NANO-WIRE ARRAYS OF Bi_2Te_3 FOR THERMOELECTRIC APPLICATIONS

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Thermoelectric Materials

- Materials which present strong thermoelectric effect
  - An electric potential creates a temperature difference
  - A temperature difference creates an electric potential.
  - Figure of Merit ZT

$$ZT = \frac{S^2\sigma}{\kappa} T$$

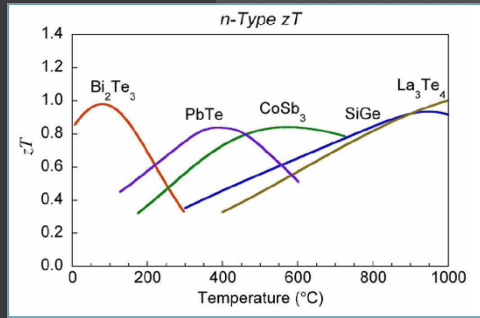
- **S** = Seebeck coefficient: high in semiconductors
- σ = Electrical conductivity : high in metals
- κ = Thermal conductivity : low in semiconductors

- Semiconductor with relative high ZT: **Bismuth Telluride**
  - 1954 : First report of Bi_2Te_3 as an effective thermoelectric material
  - High mean atomic weight
  - Low lattice conductivity
  - Low melting temperature 585 ºC

Thermoelectric Materials

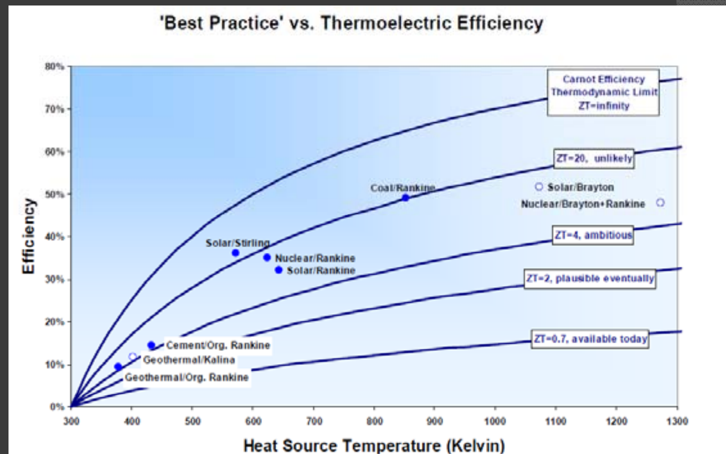
- ZT Bismuth Telluride ~ 1
  - Efficiency of 10%

$$ZT = \frac{S^2\sigma}{\kappa} T$$



C.B. Vining. Solutions Summit Nanotech. and New Mater. **8** 2 83 – 85 (2008)

- Need of improvement of the figure of merit (ZT)
  - To be competitive ZT ~ 3!
  - Unusual band structures (**S** ↑)
    - *DiSalvo, Badding, Kanatzidis, et al*
  - Control over the disorder (**S**↑, κ↓)
    - *Slack, McMillan, Pohl, et al.*



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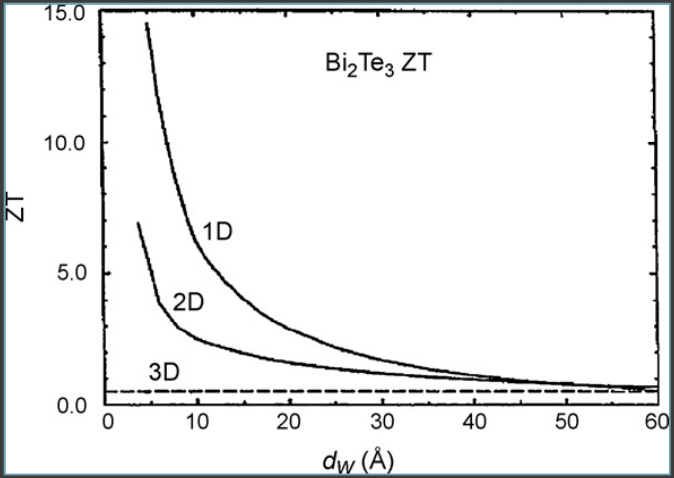
- Quantum confined structures (**S**↑, κ↓)
  - Hicks and Dresselhaus, Phys. Rev. B, 47 12727 – 12731 (1993)

Thermoelectric Materials: Low Dimensionality

- Theoretical Prediction: M.S. Dresselhaus et al.
  - Microscale Thermophysical Engineering **3** 89 (1999)



Dependence of $Z_{2D}T$ and $Z_{1D}T$ on quantum-well and quantum-wire widths d_W for Bi_2Te_3

$$ZT = \frac{S^2\sigma}{\kappa}T$$

- Effects of reduced dimensionality
  - Higher **S**: Quantum confinement effect.
  - No entanglement between **S** and σ
  - Decrease in κ : Introduction of interphases
- First experimental demonstration
  - R. Venkatasubramanian, Nature **413** (6856) 597 (2001)

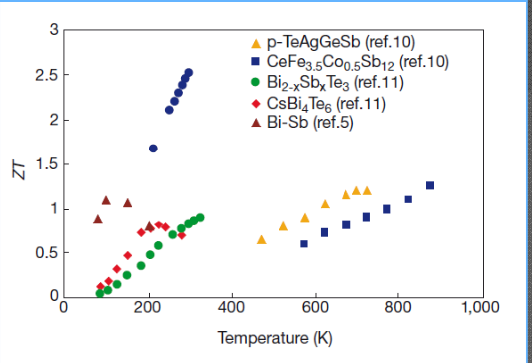
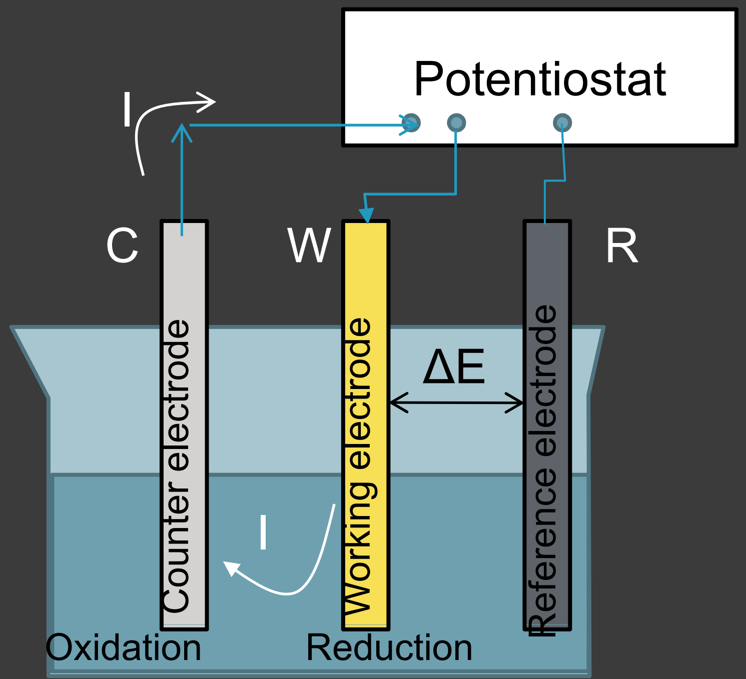


