Electrochemical Deposition of Thermoelectric Nanowire Arrays on Silicon

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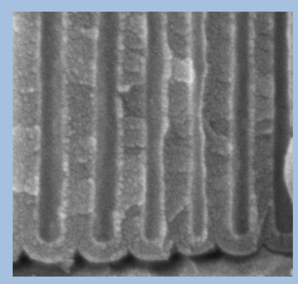
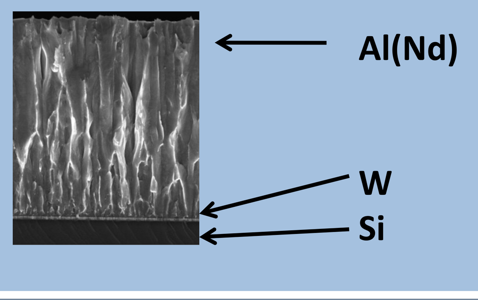
SAND2012-5933C

Thermoelectric (TE) nanowires have great promise, but by large they are not ready to be incorporated into real devices. This is mainly due to a lack of compositional and structural control that leads to poor TE performance. TE nanowire arrays deposited directly onto Si have benefits both for characterization (uniformity, controlled length) and future device integration. This poster describes our recent work in fabricating arrays of Bi_2Te_3 and $Bi_2(Te,Se)_3$ nanowires directly on Si substrates.

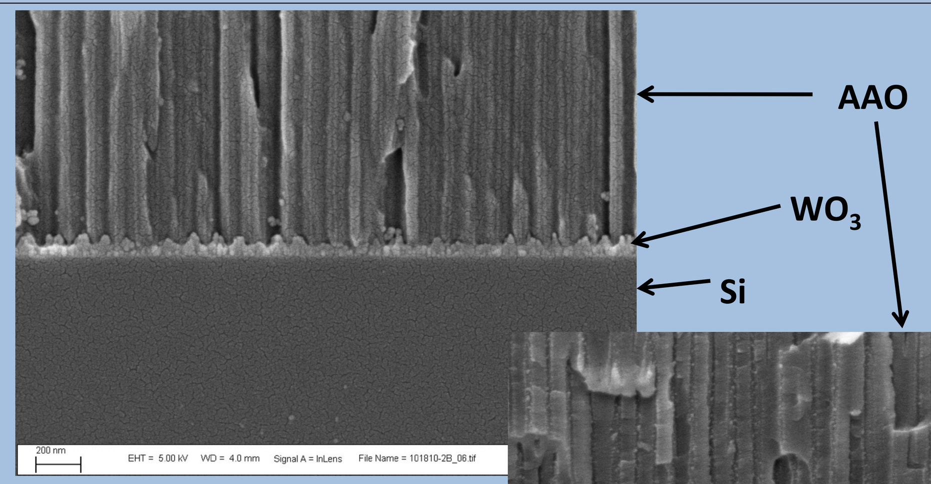
Fabricating anodic aluminum oxide (AAO) templates on Si:

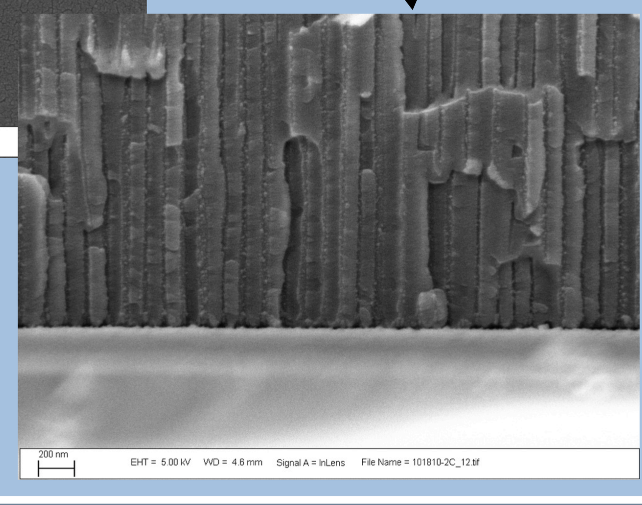
- Pores in AAO tend to have a "test-tube" shape; open at one end with an oxide cap at the other end
- This barrier oxide interferes with electrodeposition
- Attempts to form AAO directly on a conductive substrate (Au, Si, ITO…) tend to delaminate
- Using a valve metal layer (e.g. W, Nb, Ta) under the Al alleviates this problem





