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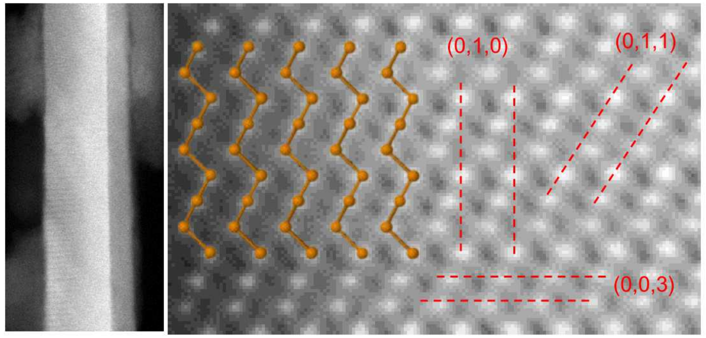

Electrical and Optical Characterization of Ultrathin Tellurium Nanostructures Synthesized by Vapor Phase Deposition

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Outline

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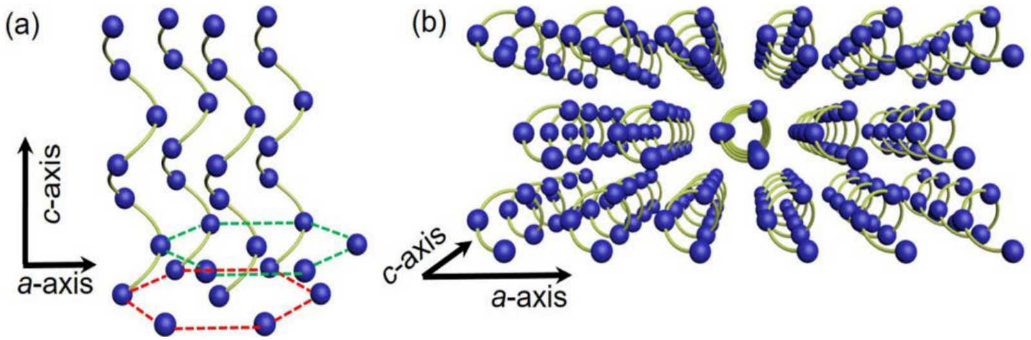
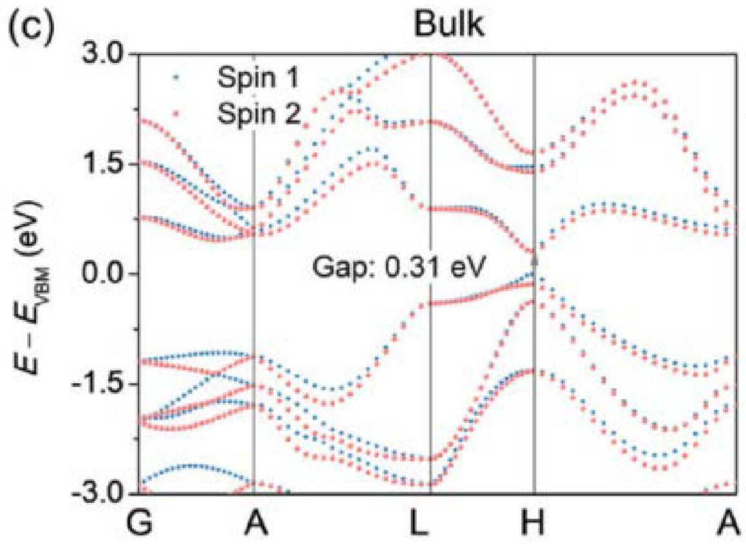
- Motivation: Te from bulk to layered structures
- Previous synthesis approaches
- High temperature synthesis of ultrathin Te nanostructures
- Structural, electrical, and optical characterization
- Conclusions

Bulk Tellurium

- 1D helical chains of Te atoms staked together on 2D hexagonal plane
- Covalent bond between neighboring atoms in the same chain
- van der Waals type bond between neighboring atoms across the chain