Figure 3 Temperature dependence of *ZT* of 10Å/50Å p-type Bi_2Te_3/Sb_2Te_3 superlattice compared to those of several recently reported materials.

Venkatasubramanian, Nature **413** (6856) 597 (2001)

Electrochemical Deposition: Films Bi_2Te_3

- Our approach: Fabrication by Electrochemical deposition
  - Room Temperature fabrication, low cost, No vacuum, high deposition rates, scalability and easy transfer to the industry.
  - Bulk electrodeposition since 1993 Takahashi et al; 1996 Magri et al



Bi_2Te_3

$S \approx -240\ \mu V/K$

$\sigma \approx 0.1\ (\mu\Omega \cdot m)^{-1}$

$\kappa \approx 2.02\ W/m \cdot K$

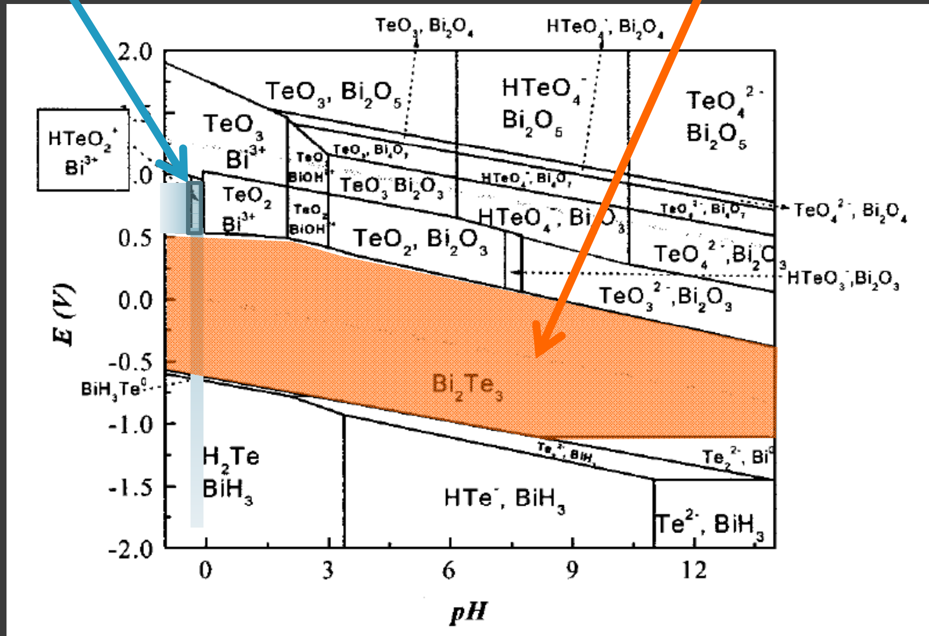
$$ZT = \frac{S^2\sigma}{\kappa} T = \frac{(240 \cdot 10^{-6})^2\ 0.1\ 10^6}{2.02} \cdot 300 \sim 0.9$$

Electrochemical Deposition: Films Bi_2Te_3

- Pourbaix- type diagram for the electrodeposition of Bi_2Te_3
  - Termodynamic stability of the dominant species as a function of pH and potential
  - We need to work at a pH and potential at which both species are soluble.

