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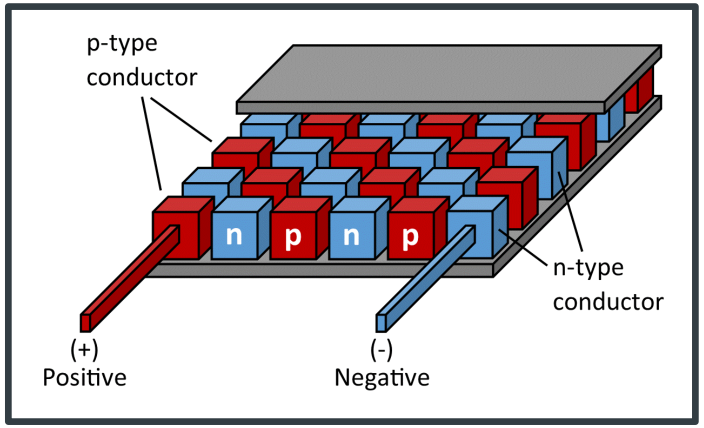
Low-pressure chemical vapour deposition synthesis of metal-chalcogenide materials for thermoelectric micro-generator applications

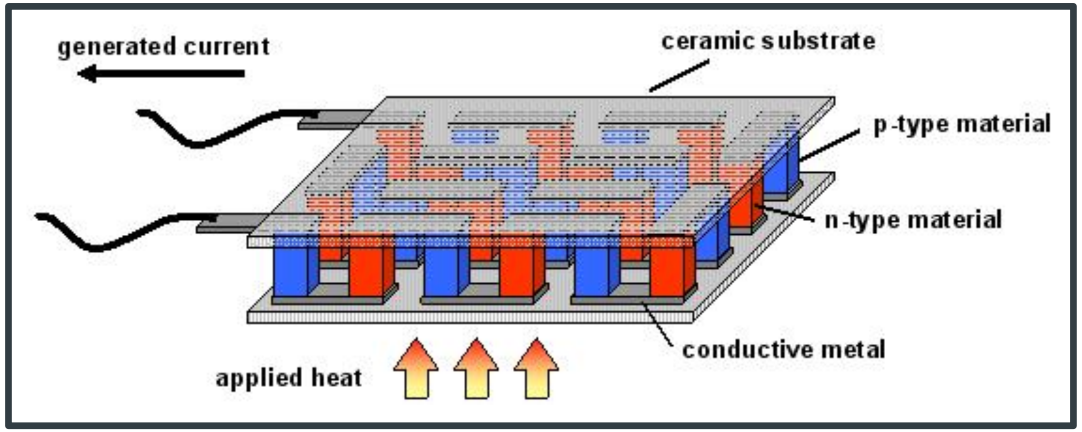
Dr Stephen Richards

14th February 2018

Context and outline

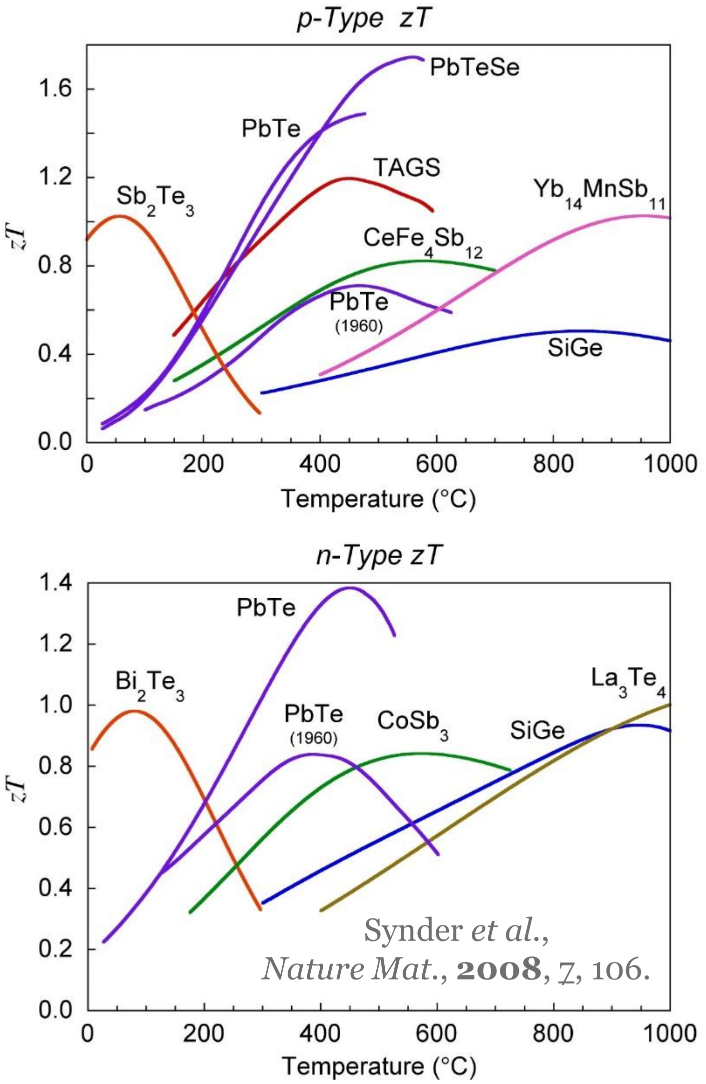


- Why Chemical Vapour Deposition (CVD)
- Binary film deposition/characterisation
- Area selective deposition study trials
- Selective CVD in test device construction
- *Ternary materials - tuning of properties*



Dimensionless figure of merit

$$ZT = \frac{\alpha_{eff}{}^{2}\sigma_{eff}}{k_{eff}}T$$



Synder *et al.*, *Nature Mat.*, **2008**, *7*, 106.

https://www.digikey.co.il/en/articles/techzone/2014/apr/thermoelectric-..energy-generation-takes-flight-for-aircraft-and-spacecraft-monitoring