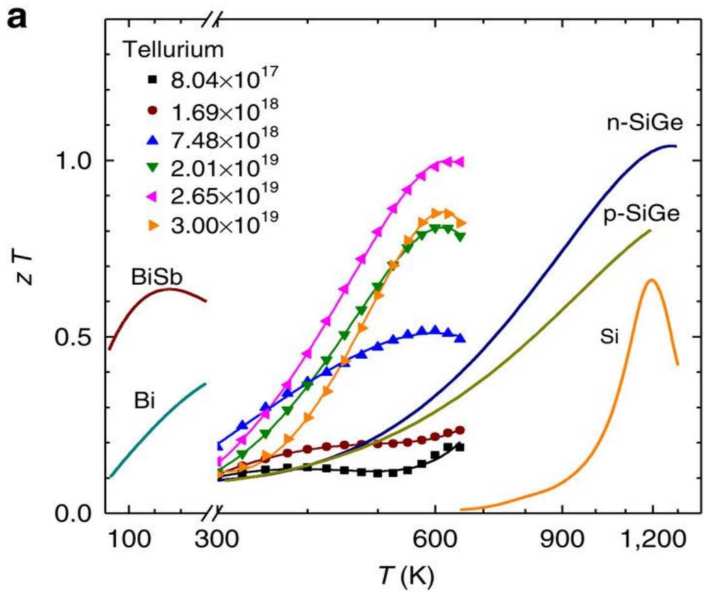




J. Qiao et al. Science Bulletin 63 (2018) 159–168

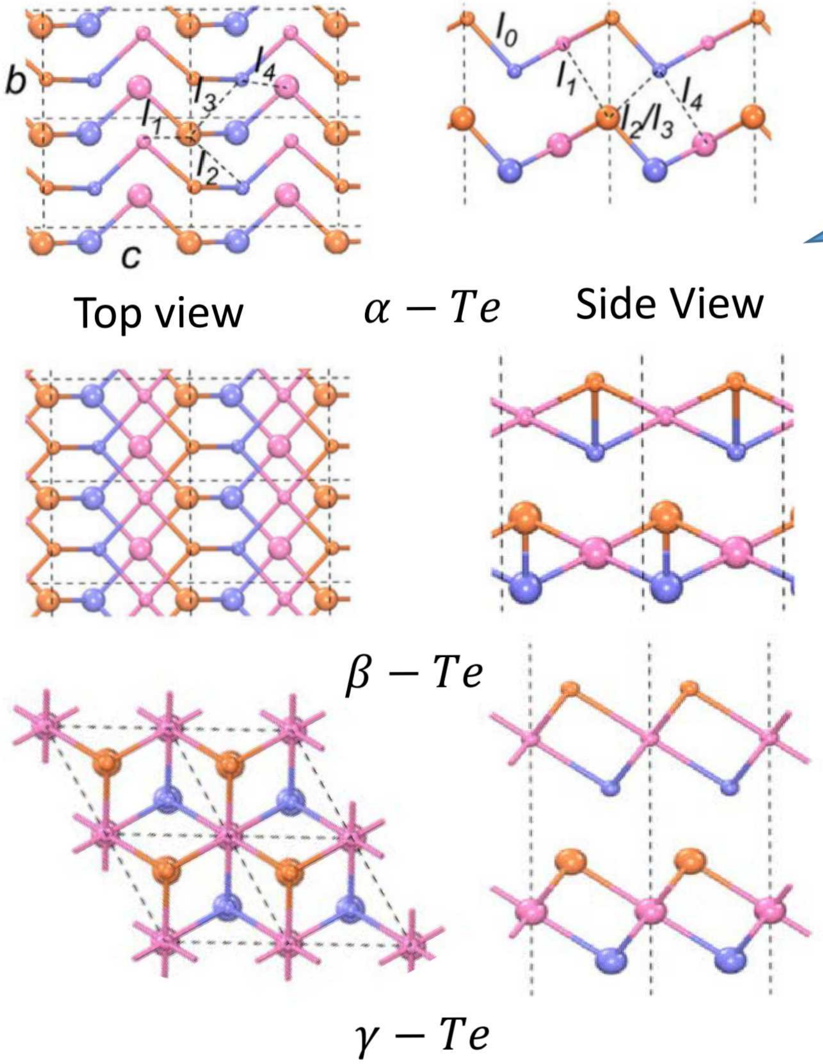
Nearly direct bulk band gap of 0.33 eV

- Te exhibits high thermoelectric performance in bulk
- Several Te based compounds are excellent thermoelectric materials e.g. PbTe



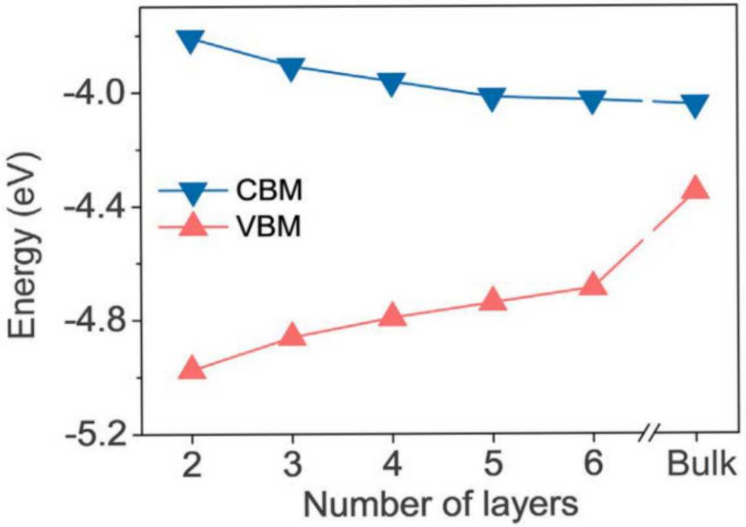
Lin, S. *et al*. *Nat. Commun.* 7:10287 10287 (2016).

Layered Structure of Tellurium



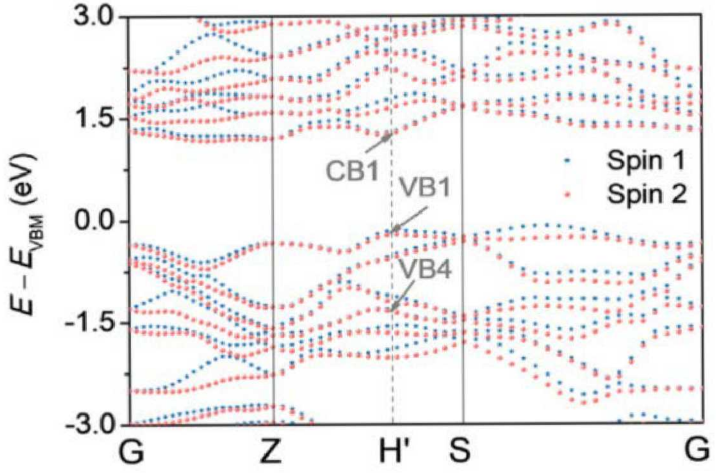
- Unique crystal structure allows to synthesize Te in 1D and 2D form
- 2D tellurium is equivalent to transition metal dichalchogenides of formula MX_2 (e.g. MoS_2) where M is replaced by Te.

Prediction*: 2D structure of Te (Tellurane) exists in 3 phases: α-, β-, and γ-Te



Tunable bandgap with Te thickness

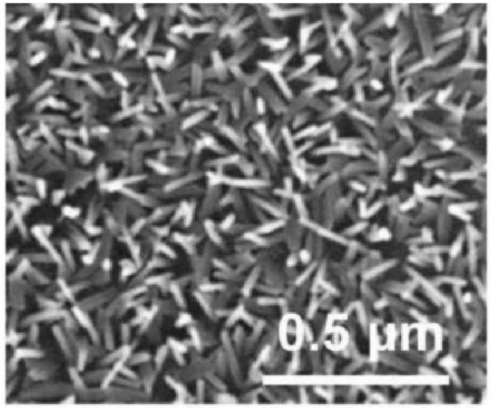
2 Layers of Te



*J. Qiao et al. Science Bulletin 63 (2018) 159–168

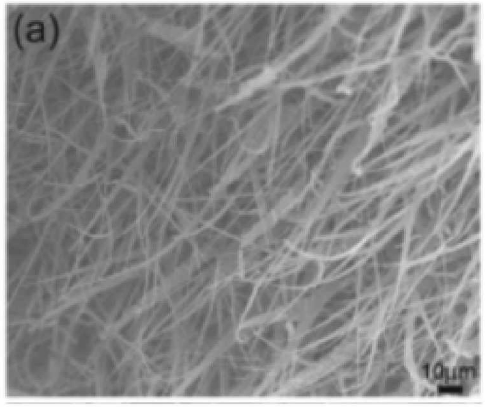
High hole mobility predicted along surface: ~$10^5 cm^2/V.s$