$$3\ HTeO_2^+ + 2\ Bi^{3+} + 18e^- + 9H^+ \rightarrow Bi_2Te_3 + 6\ H_2O$$

pH 0
E (V) 0.5 - 1

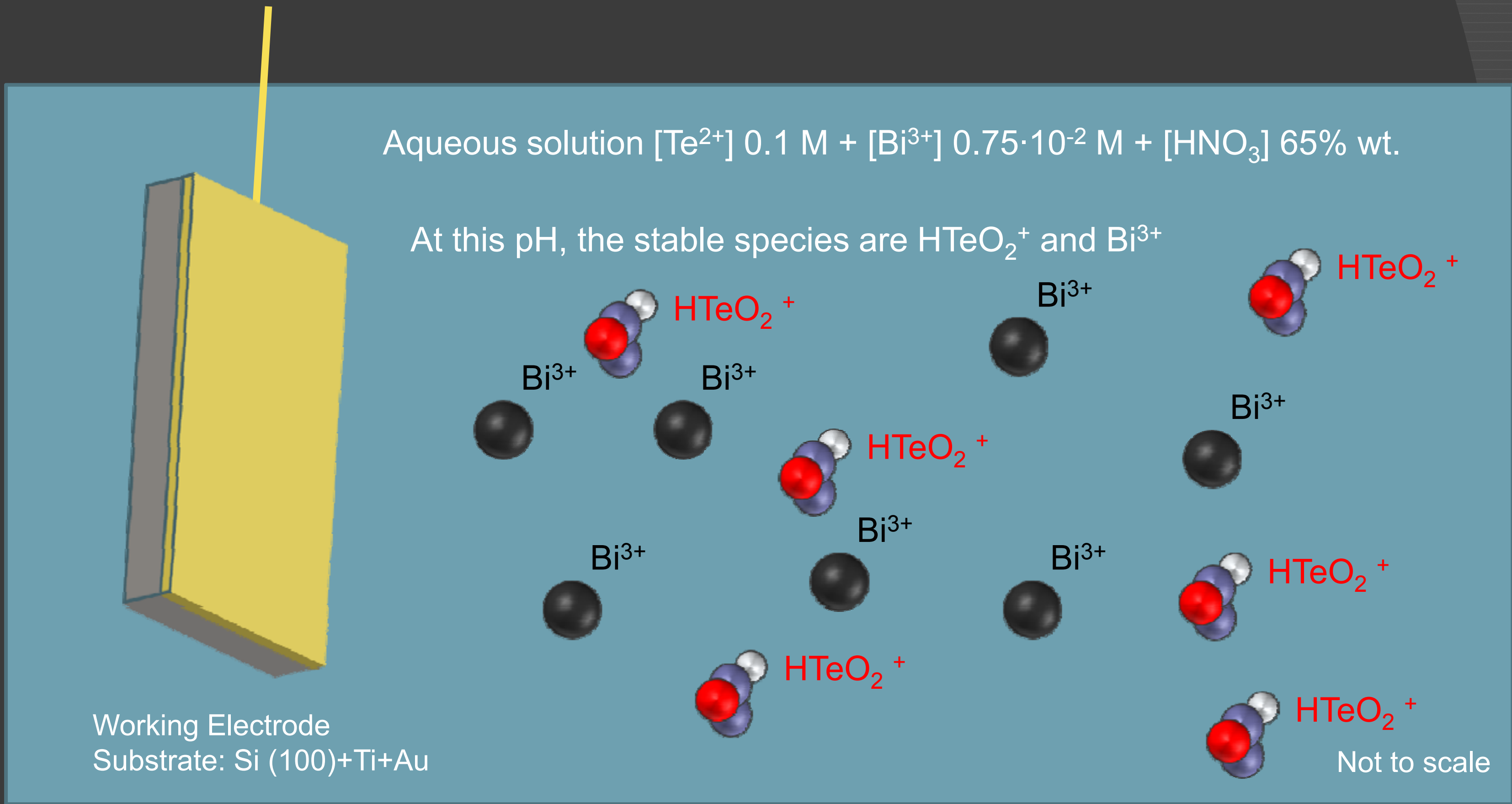


M. Martin-Gonzalez, A.L. Prieto, R. Gronsky, T. Sands and A.M. Stacy, *Journal of the Electrochemical Society* **149** (2002), p. C546.

Electrochemical Deposition: Films Bi_2Te_3

- Electrodeposition Mechanism

$$3\ HTeO_2^+ + 2\ Bi^{3+} + 18e^- + 9H^+ \rightarrow Bi_2Te_3\ (s) + 6\ H_2O$$



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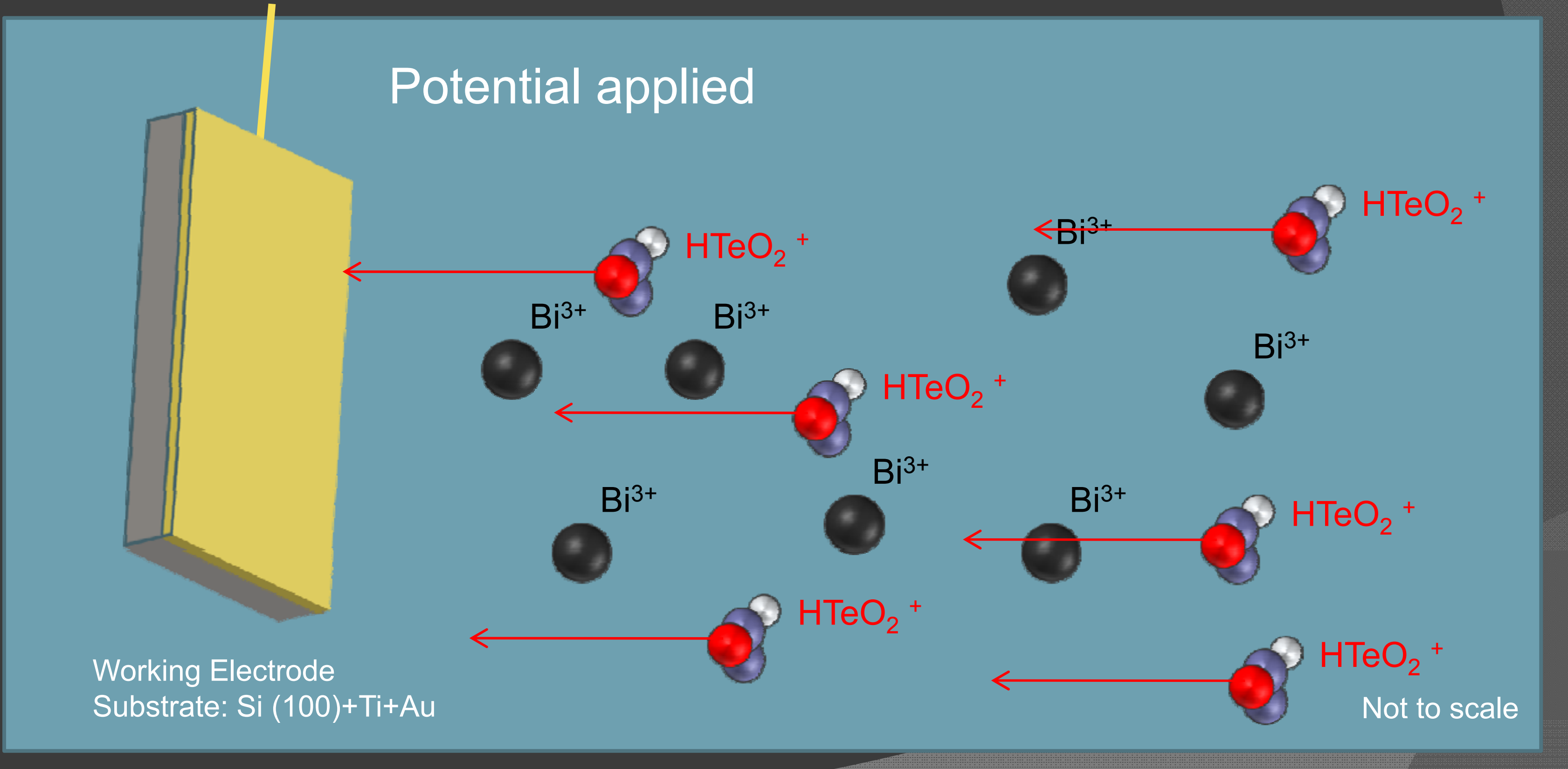
Induced electrochemical reduction $3\ HTeO_2^+\ 12\ e^- + 9H^+ \rightarrow Te^0 + 6H_2O$



