Large Area, Oriented Bi_2Te_3/Sb_2Te_3 Superlattices through Electrodeposition

SAND2011-4854C

Sandia National Laboratories

D. Banga, J. Lensch Falk, D. Robinson, D. Medlin and P. Sharma

07/20/2011

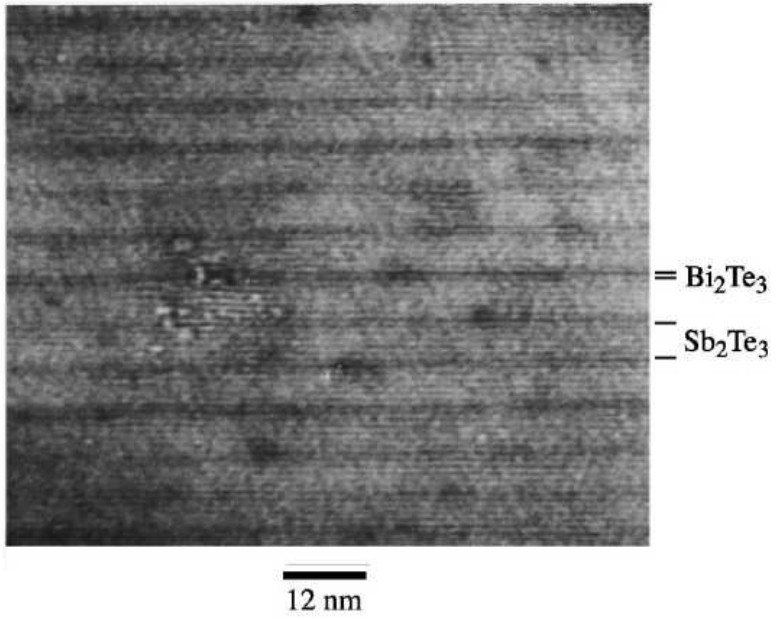
ICT2011 – Traverse City, Michigan

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. Support was provided in part by the Sandia LDRD Office

Thermoelectric Efficiency Improved through Superlattice Nanostructuring

- Nanostructured materials have shown enhanced efficiency[1,2]
- MOCVD-based Superlattices have been found as structures which improve ZT[3] due to reduced κ
- But vapor-phase methods are time consuming and expensive and can not be scaled up

Bi_2Te_3 /Sb_2Te_3 Superlattice grown by MOCVD



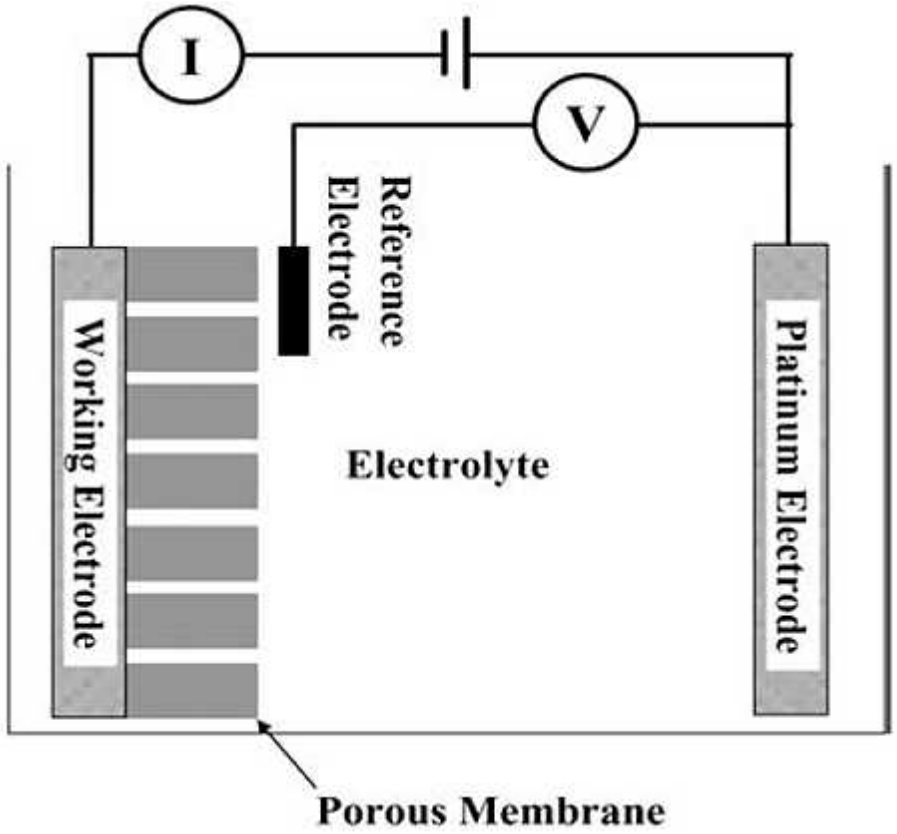
Venkatasubramanian, R.; Colpitts, T.; O'Quinn, B.; Liu, S.; El-Masry, N.; Lamvik, M. *Applied Physics Letters* **1999,** 75, (8), 1104-1106.