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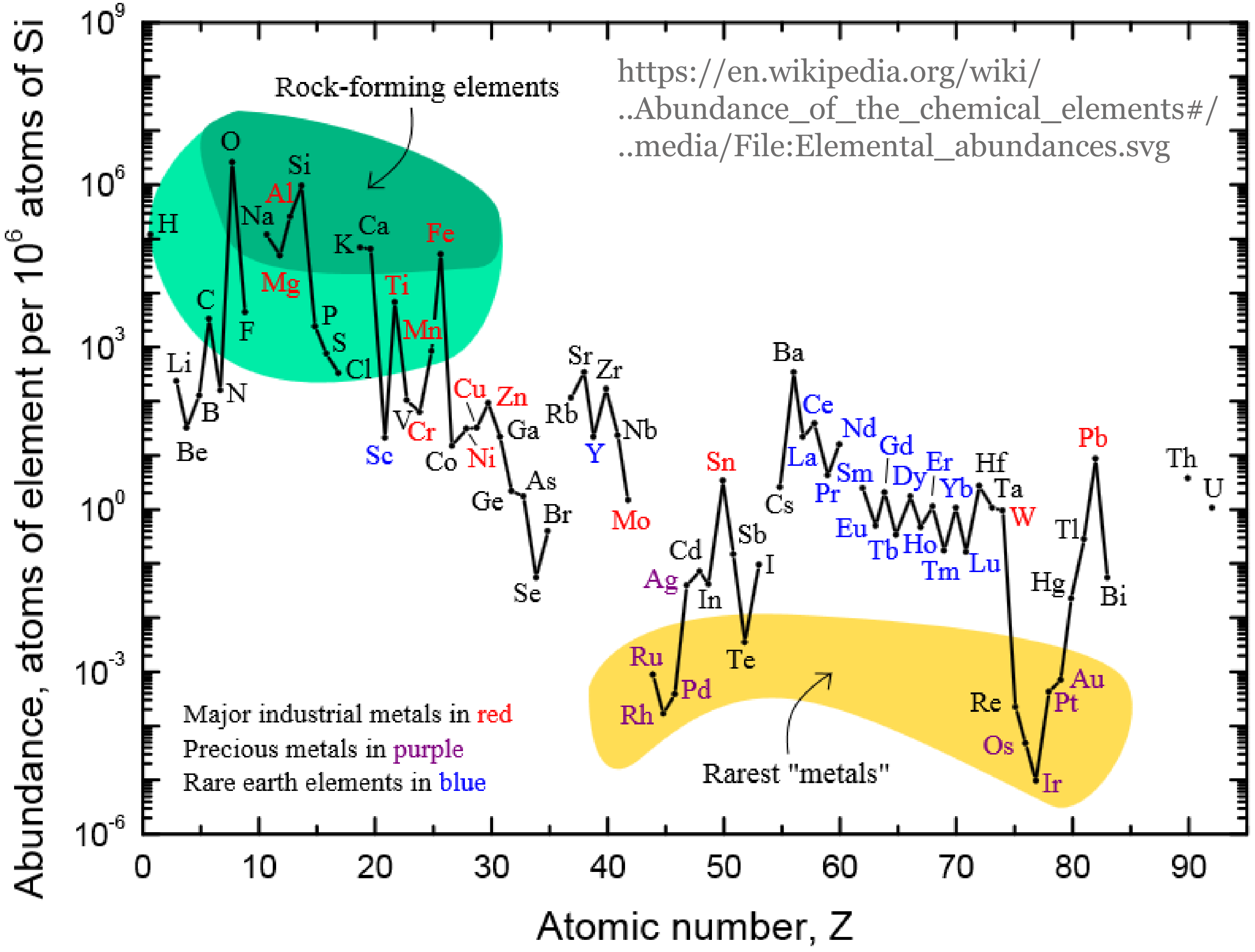
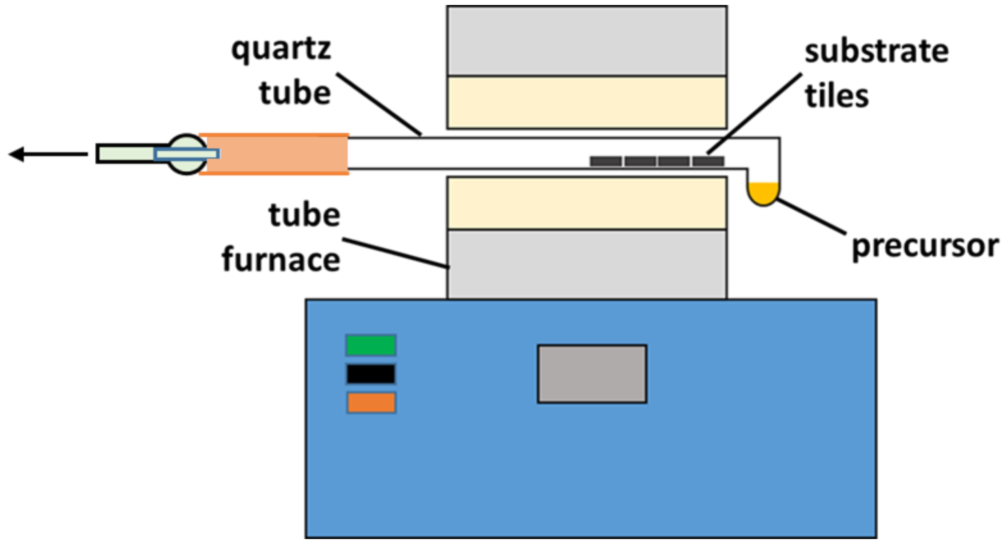
Why Chemical Vapour Deposition?



- Low abundance of Te makes *bulk* thermoelectric generator devices unaffordable – thin film devices
- Advantages of *thin film* material deposition by CVD include:
  - Low cost (ease of operation)
  - Scalability (simple engineering)
  - Good quality conformal films
  - Substrate selectivity

