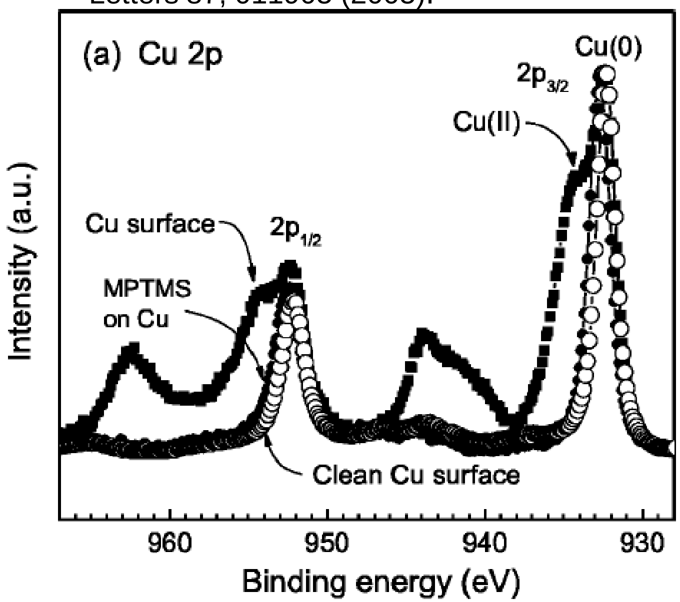
- **Stronger S signal on Cu vs Ni**
  - S readily bonds with Cu
- **O scavenged by S in Cu system**

Bonding characteristics of S-Cu & S-Ni

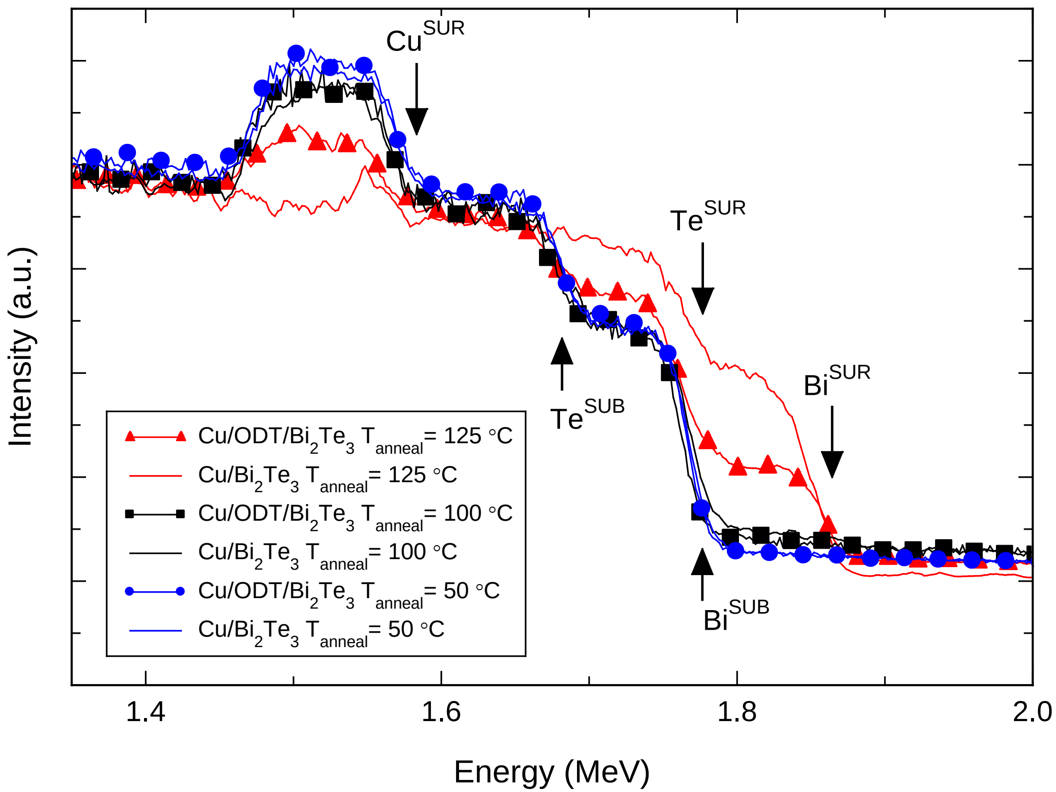


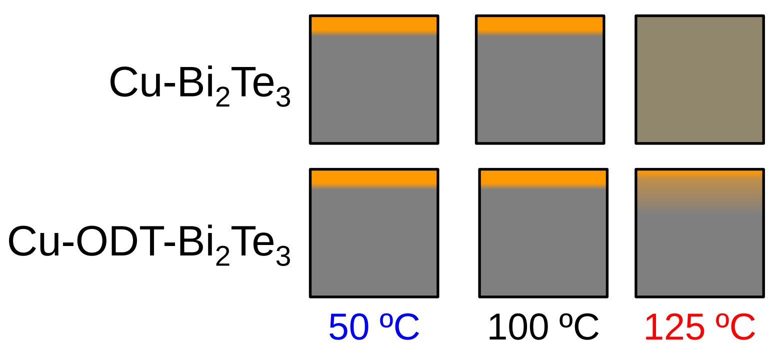
- **Broader C 1s signal on Ni**
  - Presence of C bonds other than -[CH_2]- groups
    - Ni_3C, CO-Ni, CO, CO_2
- **NiO_x band clearly present in Ni 2p**
- **Cu 2p band shows only Cu^0 state. No oxide detected.**

P.G. Ganesan, et al., Applied Physics Letters 87, 011905 (2005).