Bottom-up and Top Down Synthesis of Te Nanostructures



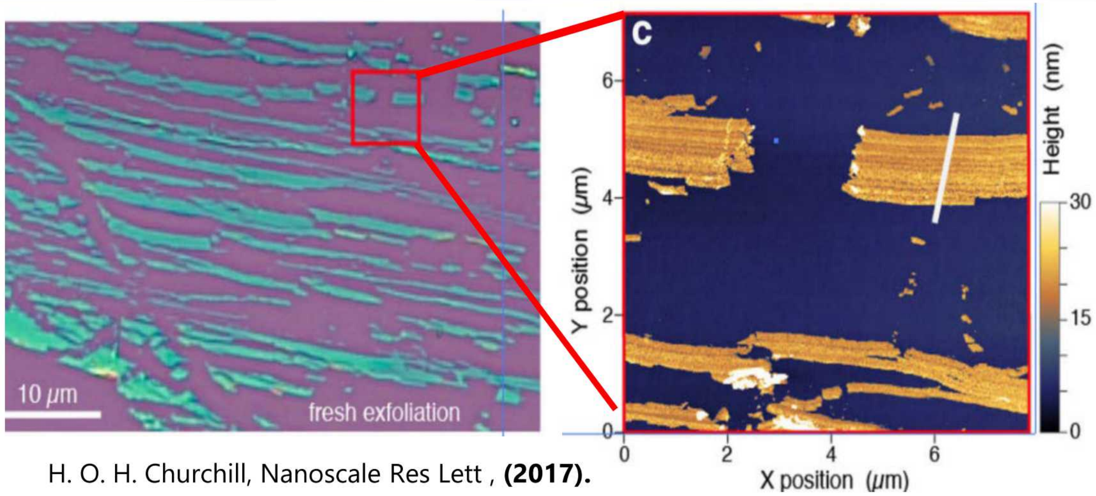
G. Zhou, Adv Mater, **(2018)**.

MBE deposited nanostructures



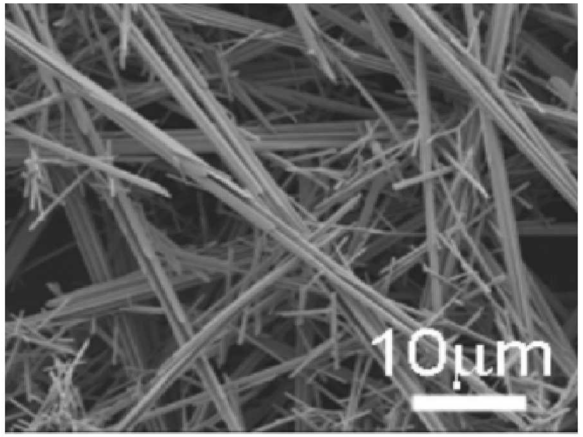
Q. Wang, J. Phys. Chem, **(2007)**.

Vapor phase deposition at 100^oC



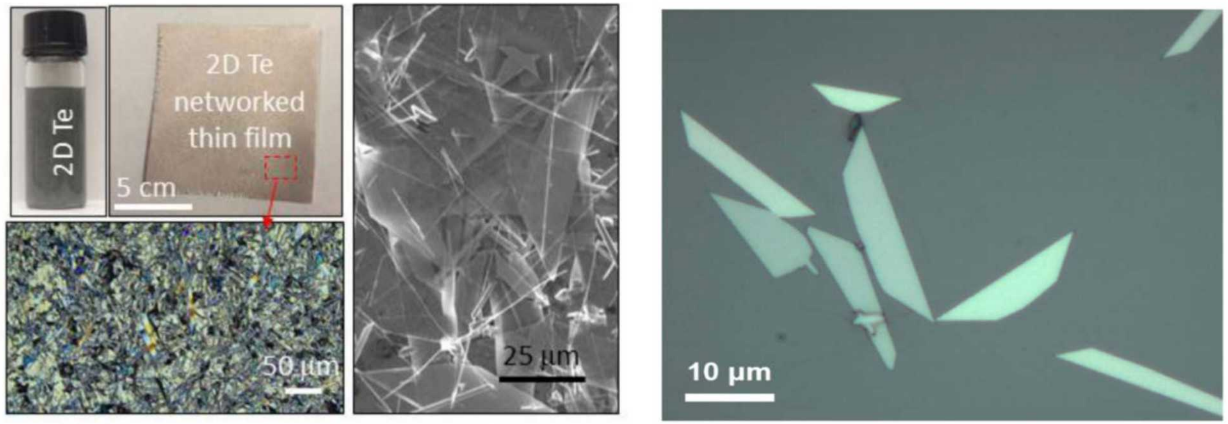
H. O. H. Churchill, Nanoscale Res Lett , **(2017).**