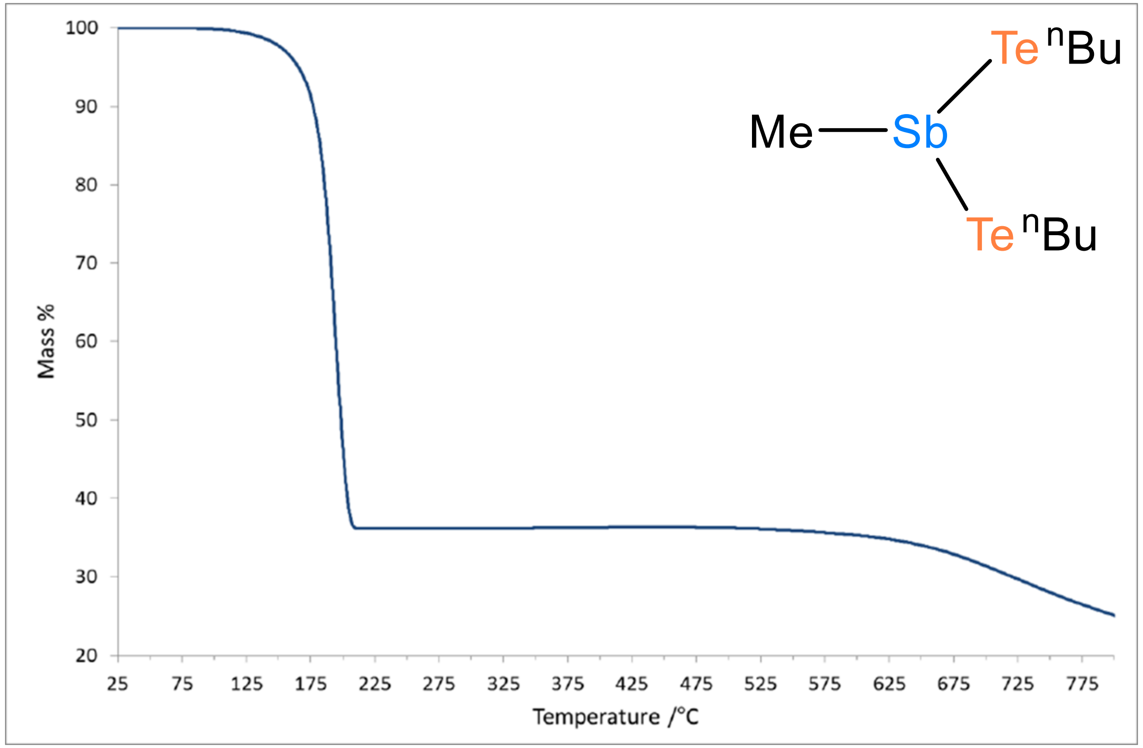
Thin film materials deposition



- Typical LPCVD process condition parameters:
  - Pressure: <0.1 Torr
  - Furnace set point (max temperature): 450 ˚C to 550 ˚C (dependent on material deposited)
  - Substrate position determines deposition temperature/precursor concentration

Single source Sb_2Te_3 precursor

- Organometallic tellurolate precursor
  - Strong bonds between constituents
  - Relatively low molecular weight
  - High purity: NMR, elemental (CHN)
  - Close to desired film stoichiometry
- TGA suggests suitability of [(Me)Sb(Te^{n}Bu)$_2$]
  - High volatility (Sb_2Te_3 c.f. 49% precursor)
  - Low decomposition temperature
- Precursor lifetime: >6 months (freezer)



Benjamin *et al.*, *J. Mater. Chem. C*, **2015**, 3, 423.

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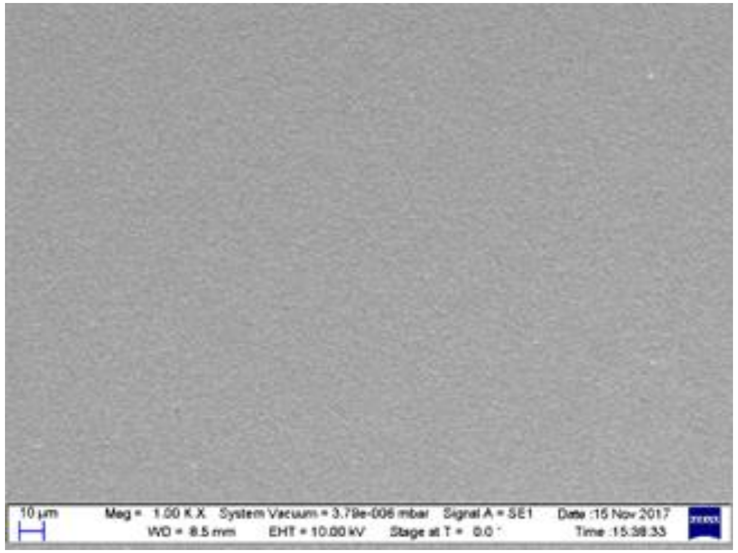
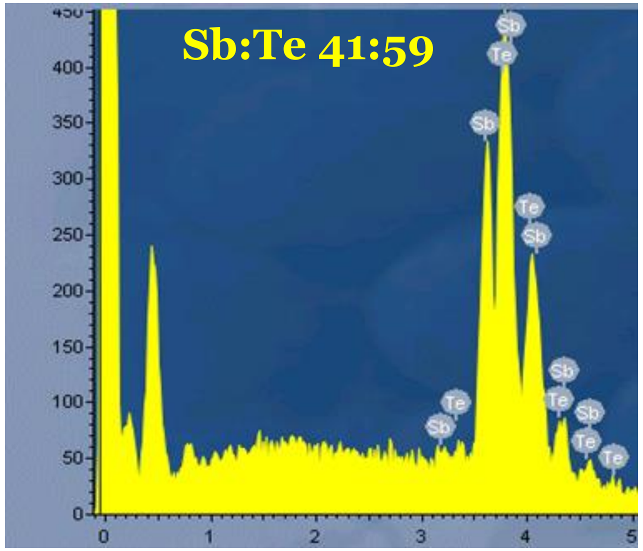
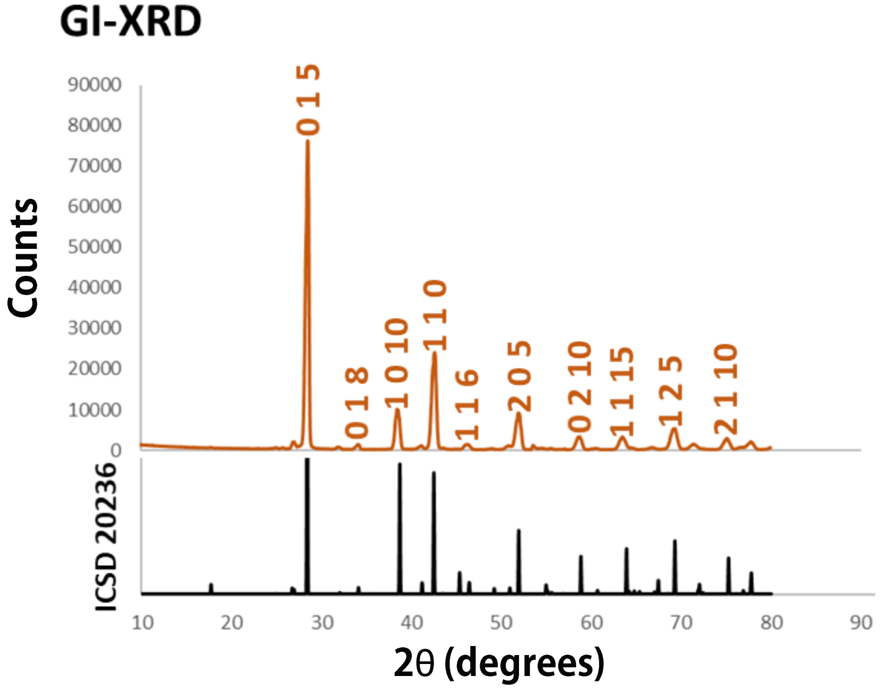
Sb_2Te_3 thin film deposition: SiO_2