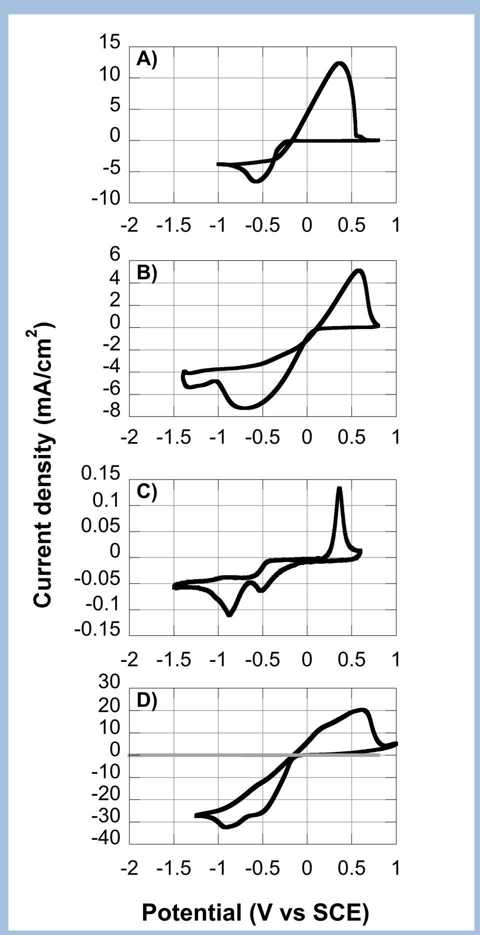
- The W oxidizes to form a "plug" of WO_3 at the pore bottom
- WO_3 "plugs" can be selectively etched, leaving pores open at both ends
- With the pore bottoms opened, it it is possible to electrodeposit nanowire arrays directly on the Si
- By carefully controlling the film stress, we have made AAO with pores up to ~10 µm depth





AAO on Si before (top) and after (bottom) removal of WO_3 plugs from pore bottoms.

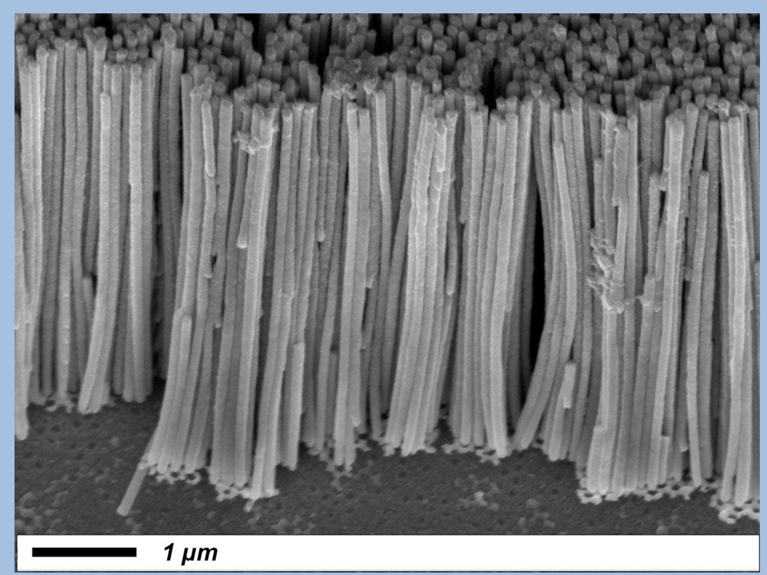
Electrodeposition of $Bi_2(Te,Se)_3$ on Si: Pulsed galvanostatic ECD from a non-aqueous (DMSO) bath