Exfoliation



J. M. Song,, Cryst Growth, **(2008).**

Solvothermal synthesis using TeO2



Y. Wang, Nature Electronics ,**1 (4), 228-236 (2018).**

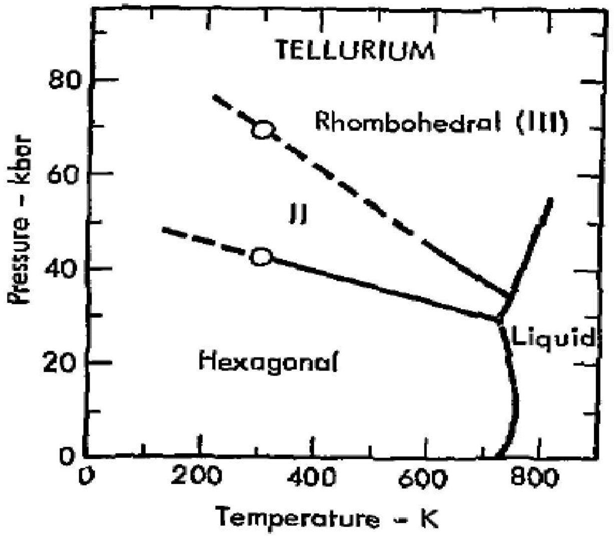
Solution based synthesis using Na_2TeO_3

High Temperature Synthesis of Ultrathin Te Nanostructures

Challenges to synthesize high quality Te nanostructures by conventional methods

- Solution based method usually contaminates the nanostructures by chemical byproducts
- Low temperature MBE/ Vapor phase deposition is susceptible to crystal defects and low quality growth

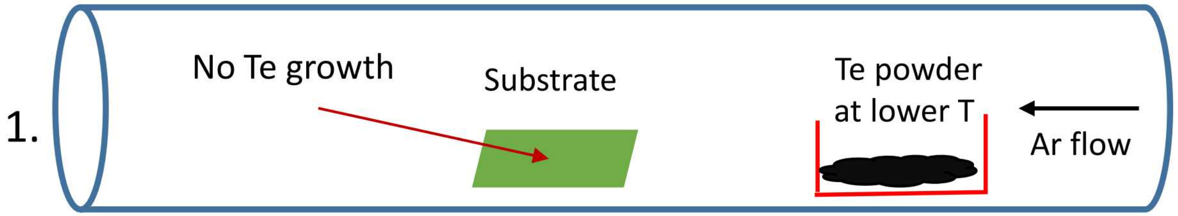
High temperature vapor phase deposition is the desired method to produce high quality Te nanostructures



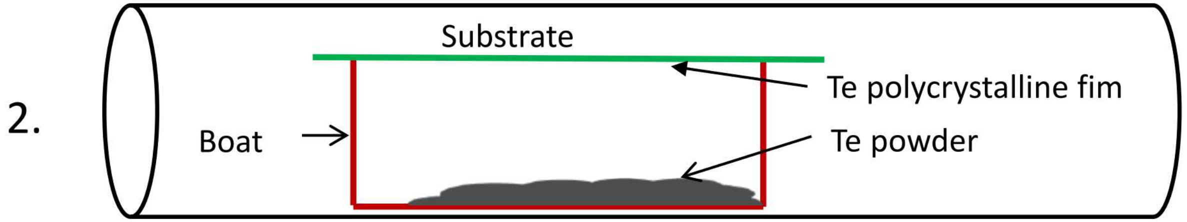
Major Challenge

Te has high vapor pressure/evaporation rate: difficult to control Te deposition and re-evaporation at high substrate temperature

Attempts to grow high temperature Te nanostructures



Substrate temperature > 600 ^{o}C



Substrate temperature > 600 ^{o}C

High Temperature Synthesis of Ultrathin Te Nanostructures

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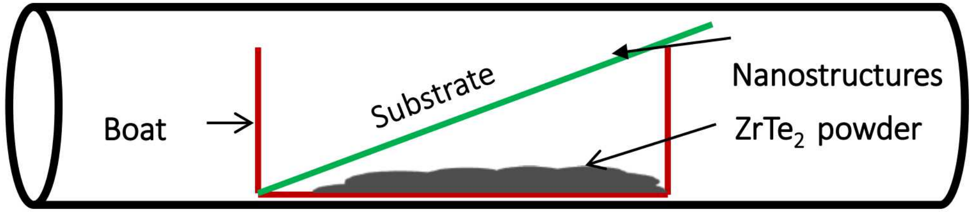
Overcoming challenges

$ZrTe_2$ powder as the Tellurium source



$ZrTe_2$ decomposes slowly at > 450 °C into crystalline Zr and Te gas*

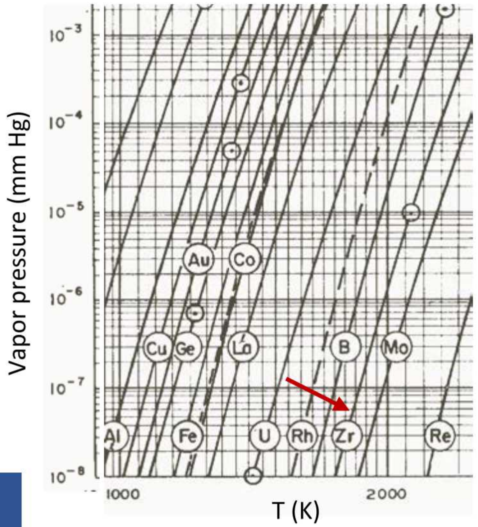
$$ZrTe_2(cr) = Zr(cr, \beta) + Te_2(g),$$

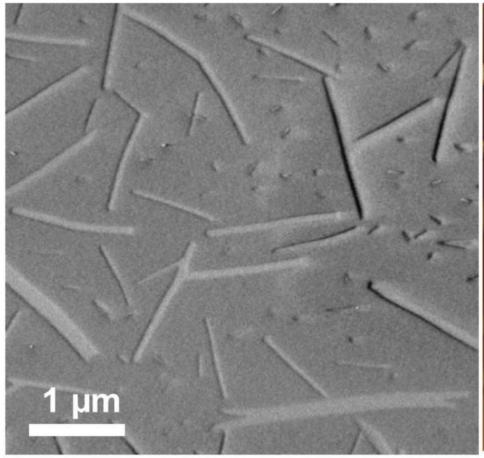
Growth temperature (T_g): **$600 \leq T_g \leq 750$ °C**