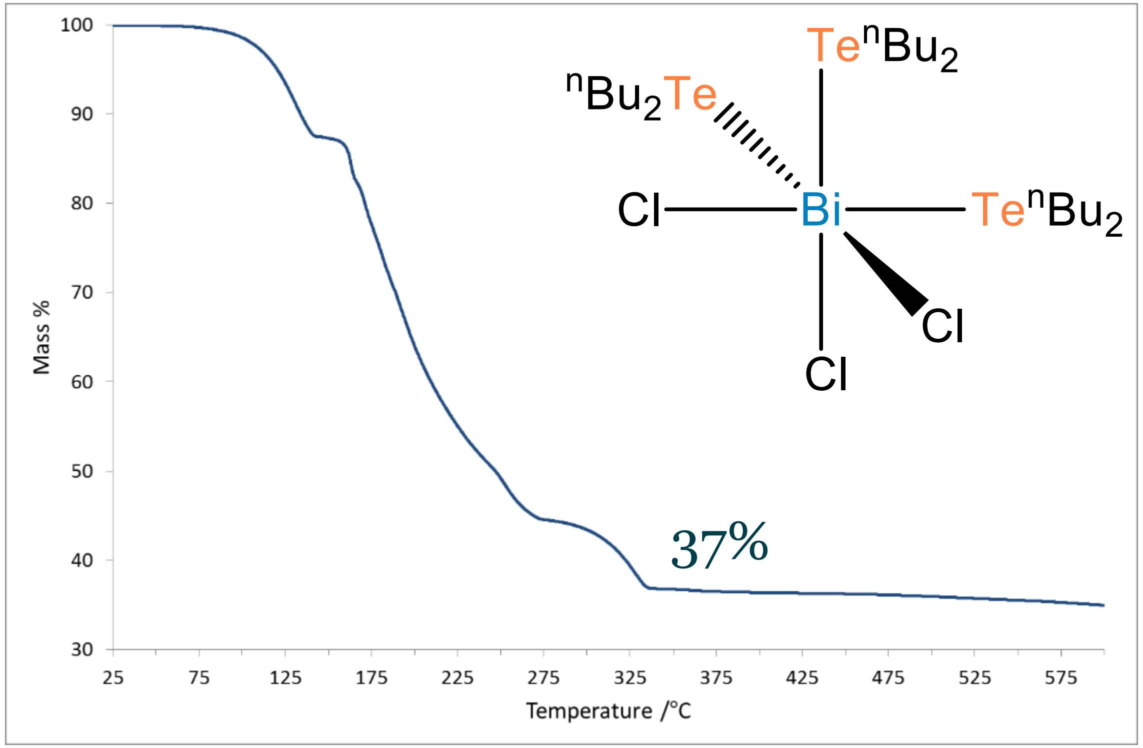




- p-type semiconductor
- Continuous thin film with no detected impurities
- Polycrystalline (tellurantimony) Sb_2Te_3 phase
  - Refined unit cell parameters: a,b = 4.239(4), c = 30.27(8) Å; α,β = 90˚, γ = 120˚

Single source Bi_2Te_3 precursor

- Direct bonds between constituent elements
  - Pure: NMR, CHN, IR [ν(Bi-Cl): 247 cm^{-1}]
  - Precise control over film composition
  - Reproducibility with simple apparatus
- TGA suggests suitability of $[(^nBu_2Te)_3BiCl_3]$
  - Residue approximating Bi_2Te_3 (c.f. 38%)
  - Low temperature decomposition
  - Clean decomposition (no contaminants)
- Precursor lifetime: >10 months (freezer)



Benjamin *et al.*, *J. Mater. Chem. A*, **2014**, 2, 4865

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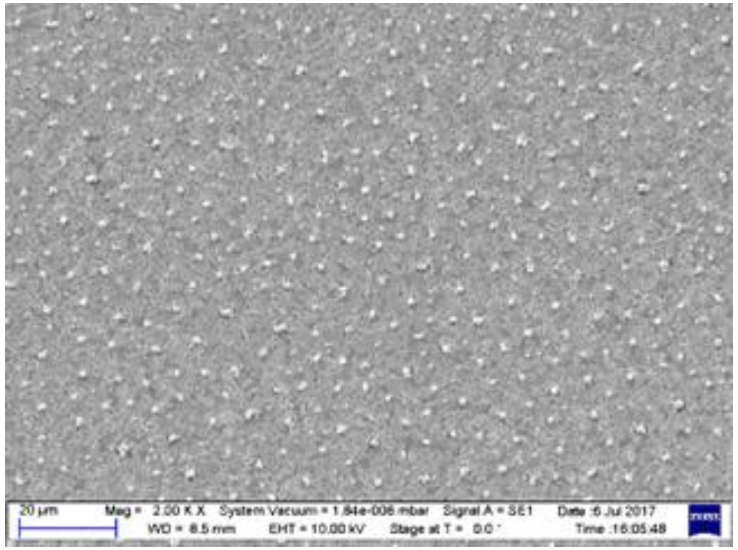
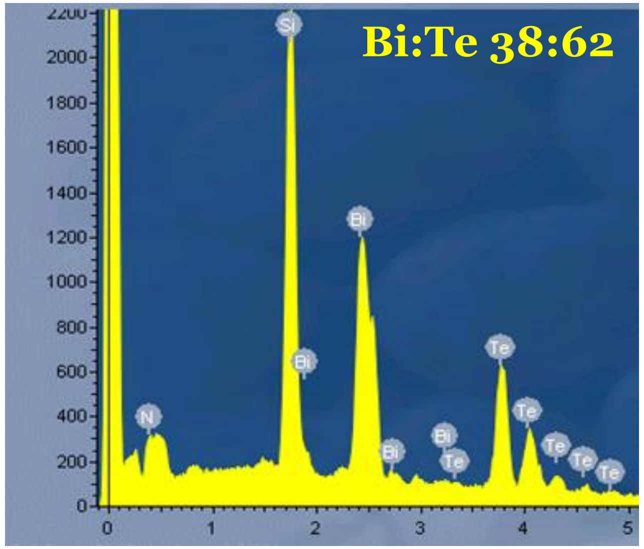
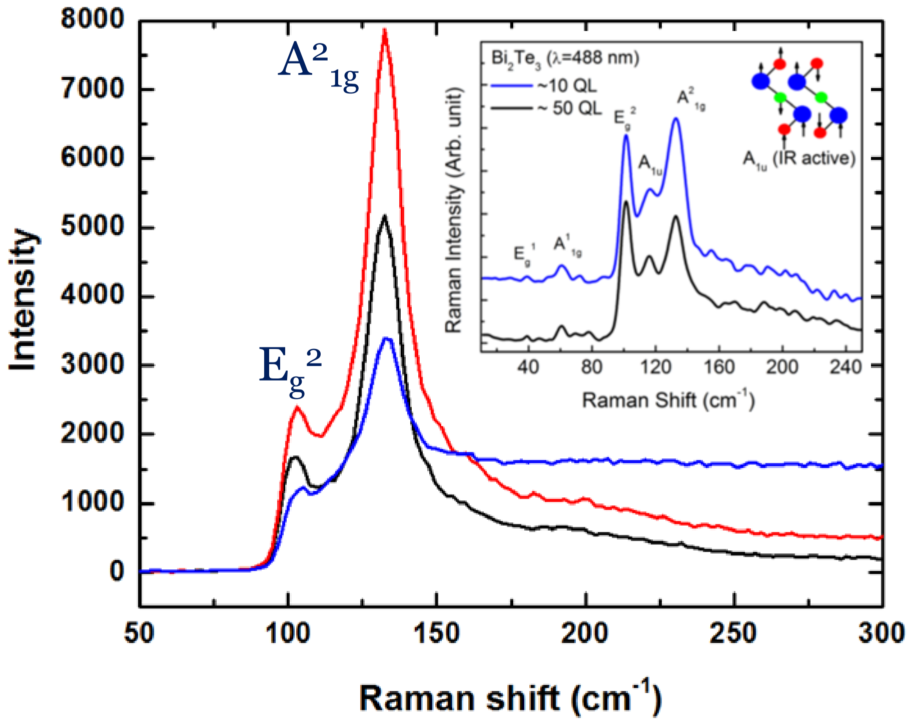
Bi_2Te_3 thin film deposition: Si_xN_y