1. **Dresselhaus, M. S.**; Chen, G.; Tang, M. Y.; Yang, R. G.; Lee, H.; Wang, D. Z.; Ren, Z. F.; Fleurial, J. P.; Gogna, P. Advanced Materials **2007**, 19, (8), 1043-1053.
2. **Snyder, G. J.**; Toberer, E. S. Nature Materials **2008**, 7, (2), 105-114.
3. **Venkatasubramanian, R.**; Colpitts, T.; Watko, E.; Lamvik, M.; El-Masry, N. Journal of Crystal Growth **1997,** 170, 817-821.

Sandia National Laboratories

Electrodeposition is Scalable, Rapid and Controllable at Nanoscale Level

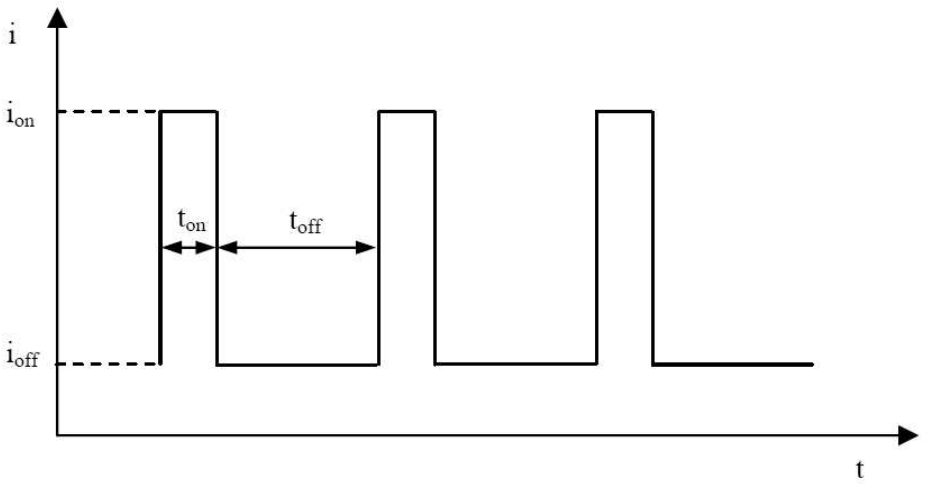
- Simple: one parameter (current or potential)
- Inexpensive isothermal process
- Scalable
- Atomic scale control
- Versatile



Sandia National Laboratories

Pulse Electrodeposition Offers More Flexibility Than Conventional Electrodeposition

- 3 independent variables
  - pulse on-time
  - pulse-off time
  - current or potential
- Numerous Advantages
  - Improvement in current distribution
  - Alteration of the prevailing mass transport conditions
  - Decrease in concentration gradients
  - Reduction in the additive requirement
  - Control of microstructure and composition of the electrodeposits