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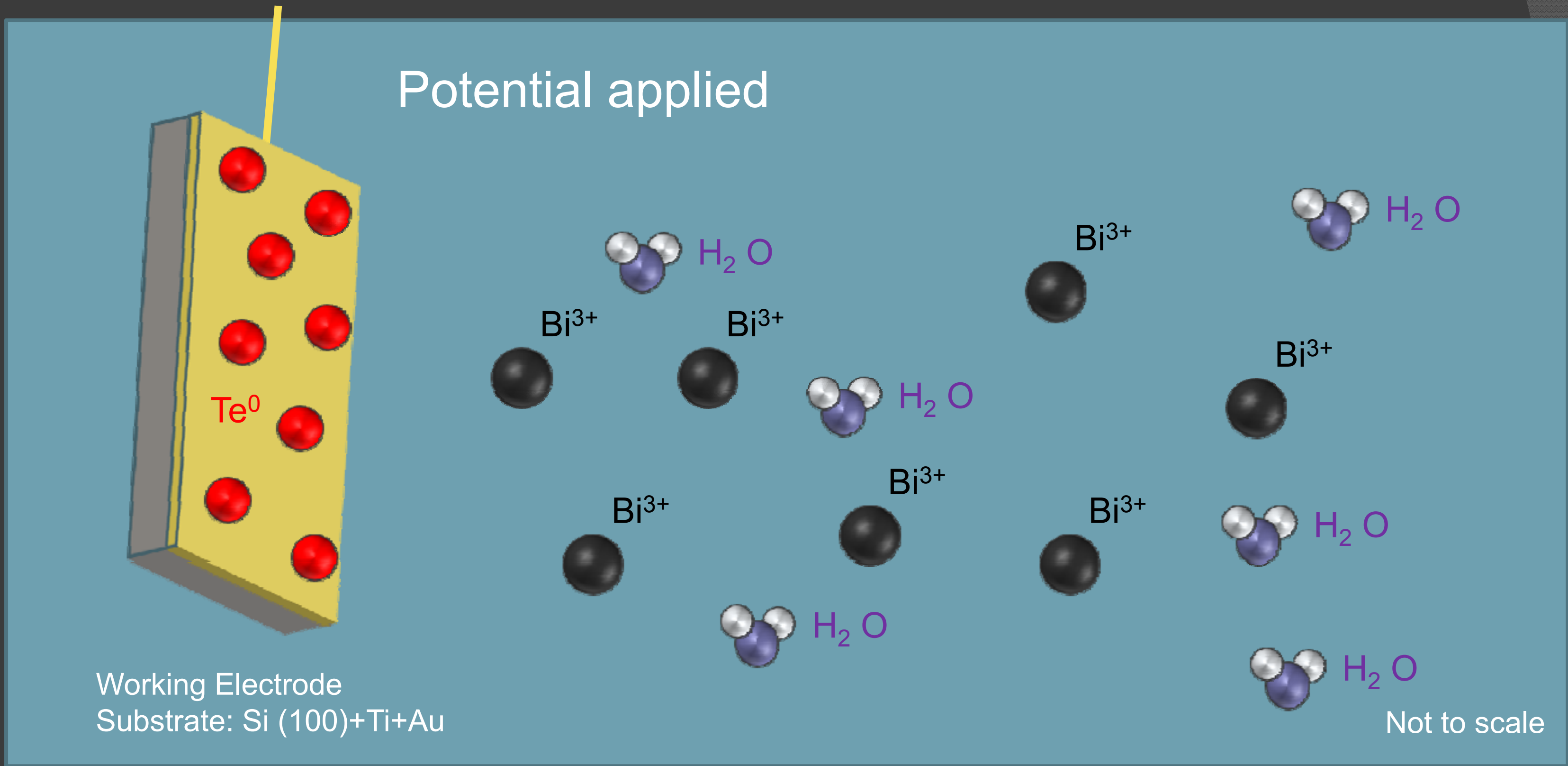
Induced electrochemical reduction $3\ HTeO_2^+\ 12\ e^- + 9H^+ \rightarrow 3Te^0 + 6H_2O$