- n-type semiconductor
- Continuous thin film with no detected impurities
- Polycrystalline (tellurobismuthite, syn) Bi_2Te_3 phase
  - Refined unit cell parameters: a,b = 4.3839(17), c = 30.52(2) Å; α,β = 90˚, γ = 120˚

Balandin *et al.*, *J. Appl. Phys.*, 2012, **111**, 054305.

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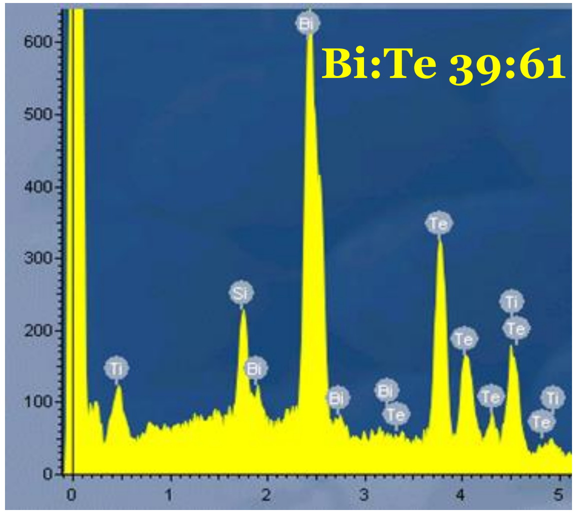
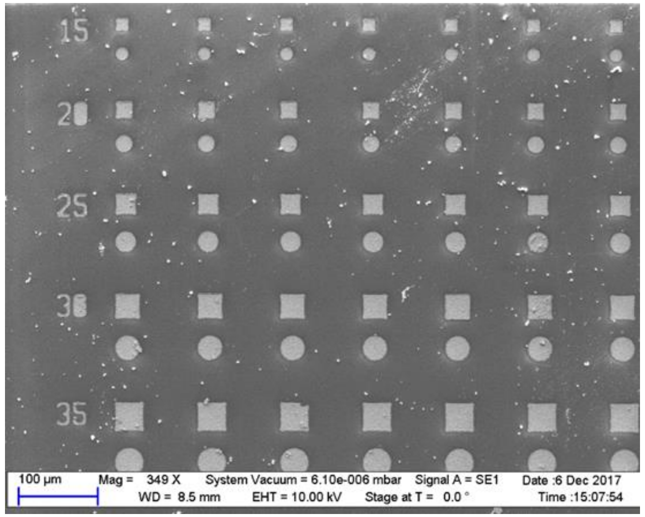
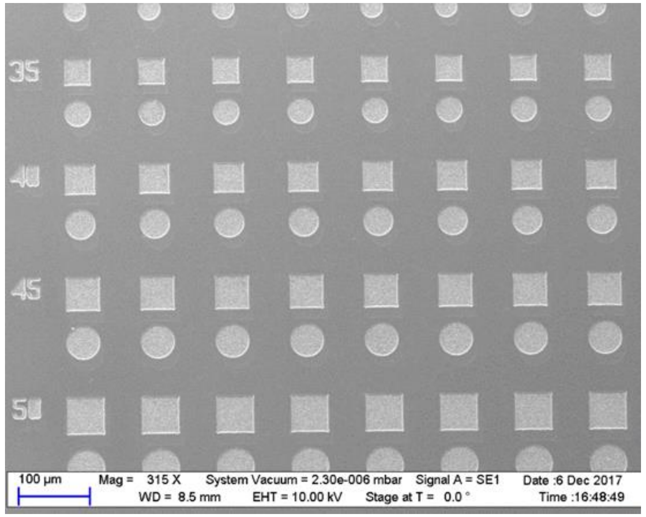
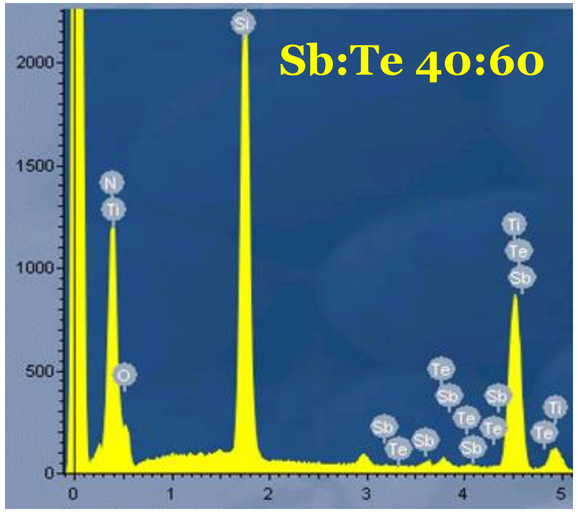
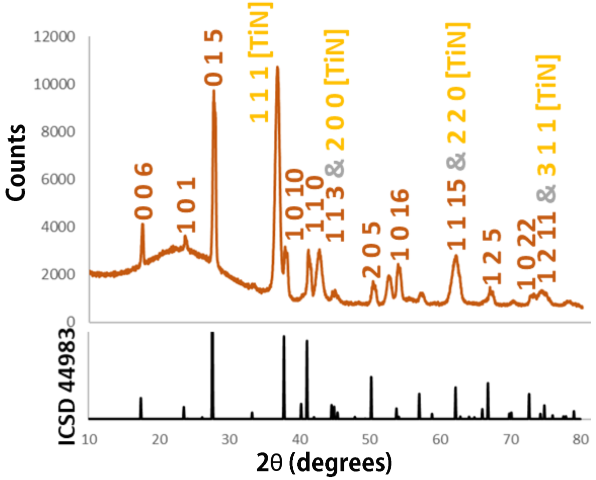
Selective deposition: Ti_xN_y/SiO_2