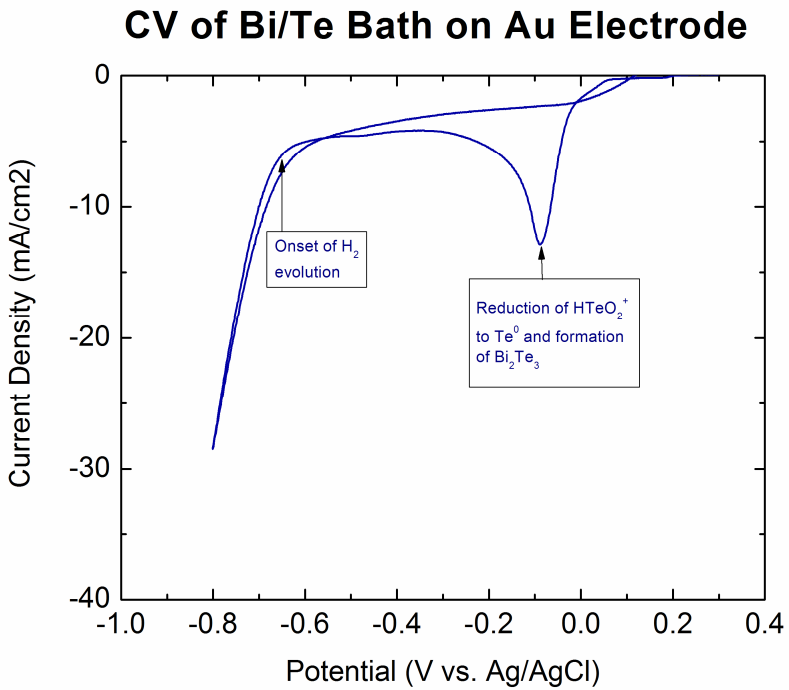
Duty cycle = t_{on} / (t_{on}+ t_{off})

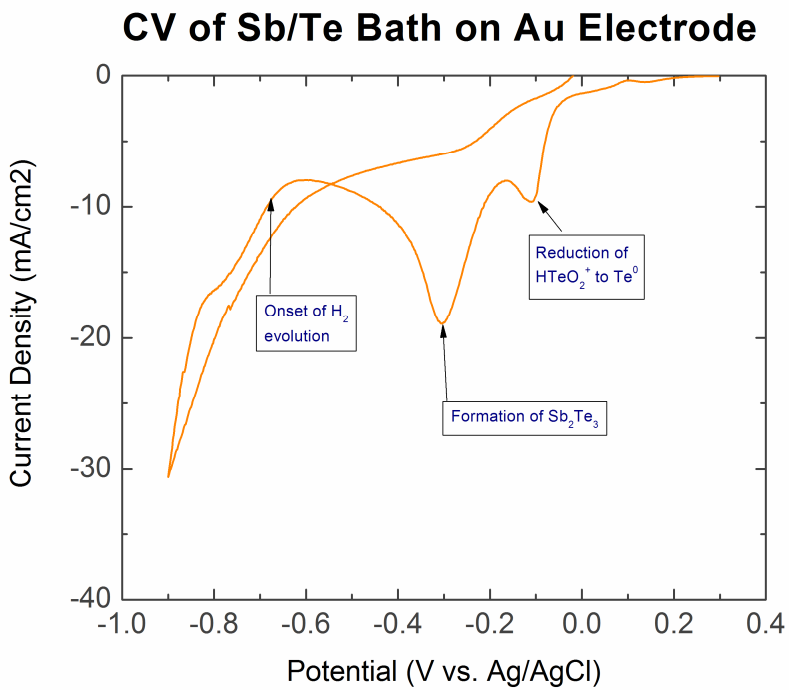
Parameters used

- Ag/AgCl RE, Pt CE and Au WE
- RT environment
- No agitation
- 25 – 500 ms t_{on}, 0.5 – 4.5 s t_{off}