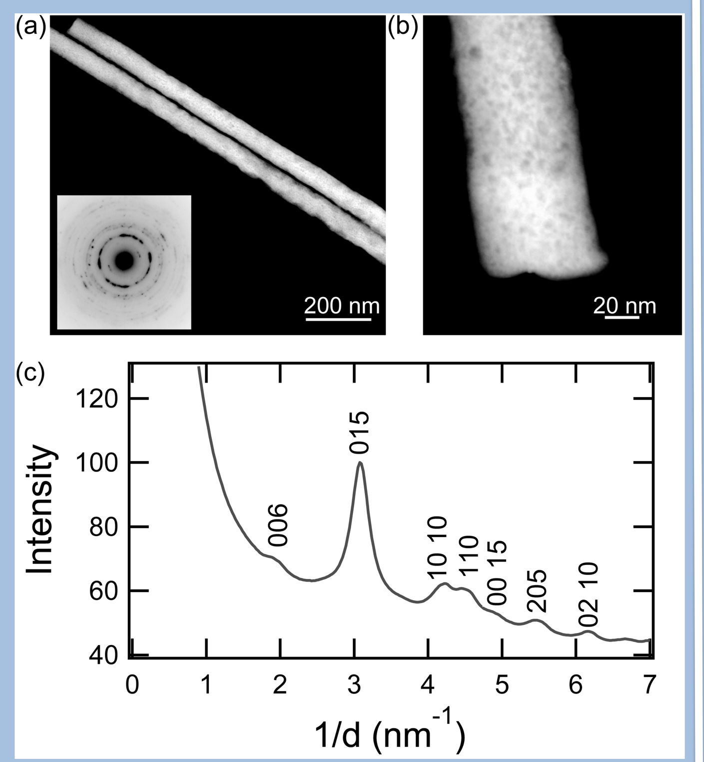


CV scans of the bath components (with 0.1 M $KClO_4$ supporting electrolyte) at 10 mV/s on Pt disk electrodes. A) 80 mM $Bi(NO_3)_3$. B) 60 mM $TeCl_4$. C) 1 mM SeO_2. D) Full bath (80 mM $Bi(NO_3)_3$, 60 mM $TeCl_4$, 1.1 mM SeO_2 and 0.1 M $KClO_4$) in black, and background (0.1 M $KClO_4$) in gray.

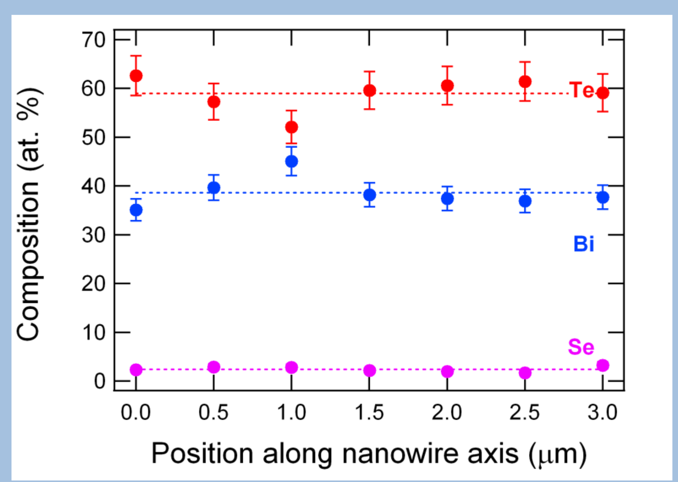
Deposition at −10 mA/cm² with 500 ms pulses (1 s off) from an 80 mM $Bi(NO_3)_3$, 60 mM $TeCl_4$ and 1.1 mM SeO_2 bath yields nanowires of nominal composition $Bi_2(Te_{0.95}Se_{0.05})_3$