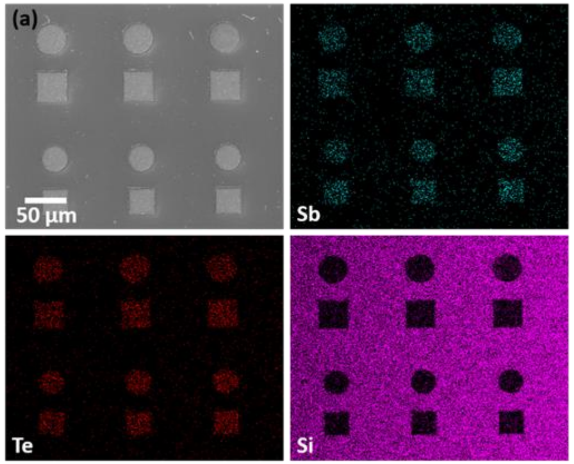


Above: Selective deposition
Top left: EDX spectrum
Left: Grazing incidence XRD

Bi_2Te_3

Above: Selective deposition
Top right: EDX spectrum
Right: EDX element map

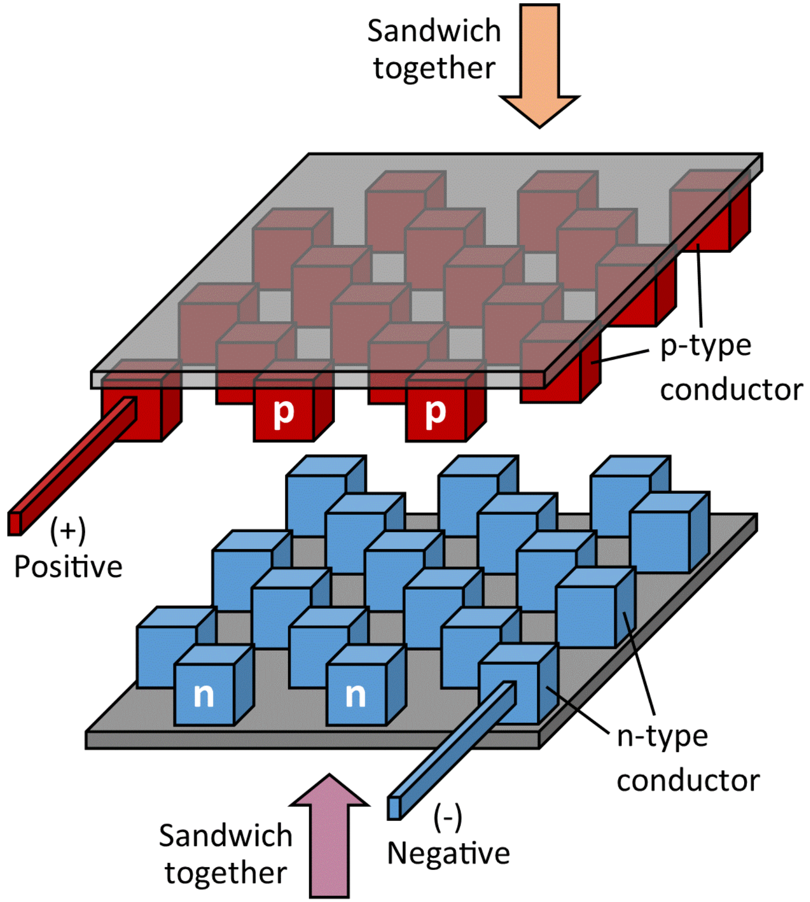
Sb_2Te_3



Micro-generator fabrication

- Conventional fabrication is laborious, complicated and costly
  - Deposition (separate lithographic processing steps for both n- & p-type materials)
  - Wasteful additional patterning (both n- & p-type materials)
  - Soldering and bonding
- Impacts on thermoelectric micro-generator performance
  - Thermoelectric material damage (etching/contacting)
  - Parasitic contact resistance due to soldering
  - Problematic limited thermoelectric performance often the case with contacted sputtered materials

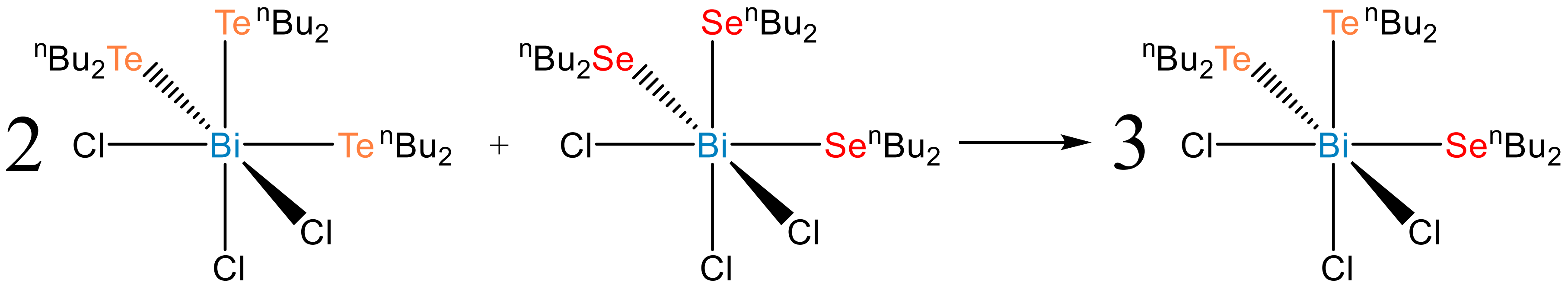
➢ *Selective deposition* confined to conductive domains within device-patterned substrates a simpler more elegant approach