Sandia National Laboratories

Reductive Features Evident in Cyclic Voltammetries of Bi/Te and Sb/Te Baths





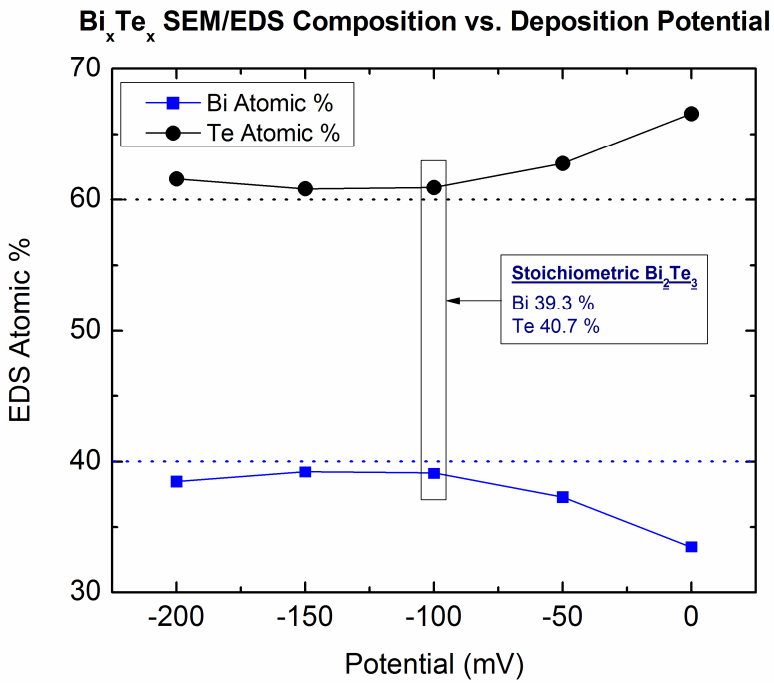
Bi/Te Bath Composition
6 mM $Bi(NO_3)_3.5H_2O$, 7 mM Na_2TeO_3, 0.3 M $C_4H_6O_6$, 2 M HNO_3

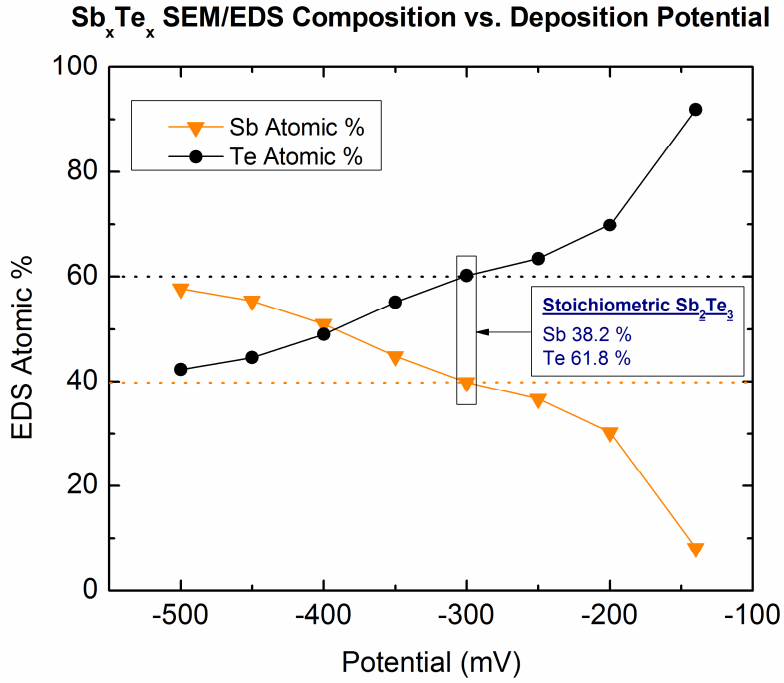
Sb/Te Bath Composition
16 mM Sb_2O_3, 7 mM Na_2TeO_3, 0.3 M $C_4H_6O_6$, 2 M HNO_3