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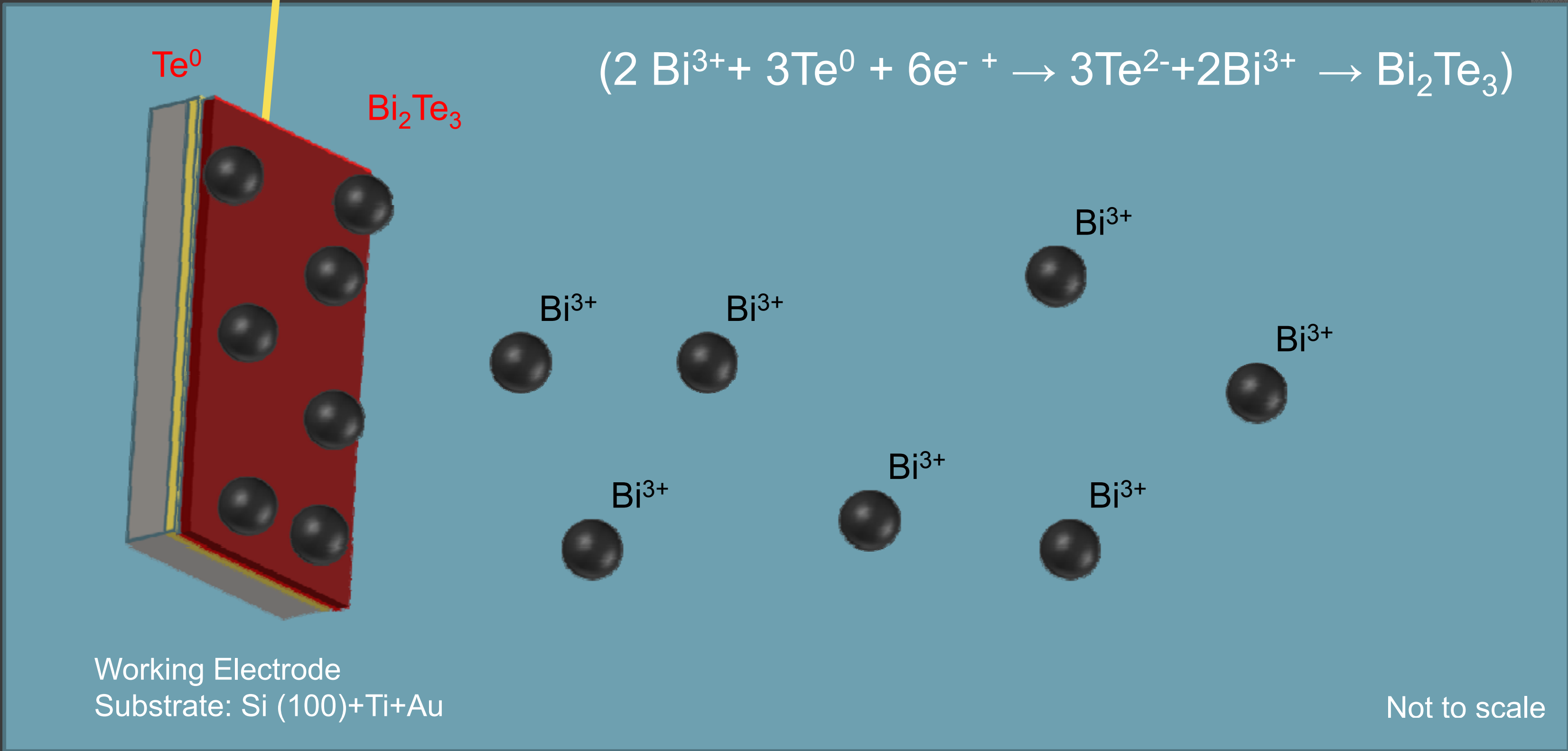
Reaction between the Te^0 at the electrode and the Bi^{3+}



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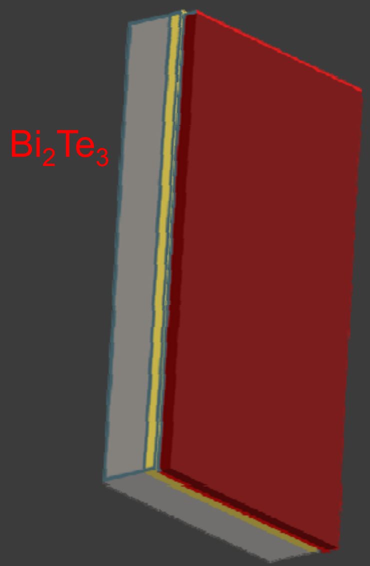

a) $3\ HTeO_2^+ \quad 12\ e^- + 9H^+ \rightarrow Te^0 + 6H_2O$

b) $2\ Bi^{3+} + 3Te^0 + 6e^-\ ^+ \quad \rightarrow\ Bi_2Te_3$

$$3\ HTeO_2^+ + 2\ Bi^{3+} + 18e^- + 9H^+ \rightarrow Bi_2Te_3\ (s) + 6\ H_2O$$

Thickness of the films: Faraday's Law

$$m = Q \cdot M / (F \cdot z)$$

m = mass liberated at the electrode
Q = Charge. We record I vs t, thus $Q = \int I\, dt$
M = molar mass
F = Faraday's 96485 $C \cdot mol^{-1}$
z = "valence" of the reaction, 18 in our case