Ternary bismuth chalcogenides

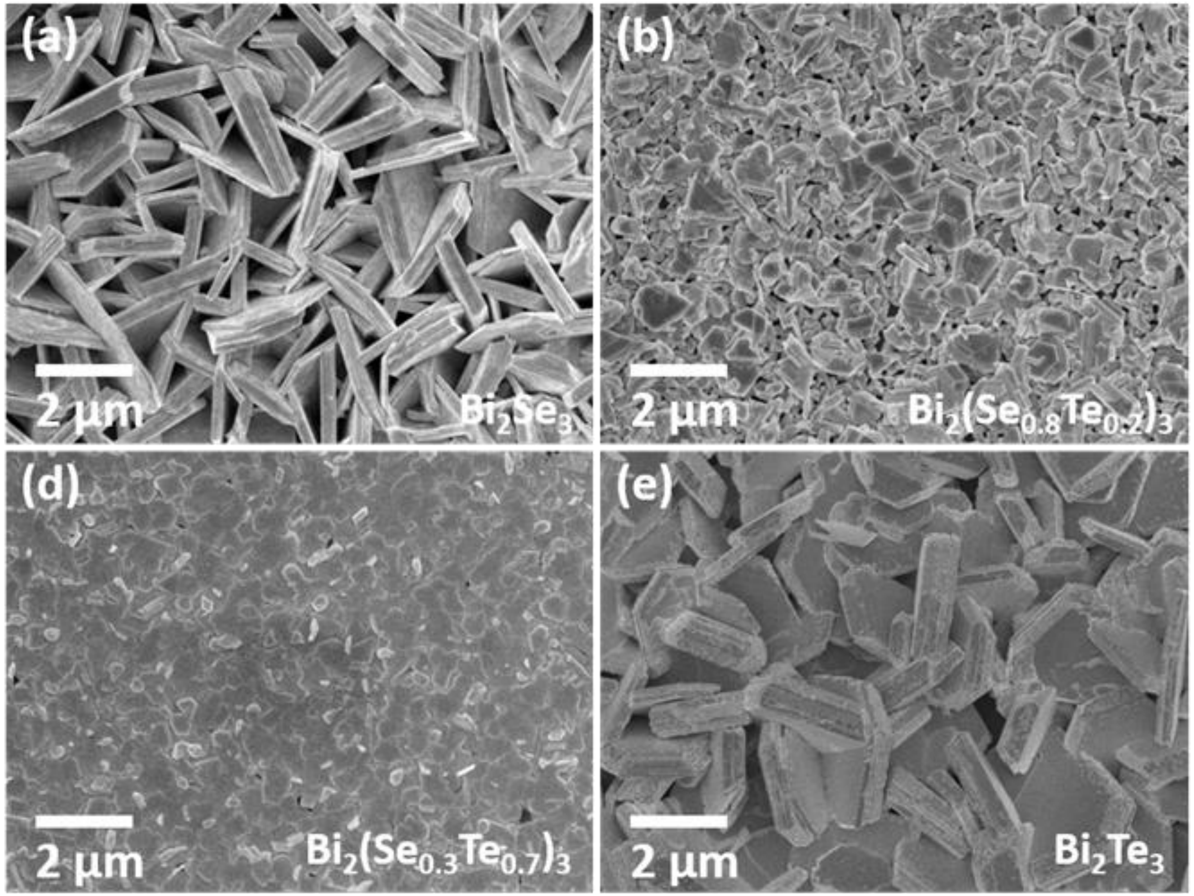
$(Bi,Sb)_2(Te,Se)_3$

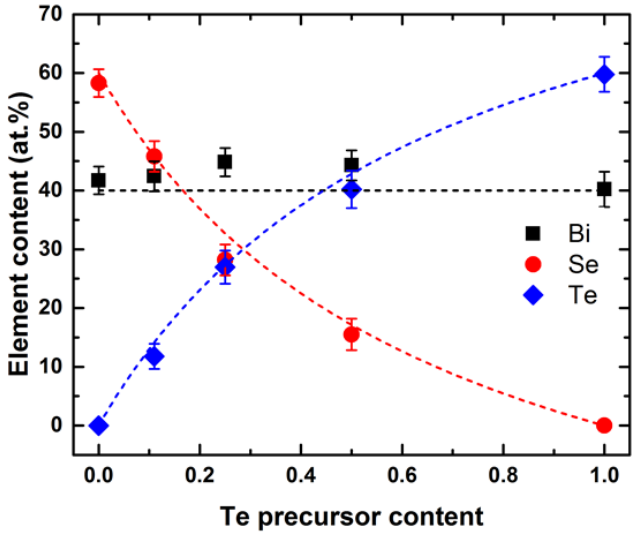
- Tuning of thermoelectric material properties (esp. relative to metal interconnects)
- Tight control over stoichiometry (compatible reagents, or preferably single reagent)



- Take advantage of lability of $[(^nBu_2E)_3MCl_3]$ systems – where E = Te, Se; M = Bi, Sb
  - Mixing $[(^nBu_2Te)_3BiCl_3]$ and $[(^nBu_2Se)_3BiCl_3]$ causes ligand scrambling – statistical mixture

$Bi_2(Se_{1-x}Te_x)_3$ thin film deposition

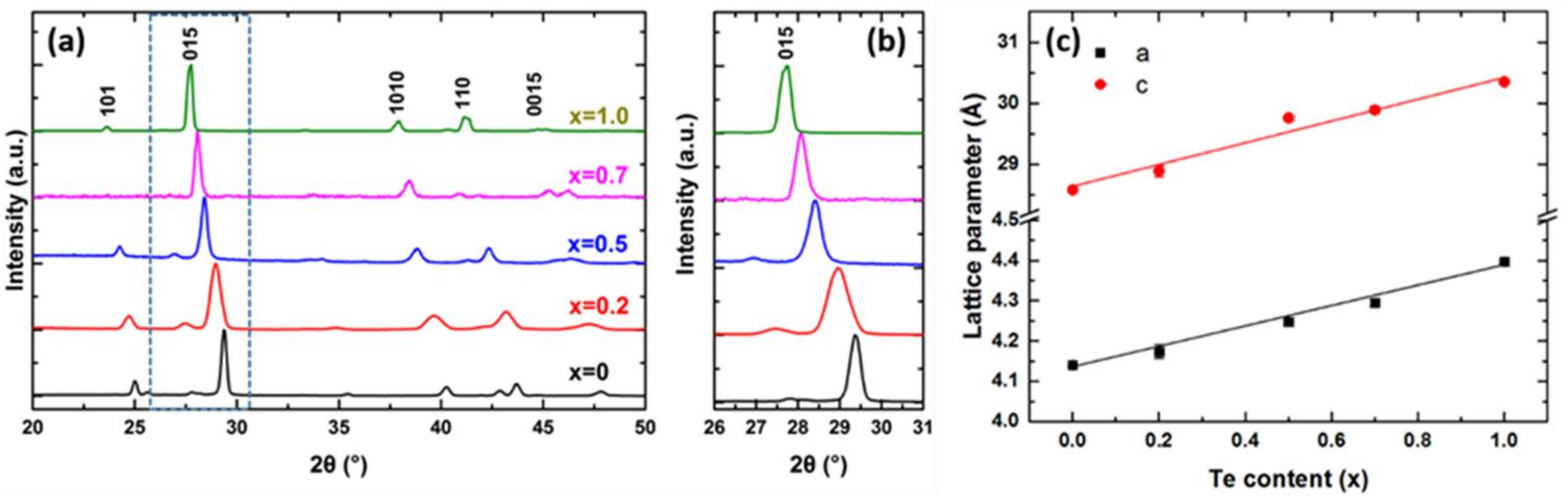




- All depositions at 550 ˚C
- Stoichiometry/composition (by EDX) of solid solution follows trend precursor formulation with enhancement in Te

Benjamin *et al.*, submitted

$Bi_2(Se_{1-x}Te_x)_3$ thin film XRD



- Vegard's Law behaviour *vs* EDX analysed compositions for solid solutions
- Some broadening of reflections in solid solutions c.f. binary material phases

Benjamin *et al.*, submitted.