100 mV/s CV scan rate

Sandia National Laboratories

The Stoichiometry of Compounds Controlled Through the Applied Potential



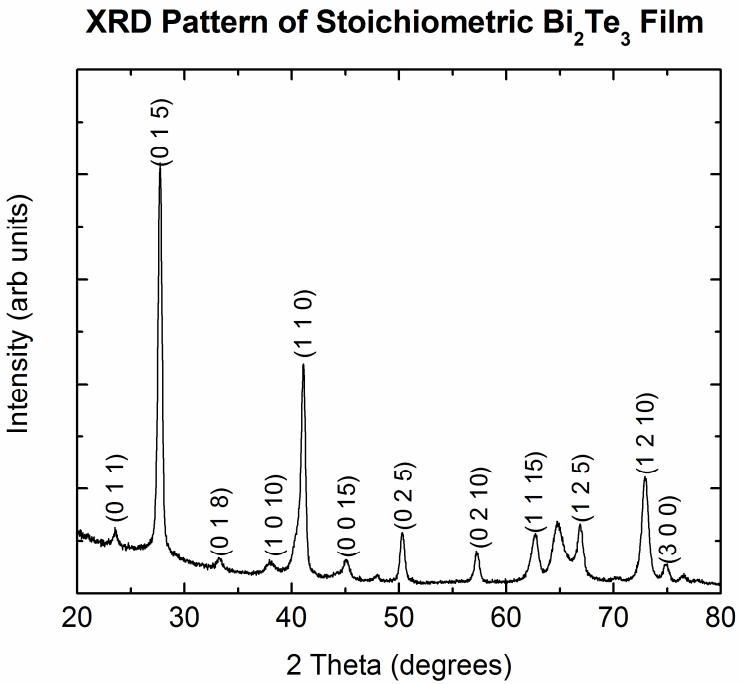


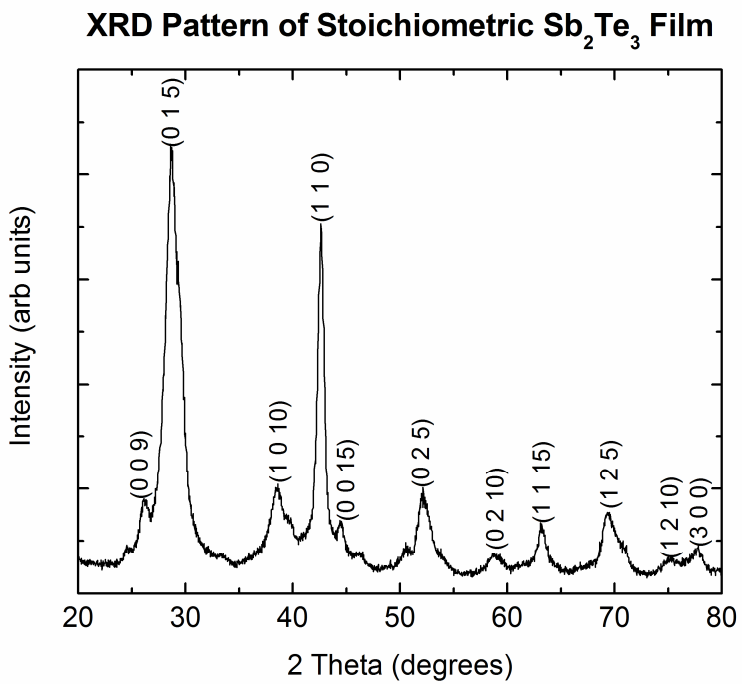
Deposition Parameters

100 ms t_{on}, 4.5 s t_{off}, 30 minute total deposition time, No agitation, RT

Sandia National Laboratories

XRD: As-deposited Stoichiometric Films Possess Correct Crystal Structure