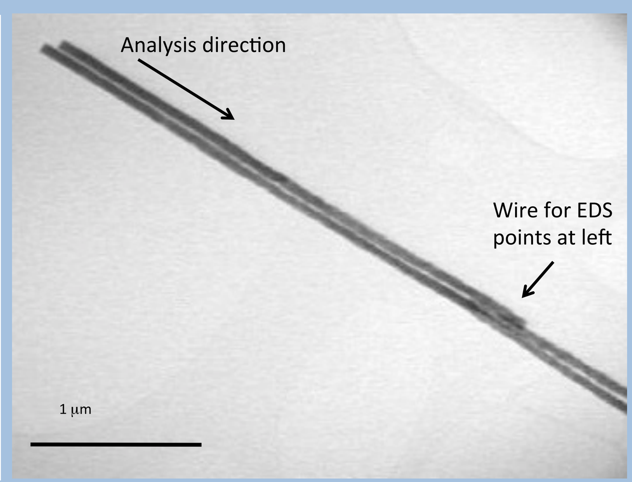
SEM image of $Bi_2(Te,Se)_3$ nanowires on Si. These nanowires are ~75 nm in diameter and ~ 5 µm long.



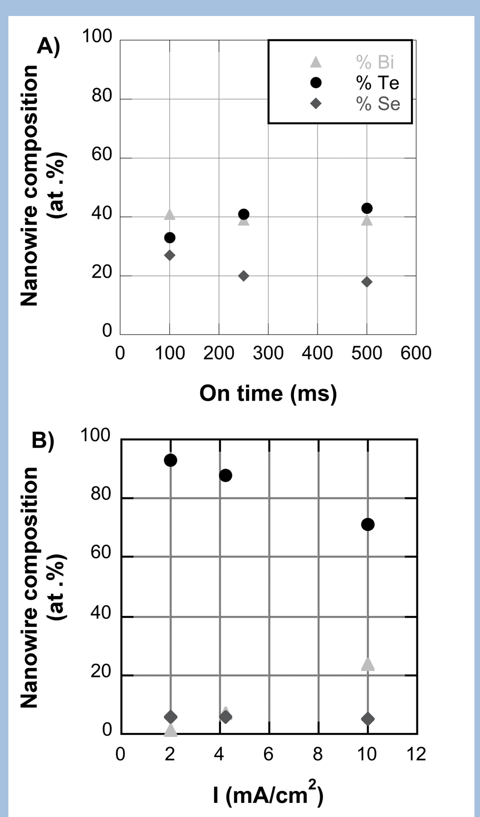


HAADF STEM images of $Bi_2(Te,Se)_3$ nanowires showing a polycrystalline structure. The inset in (a) is the SAED pattern for these nanowires, which confirms that the nanowires are polycrystalline. (c) The azimuthal average of the SAED pattern in (a) is indexed and indicates that the material has the Bi_2Te_3 tetradymite crystal structure.



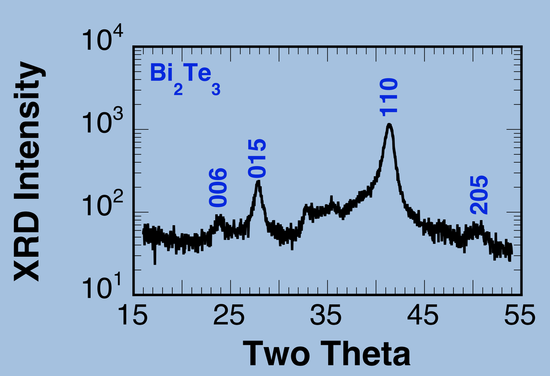


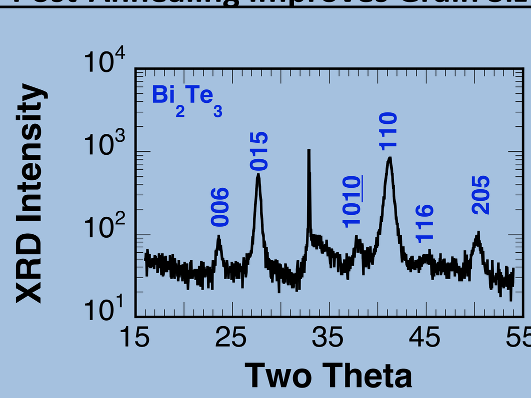
Composition along the length of an individual nanowire measured by STEM/EDS. Dotted lines show the overall average composition of a number of nanowires.