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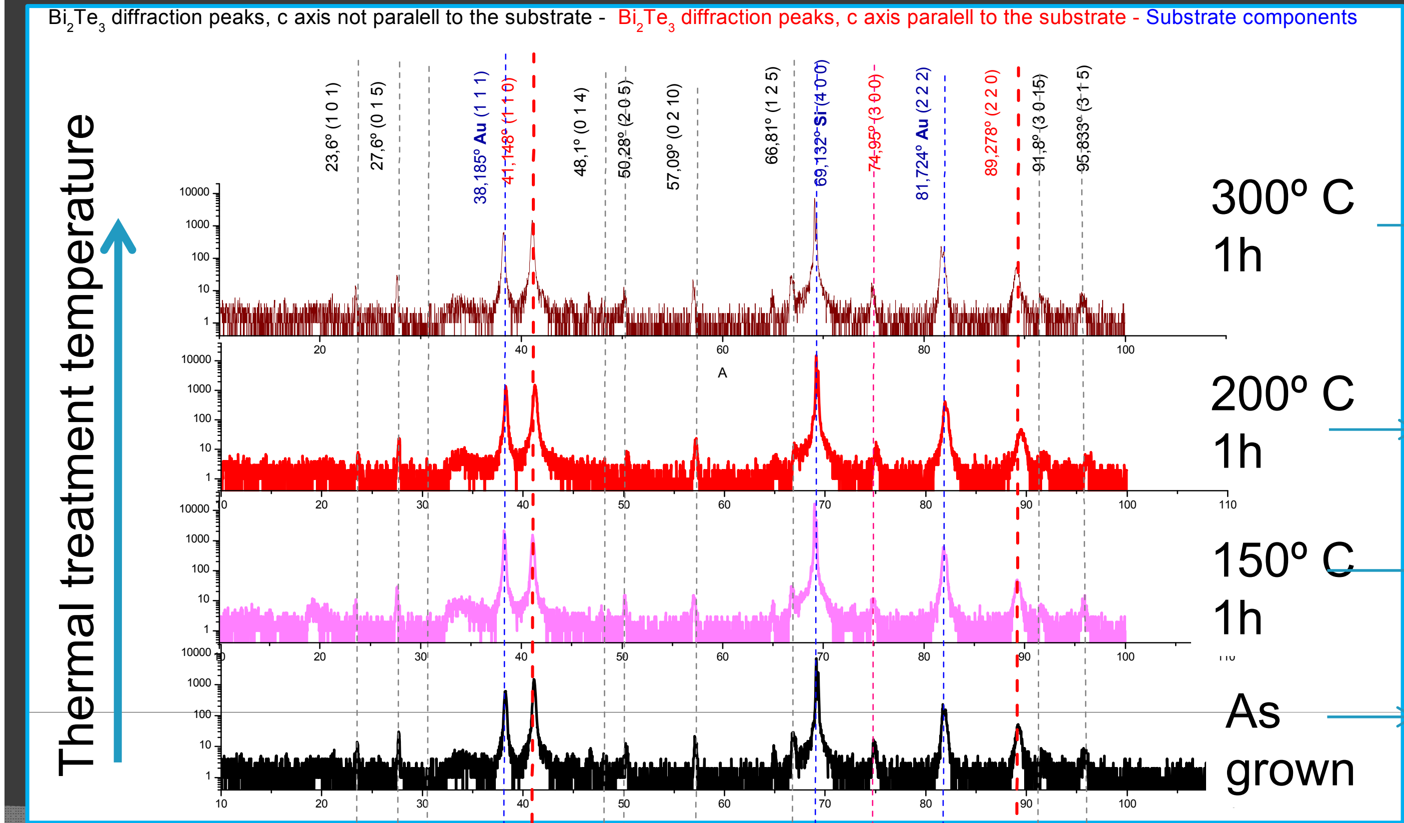
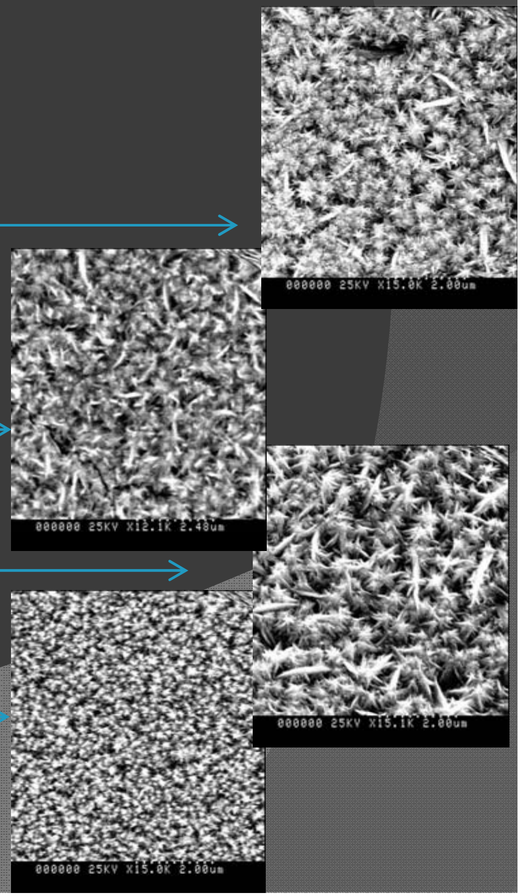
Electrochemical Deposition: Films Bi_2Te_3

- Optimization of films grown by electrochemical deposition.
  - Final Aim: Preferential crystal orientation
    - Higher thermoelectrical efficiency: c-axis paralell substrate
  - Best results: 60 mV applied potential
  - Thermal treatments to improve crystal orientation.

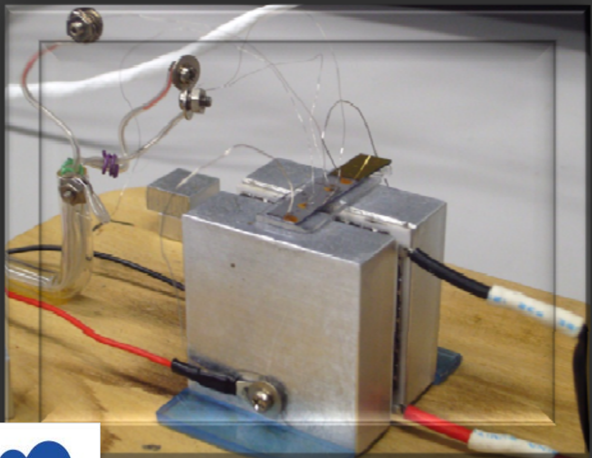


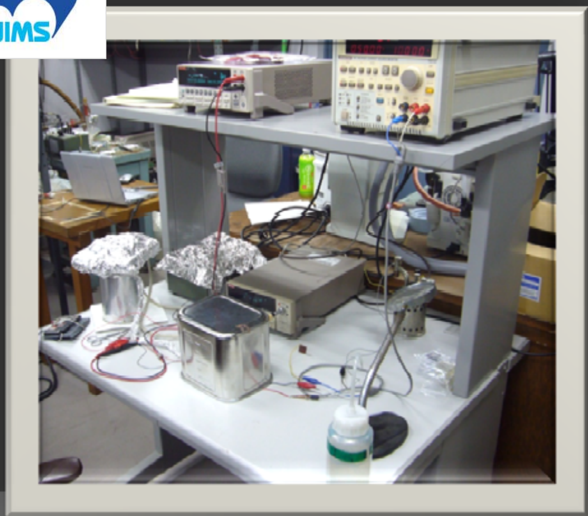


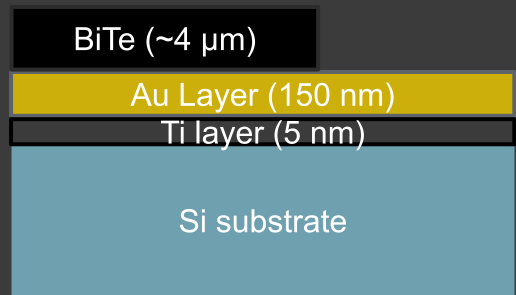
XRay Diffractogram of a Bi_2Te_3 film grown by electrochemical deposition for 2 hours at -60 mV applied potential (resp Ag/AgCl)