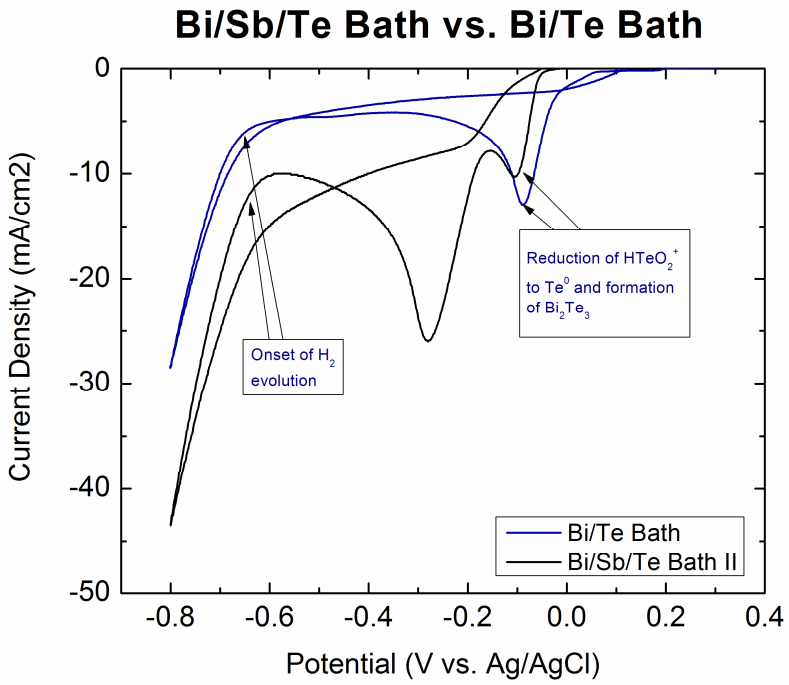


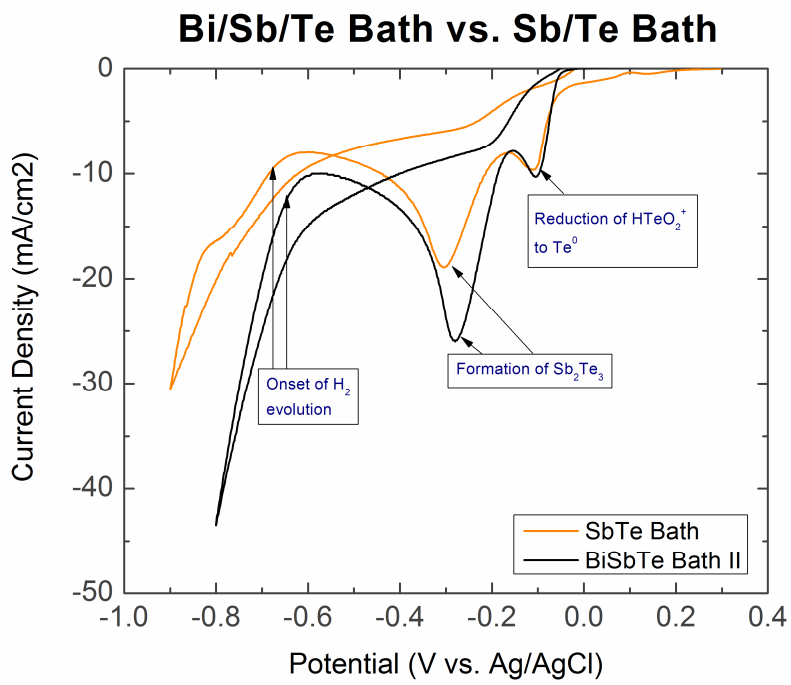


Right structure and good crystallinity with no annealing

Sandia National Laboratories

Reductive Features in Bi/Sb/Te Bath Overlap with those found in Bi/Te and Sb/Te Baths





Bi/Sb/Te Bath Composition

4 mM $Bi(NO_3)_3.5H_2O$, 20 mM Sb_2O_3, 7 mM Na_2TeO_3, 0.3 M $C_4H_6O_6$, 2 M HNO_3