*G.K. Johnson, ***17 (1985)***

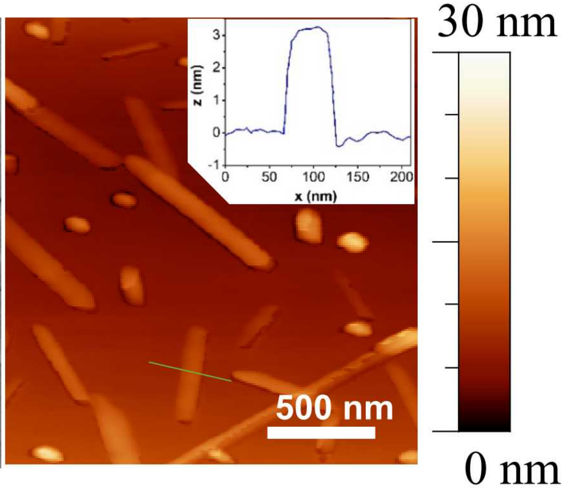
Crystalline Zr evaporate only above 1500 °C

Slow decomposition of $ZrTe_2$ controls the Te vapor pressure at high temperature and containment of Te evaporation by covering with substrate successfully grew Te nanostructures at > 600 °C .





SEM image



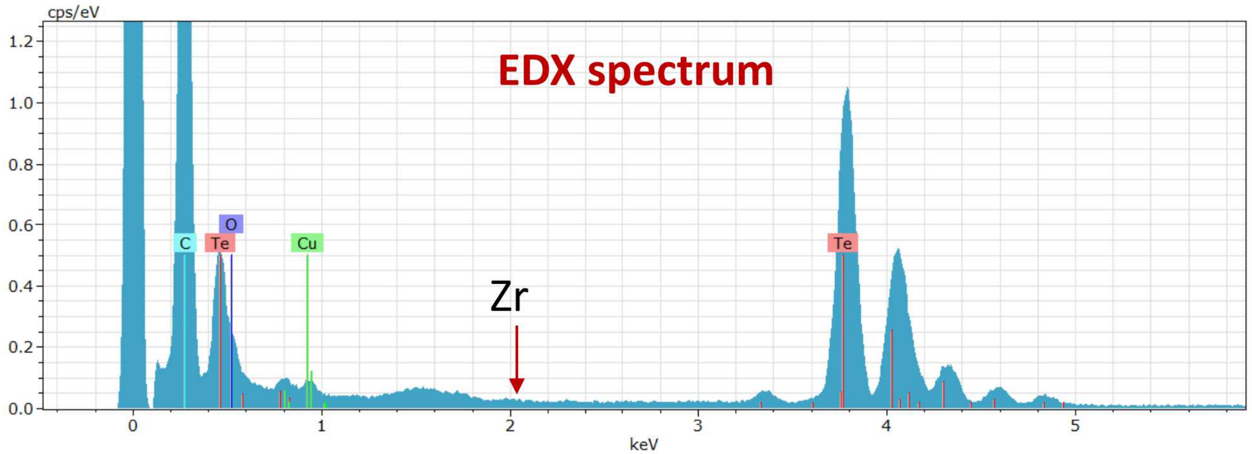
AFM image

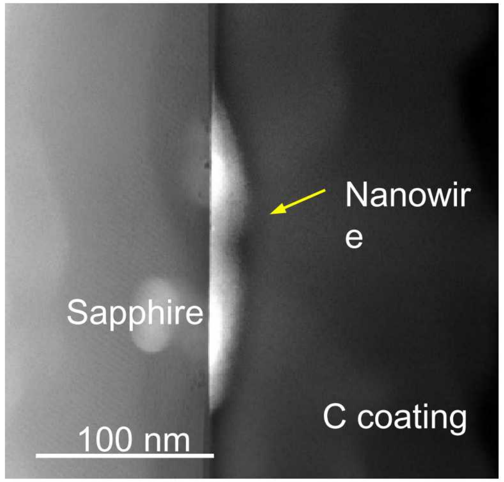
Te nanostructures thickness: down to 3 nm
Width and length: few hundred nm and few μm

Structural Characterizations

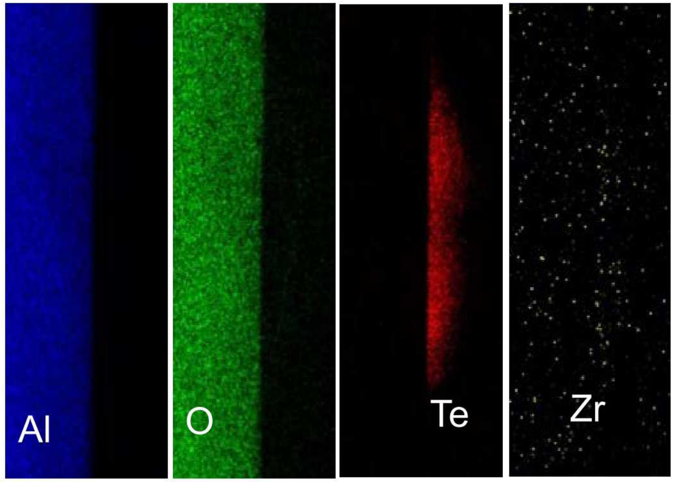
Source material $ZrTe_2$ ➔ Are these nanostructures pure Te?

- Te nanostructures are studied under STEM
- Electron Dispersive X-ray studies could not reveal any presence of Zr on the nanostructures to the detection limit of instrument
- **Nanostructures are pure Te**

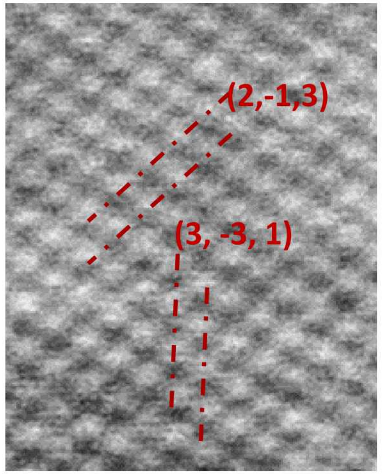




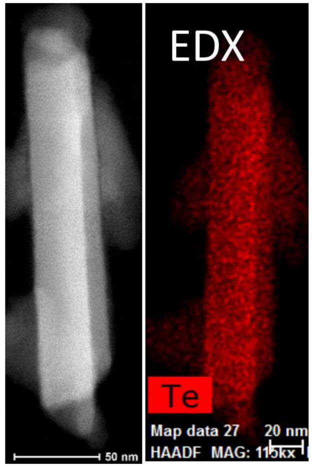
Cross-sectional STEM image of Te Nanowire