Electrochemical Deposition: Films Bi_2Te_3

- Preliminar measurements
  - Four probe conductivity

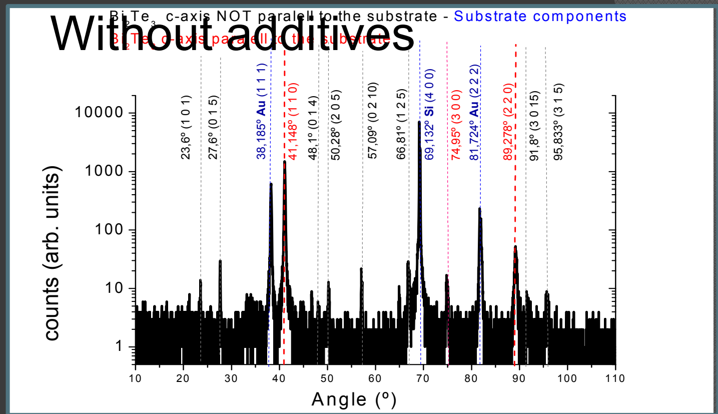


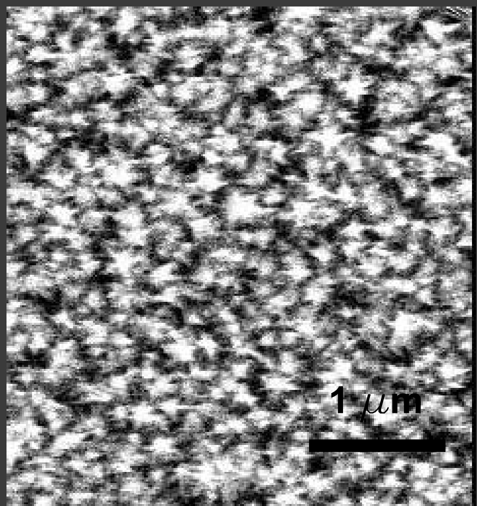




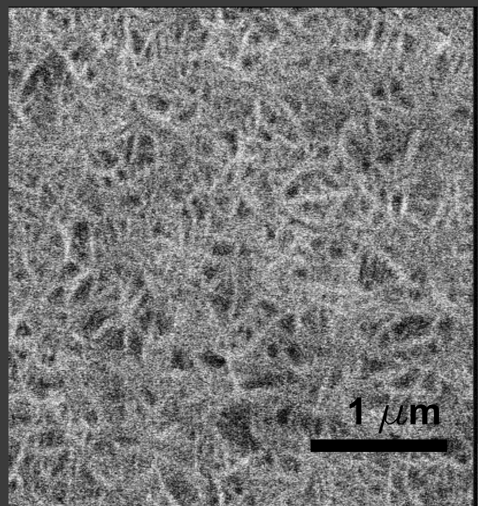
Electrochemical Deposition: Films Bi_2Te_3

- Further optimizations
  - Use of aditives
    - Problems with adhesion
    - Different substrates used (Au, Pt, Ag…)
    - Different concentrations
    - Preferential crystal orientation
      - C-axis paralell to the substrate