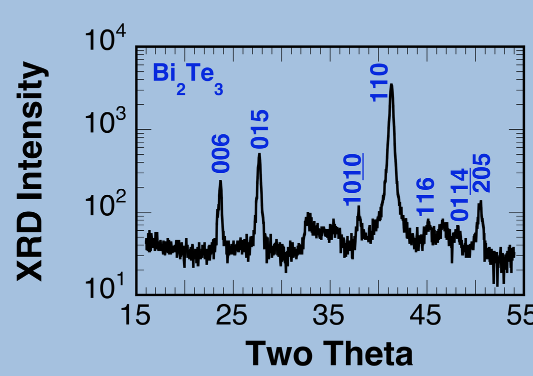


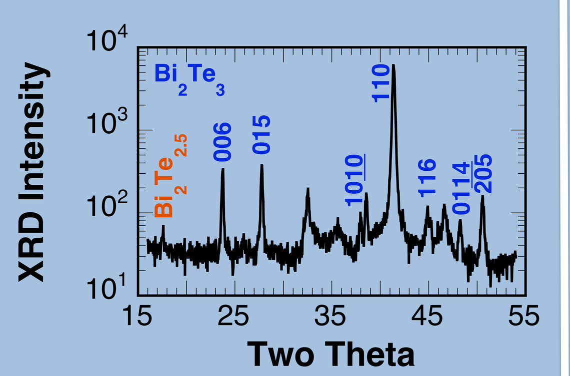
Nanowire composition is influenced by bath, pulse time and current density. A) Influence of "on" time on the nanowire composition (2 mA/cm² in a bath with 80 mM Bi^{3+}, 40 mM Te^{4+} and 1.2 mM Se^{4+}). B) Influence of current density on the nanowire composition (500 ms "on" time in a bath with 80 mM Bi^{3+}, 80 mM Te^{4+} and 1.0 mM Se^{4+}).

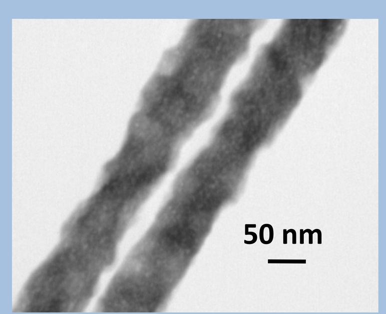
Controlling Crystallinity: Post-Annealing Improves Grain Size and Orientation *all samples annealed for 30 minutes in 3% H_2/Ar*