Elemental mapping by EDX



HRTEM image of the Te cross section



Top view

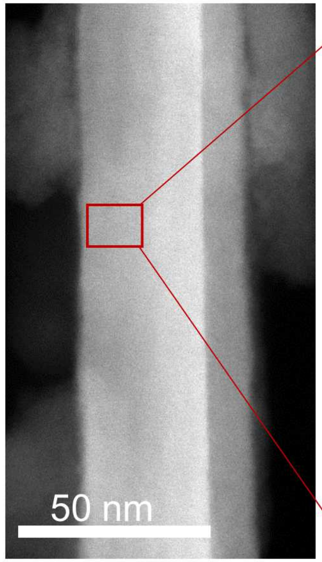
Structural Characterizations

HAADF and FFT : Te crystal structure matches with α – Te phase

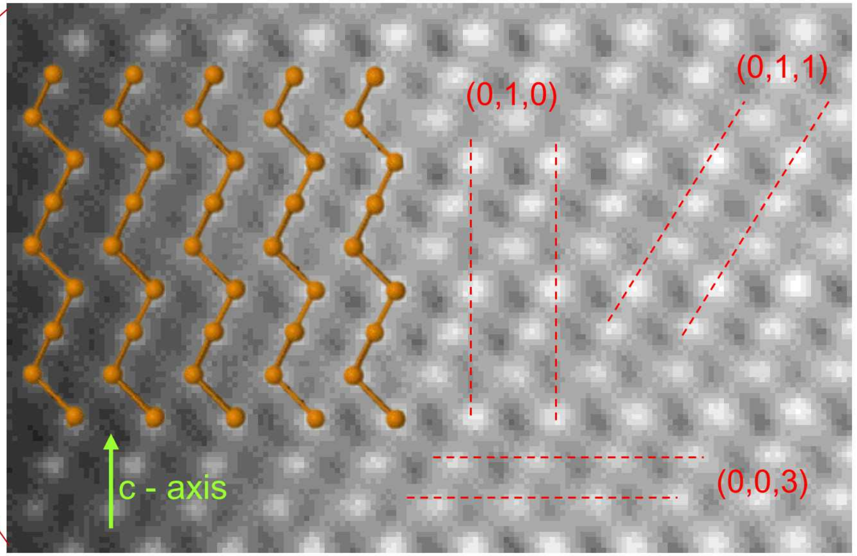
- High-angle annular dark-field (HAADF) STEM image exhibits helical chains of Te
- **Trigonal crystal structure with hexagonal cell**
- Space group $P3_121$
- Lattice parameters: a = 4.458 Å, and c = 5.927 Å

FFT analysis

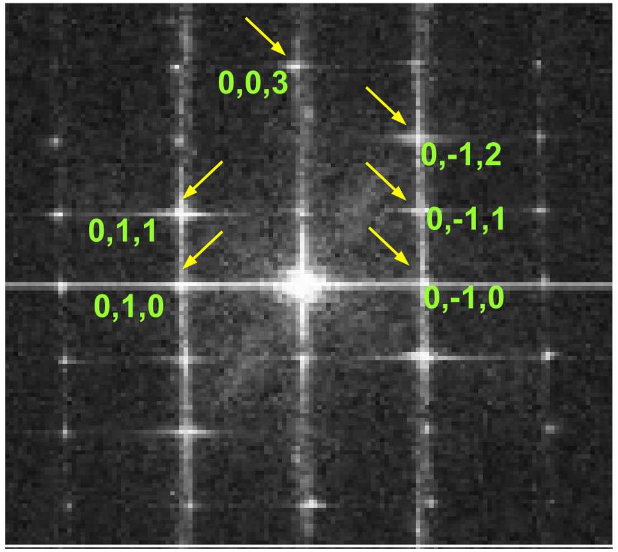
	D-spacing		
Miller index	Expected (A)	Measured (A)	Difference (%)
0,1,0	3.856	3.83	-0.67
0,1,1	3.233	3.2	-1.02
0,-1,2	2.35	2.32	-1.28
0,0,3	1.975	1.94	-1.77