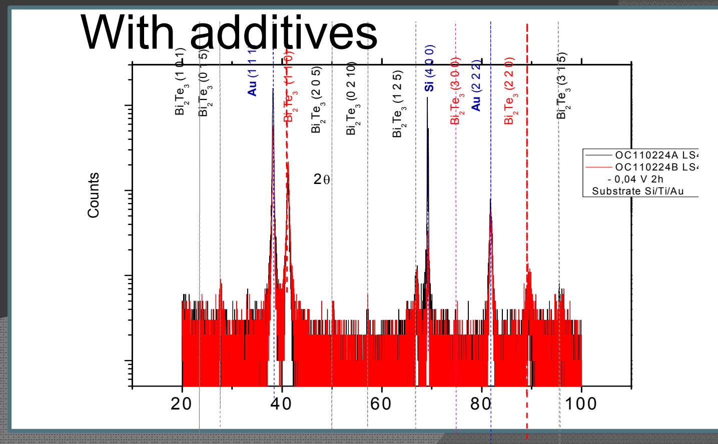




Without additives

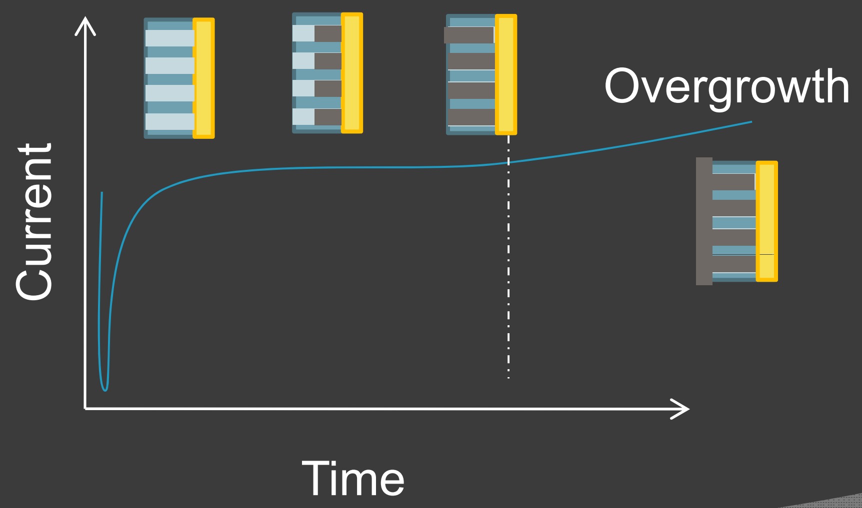


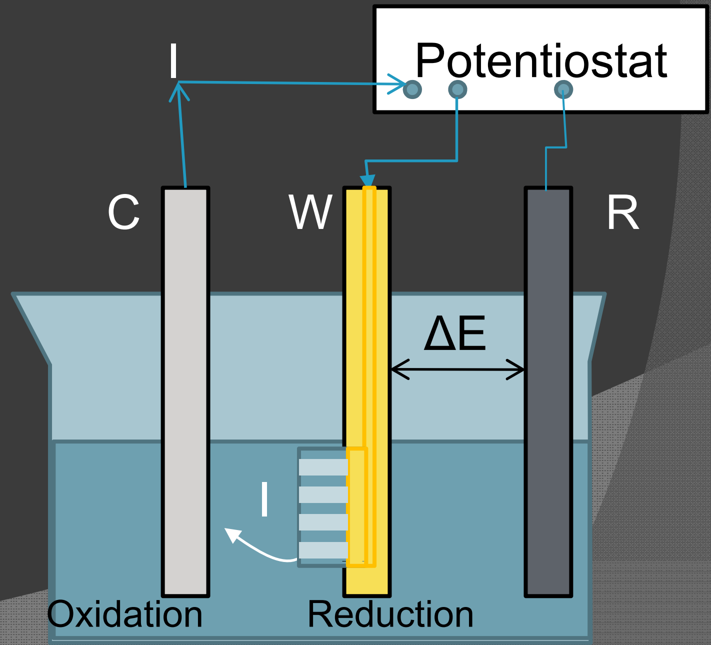
With additives



Electrochemical Deposition: Nanowires

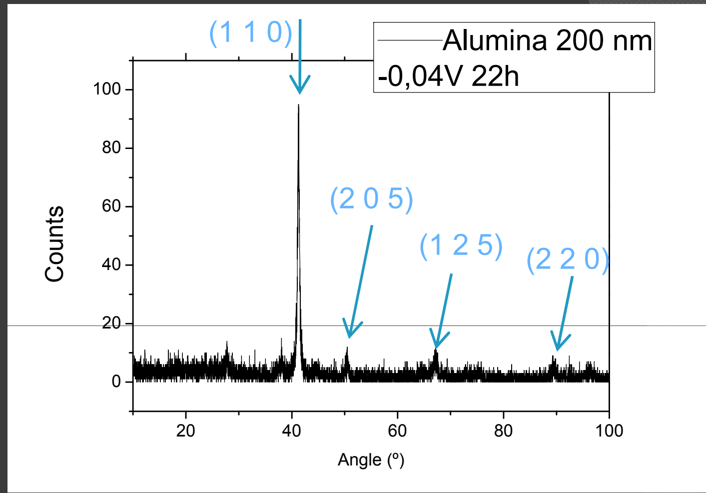
- Matrix: Anodic porous alumina
  - Fabrication process in the laboratory. Also commercial available
  - Hexagonal ordering of the pores, tunabilityof the pore diameter (~ 9 – 300 nm), porosity up to 50%
  - Electrical insulator and Thermal insulator
    - E_{gap} = 7.4 eV
    - κ = 1.7 W / m·K at 300 K
  - Electrodeposition until overgrowth

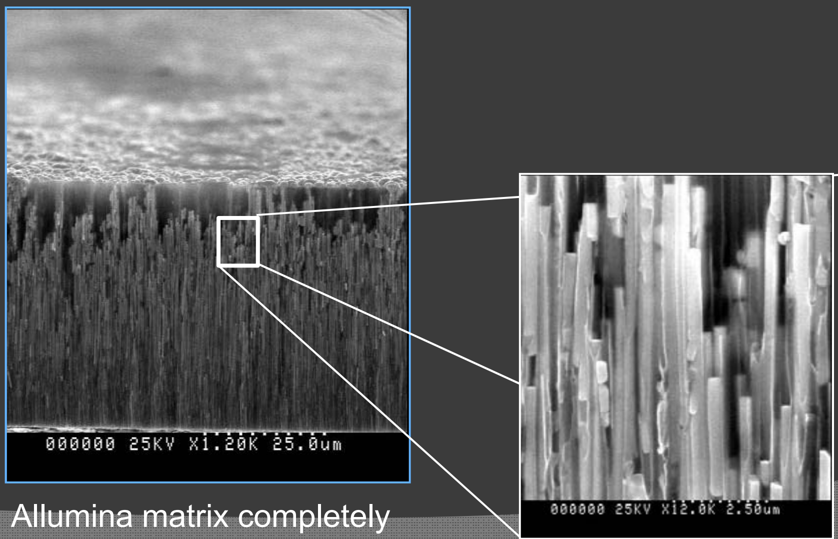




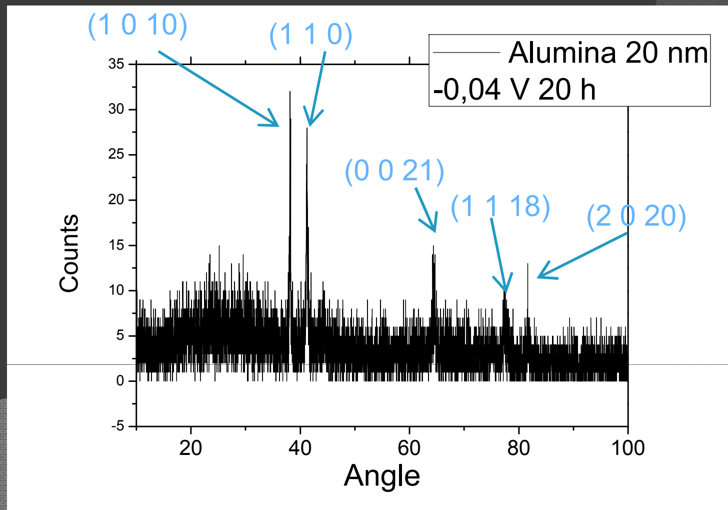
Electrochemical Deposition: Nanowires

- Bi_2Te_3 wires from 200 to 20 nm diameter.
  - Characterization techinques
    - Actually: SEM, XRD
    - Future:
      - AFM electrical measurements
      - Photoacoustic techniques
        - Thermal conductivity
      - Raman Microscope.
      - External collaborations.





Allumina matrix completely filled. Almost no overgrowth.



Conclusions and Future Work

- Films of Bi_2Te_3
  - Good reproducibility of the films
  - C-axis paralell to the substrate.
- Nanowires of Bi_2Te_3
  - Not direct transference between film growth and nanowires.
    - Ionic diffusion different in the nanopores.
  - Room for improvement
    - ECALE, pulsed deposition, additives, etc.
  - Modification of experimental setups available to measure their properties is in process.

THANK YOU