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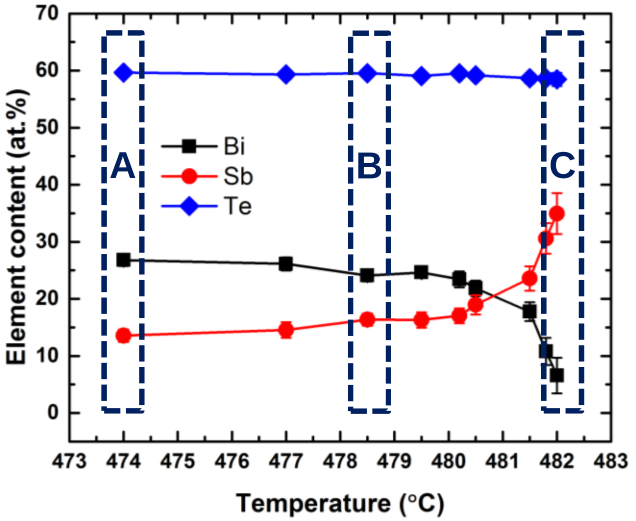
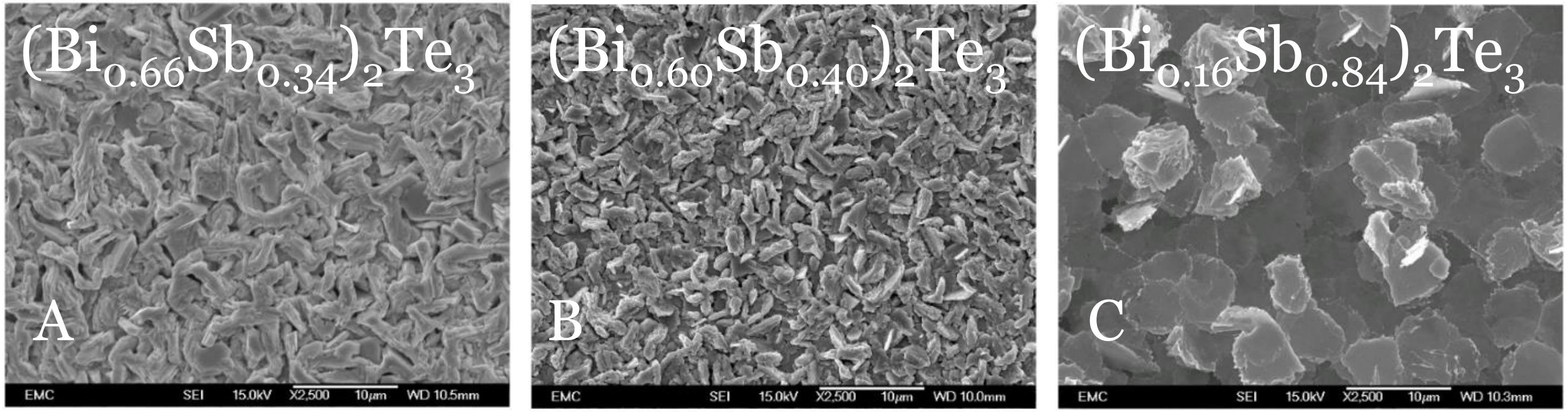
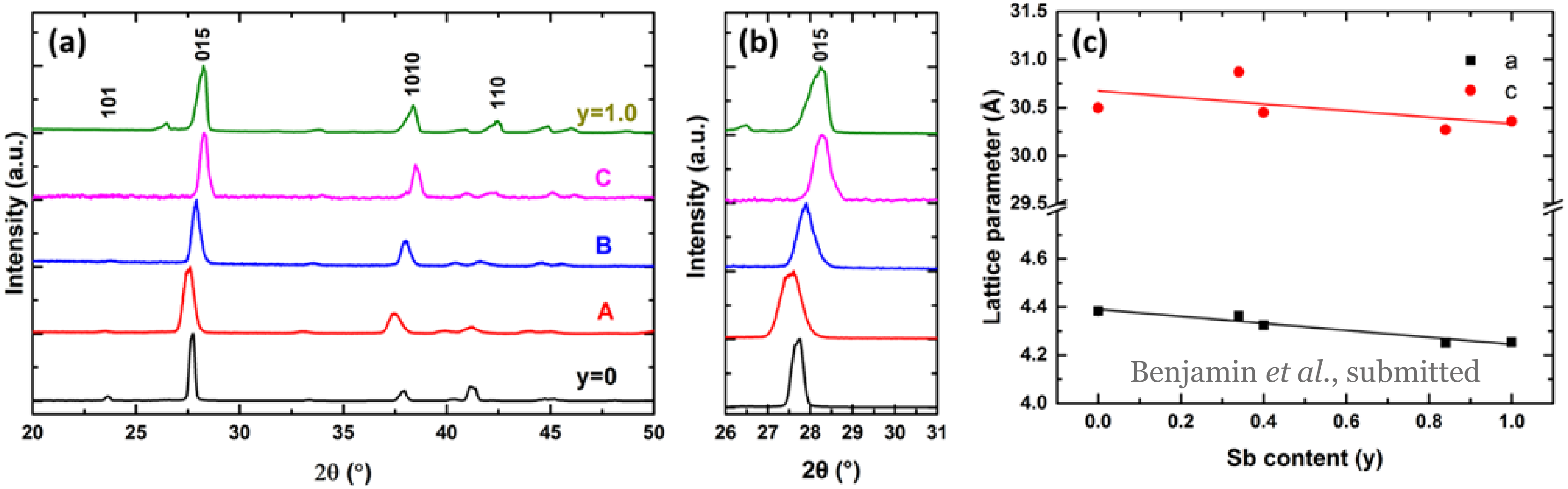
$(Bi_{1-y}Sb_y)_2Te_3$ thin film deposition







- Composition *vs* long axis of sample (function of deposition temperature)
- Increase in Sb and decrease in Te with increasing temperature

Conclusions and future work

- Good degree of control using single source precursors – high quality polycrystalline films
  - [(^{n}**Bu$_2$Te**)$_x$(^{n}**Bu$_2$Se**)$_{1-x}$BiCl$_3$] convenient single source precursors to **Bi**$_2$(**Te**,**Se**)$_3$ ternaries

- Substrate selectivity is a major advantage of LPCVD using our precursors for micro-TEGs
  - Materials efficiency to minimise wastage of expensive tellurium (Te)
  - Simpler device construction with fewer steps – anticipated better performance

- Optimisation of ternary phase deposition is ongoing to allow measurements to be undertaken
  - Efficiency requires tuning thermoelectric device element "legs" relative to interconnects
  - Working towards evaluating selective deposition of ternary materials

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