Diffusion characteristics of Cu-ODT-Bi_2Te_3 via RBS

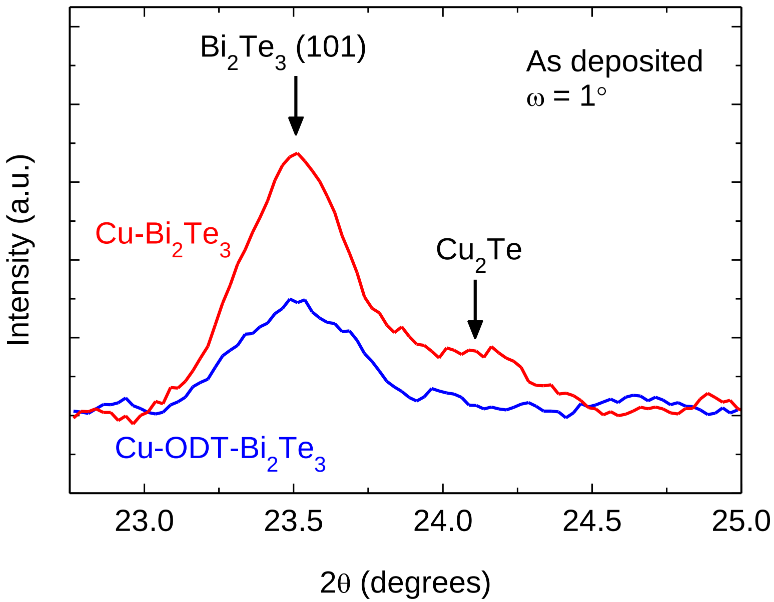




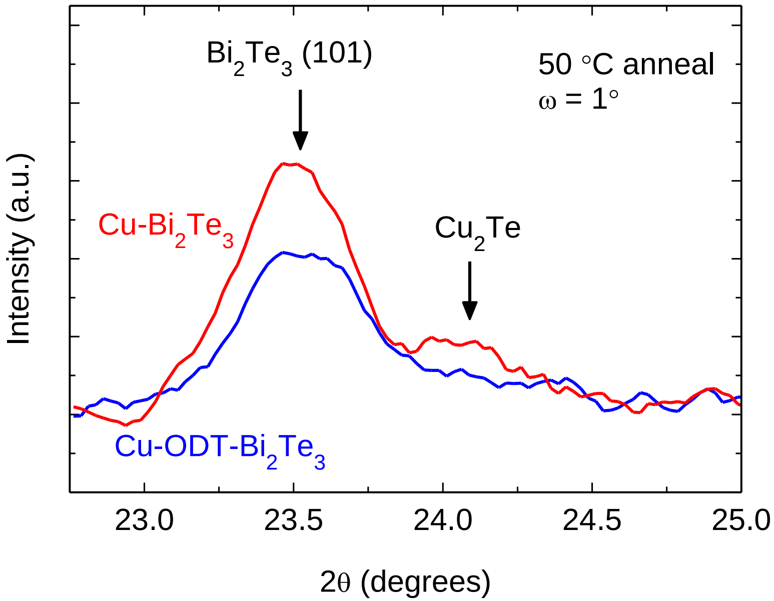
- Very little interdiffusion upon annealing at 50 ºC and 100 ºC
- Almost no Cu on surface without ODT after anneal at 125 ºC
- Considerable amount of Cu on surface with ODT after 125 ºC anneal
  - Some Bi & Te are at surface for system with ODT

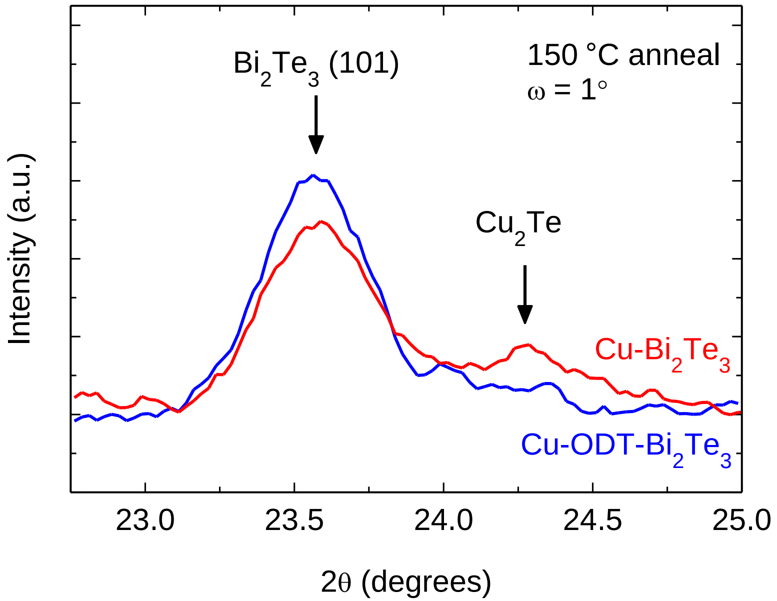
ODT is inhibiting Cu diffusion upon annealing.

Grazing Incidence XRD (GID)



- **GID reveals Cu_2Te phases not detected via standard θ - 2θ diffraction.**
- **Cu_2Te signal suppressed when ODT is present at interface upon annealing.**





Concluding remarks

- **ODT able to self-assemble on Bi_2Te_3 surface**
- **Interfacial chemistry impacts electric contact conductivity**
  - Σ_c 10 times higher when ODT at Cu-Bi_2Te_3 interface
  - 20% decrease in Σ_c when ODT at Ni-Bi_2Te_3 interface
  - Strong Cu-S bonding in comparison to Ni-S bonding
- **Σ_c enhancement for Cu-Bi_2Te_3 system due to interfacial preservation**
  - ODT found to be diffusion barrier
  - Cu_2Te formation suppressed
- **Careful selection of NML with interfacial system critical to achieve desired properties**

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