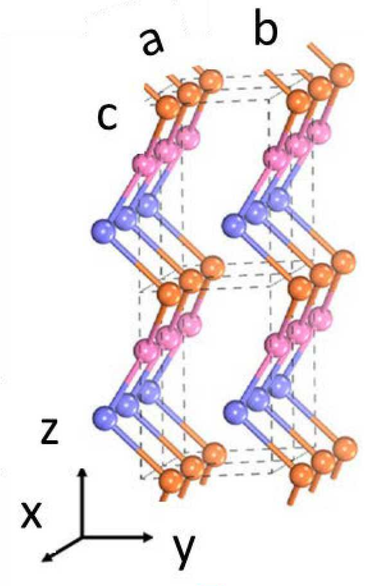
Te nanowire



High-angle annular dark-field (HAADF) STEM image



FFT patterns

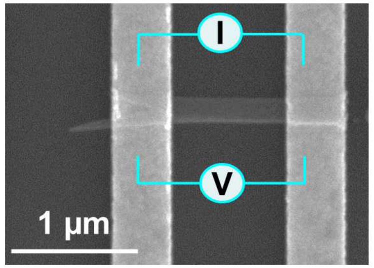


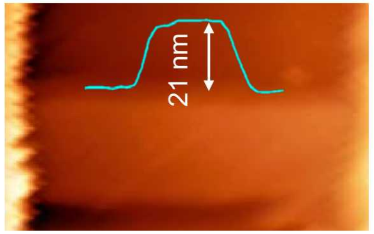
α - Te

Electrical Properties of a Te Nanostructure

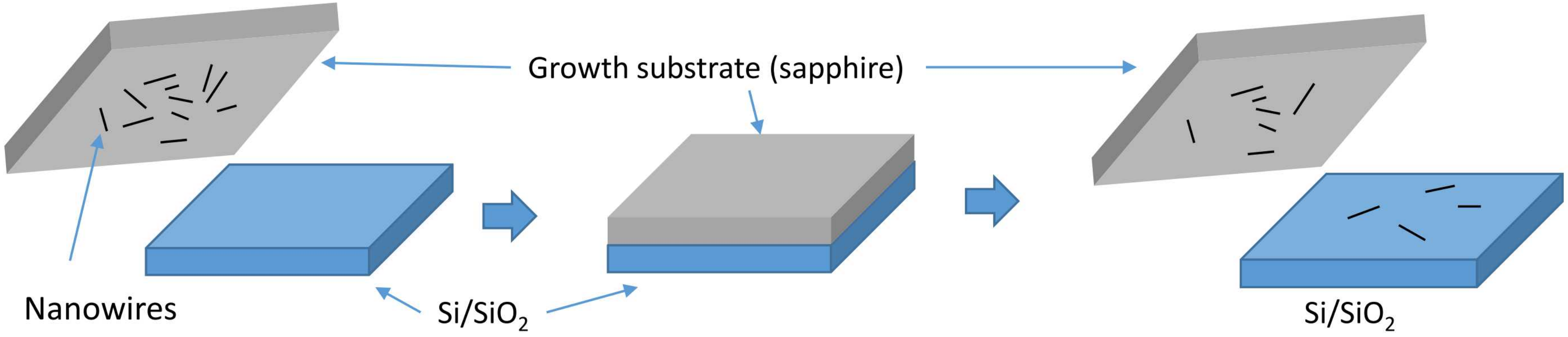
Device fabrication and measurement

- Challenging to fabricate gated device on the growth substrate (sapphire)
- Nanostructures were transferred to Si/SiO_2 substrate by contact method
- Electron beam lithography was carried out to fabricate the single nanostructure devices
- In-situ ion milling at the contact region before metallization to improve contacts
- Nanowire channel length = 830 nm and width = 180 nm, thickness = 21 nm
- I-V characteristics is linear at room temperature ➔ no Schottky barrier observed

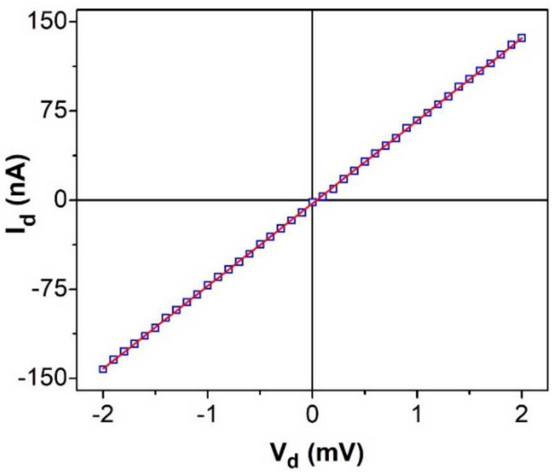




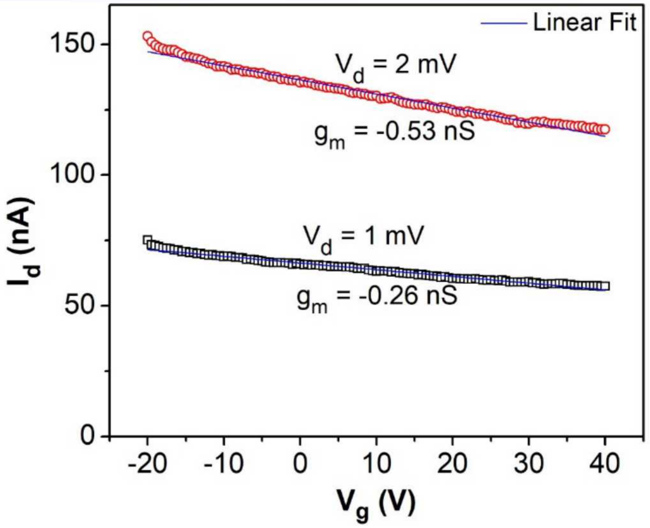
AFM image of nanowire device



Nanowire transfer by contact method. To enhance the transfer, growth substrate was soaked with DI water



Electrical Properties of a Te Nanostructure



Resistivity *(ρ)* = 645 μΩ.cm.

- **Nearly two order of magnitude lower than the resistivity of bulk-Te**
- Significantly lower than solution-based synthesized Te nanostructures

Gated measurements at room temperature

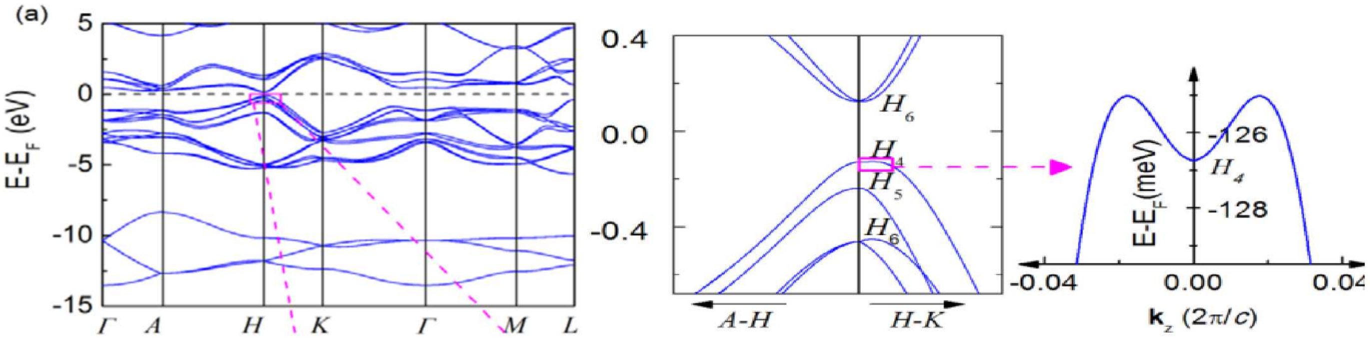
- Negative transconductance (g_m): ***p-type semiconductor***

$$g_m = d\,I_d/d\,V_g \qquad \mu_h = \frac{g_m L^2}{V_{ds} C_{get}} \qquad C_{get} = \epsilon_0 \epsilon_r w\, L/t$$