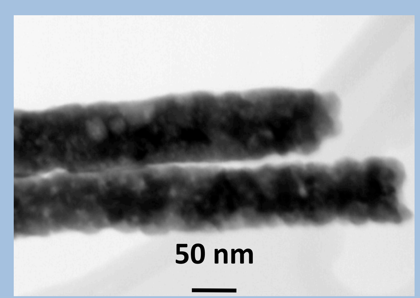




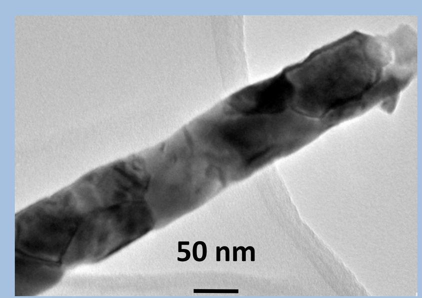




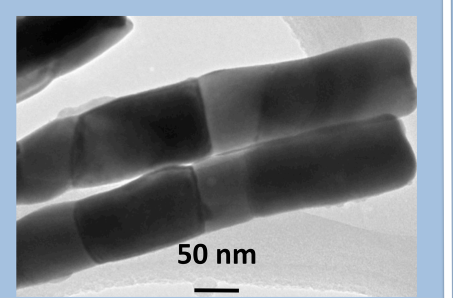
As deposited
5-10 nm grains



200 °C anneal
20-40 nm grains



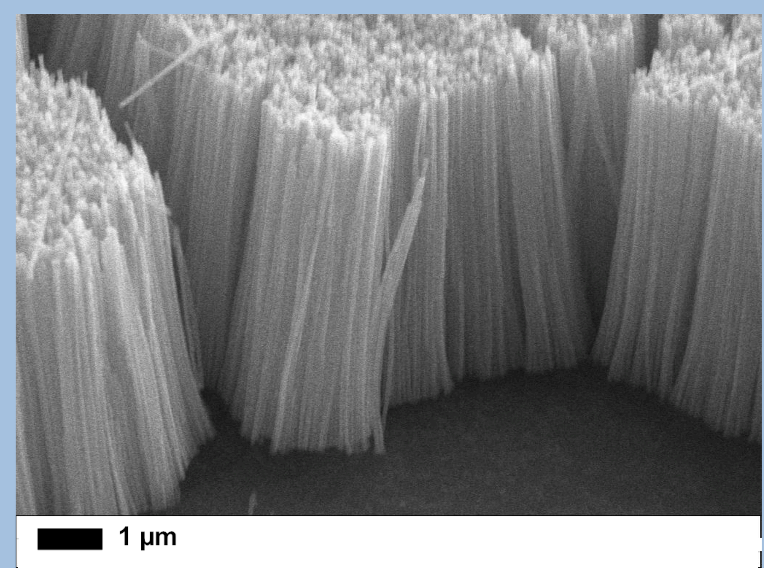
300 °C anneal
grains 56 x 98 nm to 250 nm x full width



400 °C anneal
grains 74 x 145 nm to 320 nm x full width

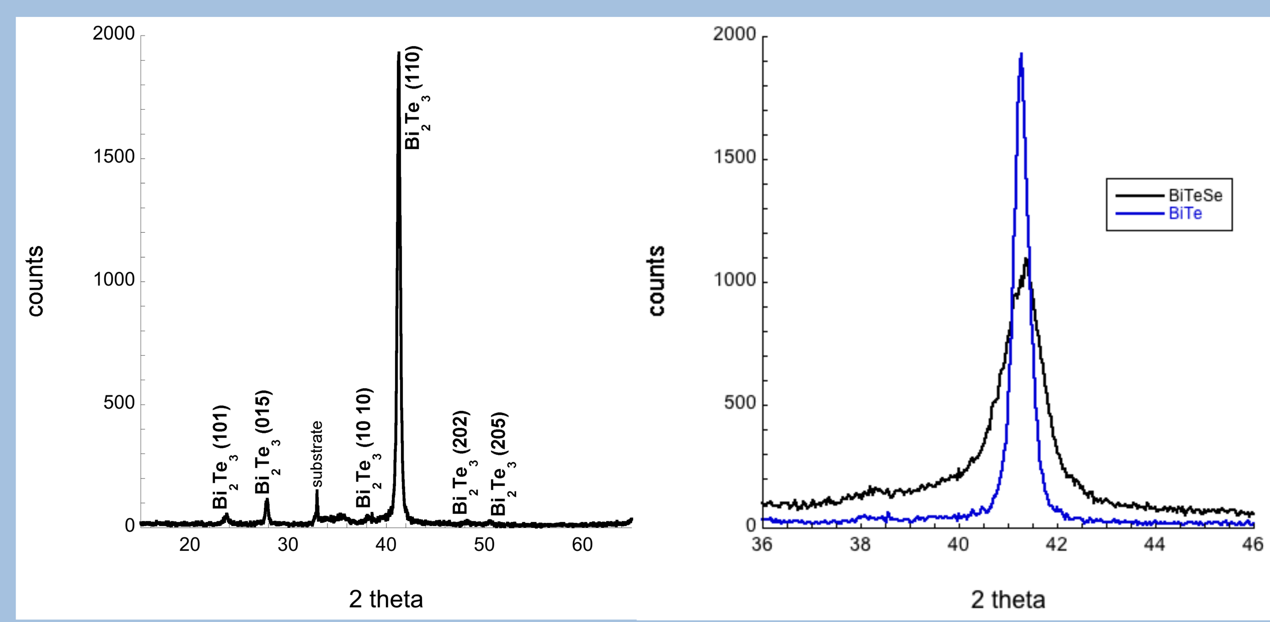
Electrodeposition of Bi_2Te_3 on Si: Pulsed galvanostatic ECD from an aqueous bath