- Hole mobility (μ_h) = 349 cm^2/V.s
- Mobility higher than of MoS_2 which is typically ~190 cm^2/V.s *(L. Ma, APL**105** (7) (2014))*

$$n_h = 1/e\,\rho\mu_h$$

- Hole concentration (n_h) = 2.78 × 10^{18} cm^{-3}



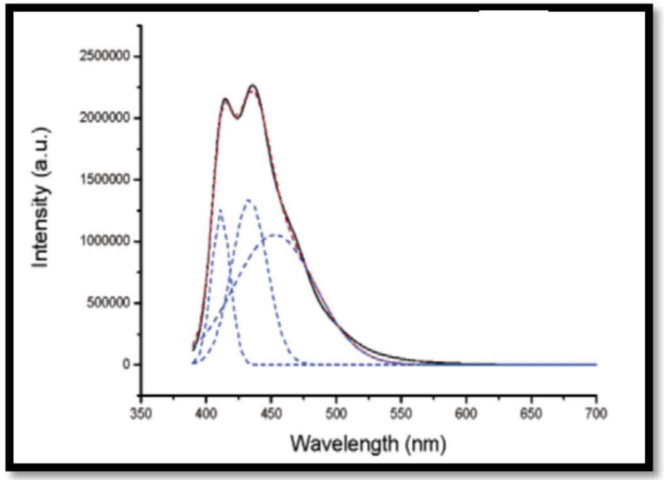
*H. Peng, PRB **89** (19) (2014)

Hole Transport Mechanism*

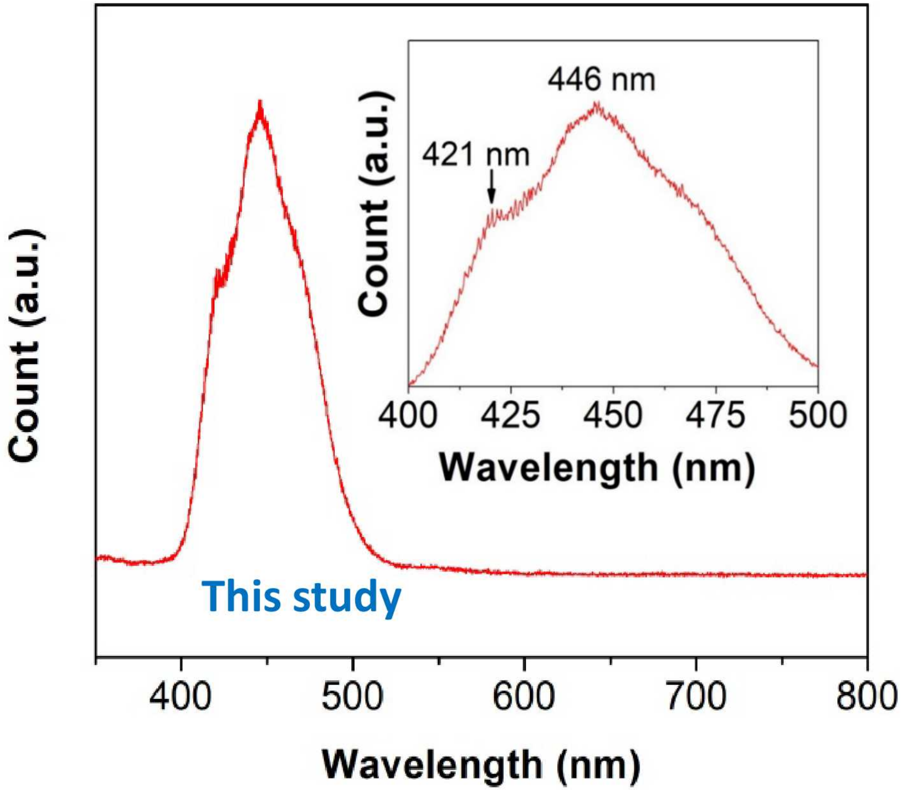
- Unique valence band structure at the H point in the Brillouin zone provides conduction channels for the holes
- The four fold degenerate valance band at H point is split into two non-degenerated H_4 and H_5 bands and a doubly degenerated lower H_6 band due to the strong spin-orbit coupling in the Te.
- Only H_4 and H_5 bands lie close to the Fermi level and thus contribute holes transport.

Micro-PL study

- Room-temperature micro- photoluminescence (micro-PL) measurements show a strong violet-blue luminescence at ~ 445 nm
- PL peak lies at a significantly higher energy level than the expected bandgap level.



Previously observed PL in Te nanowires
*H. Sheng, Langmuir, **22** (2006)*



- Hartee-Fock-Slater model:
  - Peaks in the energy range of 0-3 eV can be assigned to the transition form valence band p-bonding (VB3) to conduction band p-antibonding (CB1).*

T. Ikari, Mater. Res. Bull. **21, 99 (1986)*

Conclusions

- Te can be synthesized in 2D form which can exists in 3 phases: α-, β-, and γ-Te
- 2D Te is equivalent to transition metal dichalchogenides of formula MX_2 (e.g. MoS_2) where M is replaced by Te
- High temperature vapor phase deposition of Te nanostructures was realized by using $ZrTe_2$ as Te source
- Ultrathin nanostructures were obtained down to 3 nm thickness
- The synthesized Te nanostructures exhibited α – Te phase
- The high quality Te nanostructures exhibited 2 order lower resistivity that than of bulk Te and chemically synthesized Te nanostructures
- High hole mobility was observed (349 cm^2/V.s) which is greater than for typical 2D van der Waal materials
- Micro-PL exhibits luminescence at ~ 445 nm which is significantly deeper energy level than expected bandgap