Deposition at −20 mA/cm² with 100 ms pulses (0.9 s off) from 6 mM $Bi(NO_3)_3$ and 7 mM Na_2TeO_3 in 0.3 M tartaric acid + 2M HNO_3 yields nanowires of nominal composition Bi_2Te_3



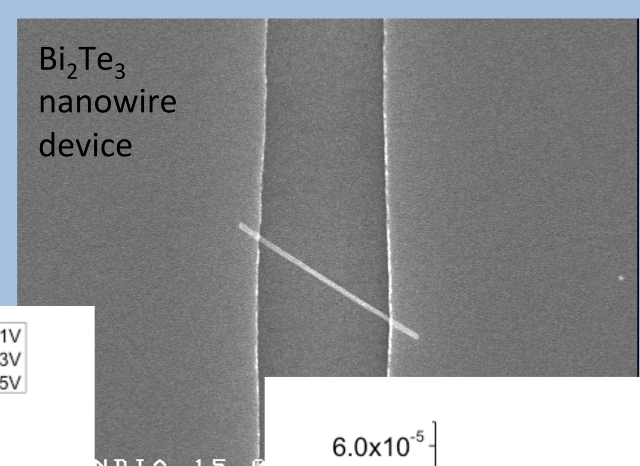
SEM image of Bi_2Te_3 nanowires on Si. These nanowires are ~75 nm in diameter and ~ 6 µm long.

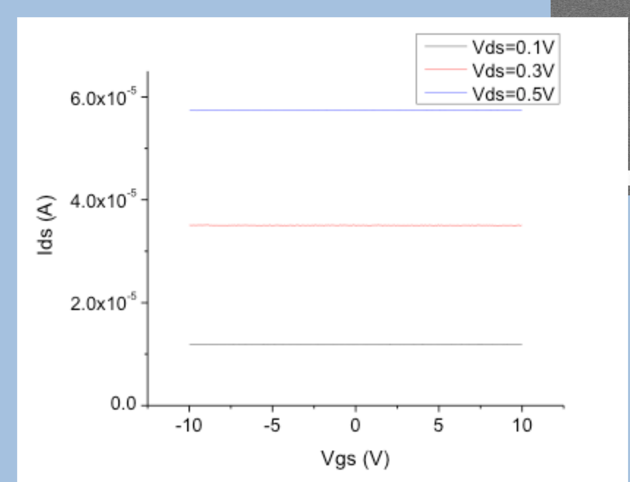
These nanowires are very uniform in length. Pulsed potentiostatic deposition from this bath yielded a less uniform length distribution.

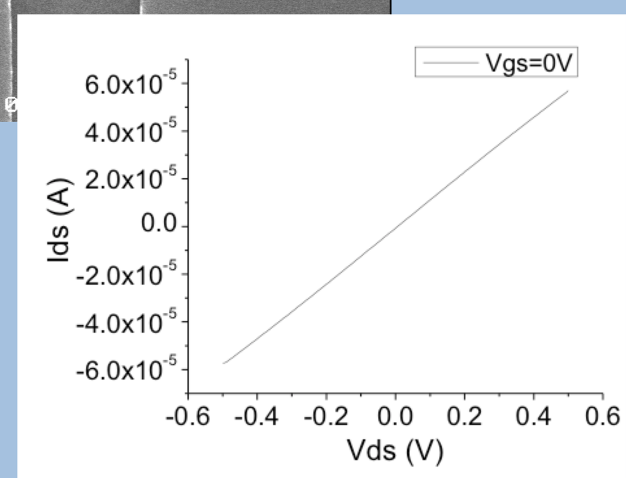


Nanowires from this bath have a more pronounced (110) orientation. Sharper XRD peaks imply a larger grain size than in the $Bi_2(Te,Se)_3$ nanowires

Measurements of single nanowires (annealed at 200 C) show a resistivity of ~1.5×10^{-3} Ω-cm, which is comparable to bulk values.







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