100 mV/s CV scan rate

Sandia National Laboratories

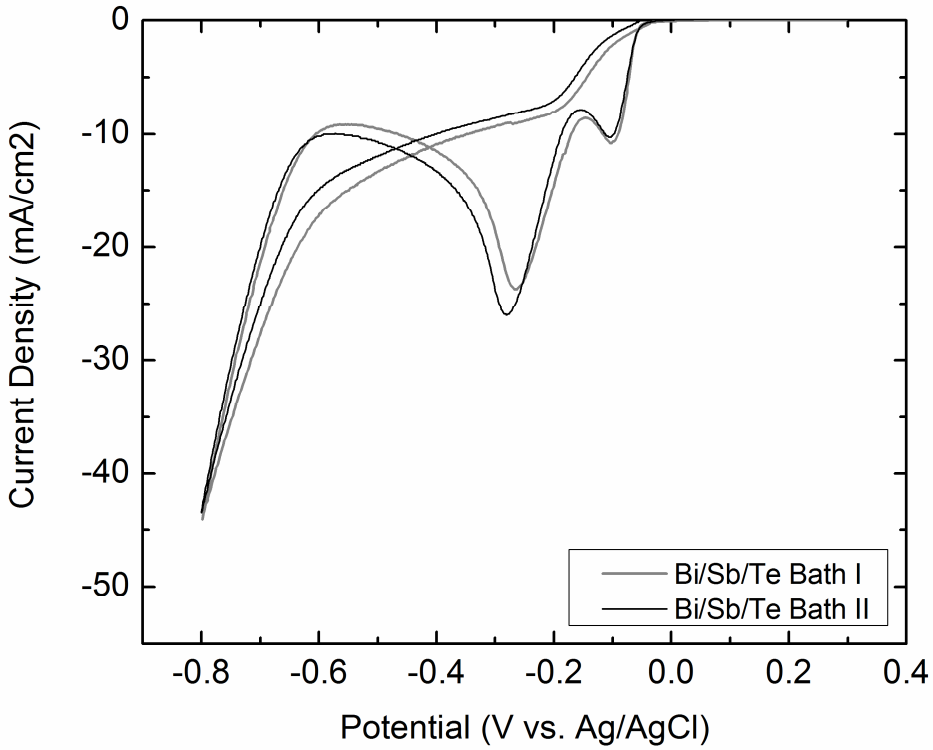
The Positions of Reductive Peaks Unchanged with Te/Sb Content in Bi/Sb/Te Baths

Bi/Sb/Te Bath Compositions

Bath I	Bath II
4 mM $Bi(NO_3)_3.5H_2O$	4 mM $Bi(NO_3)_3.5H_2O$
16 mM Sb_2O_3	20 mM Sb_2O_3
5 mM Na2TeO3	7 mM Na_2TeO_3
300 mM $C_4H_6O_6$	300 mM $C_4H_6O_6$
2 M HNO_3	2 M HNO_3

Less Te and Sb in the bath resulted in a less intensive peak at around -0.3 V due to the formation of Sb_2Te_3

Comparison of the CVs of the two Bi/Sb/Te Baths



100 mV/s CV scan rate

Sandia National Laboratories

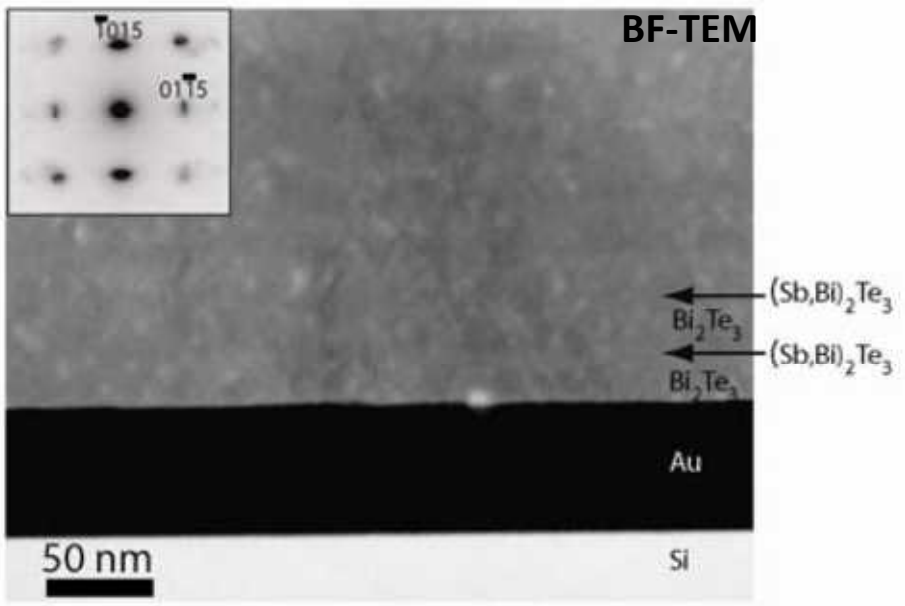
Bright Field TEM: 10 Period Superlattice – EDS Linescan Modulation

Plating Parameters

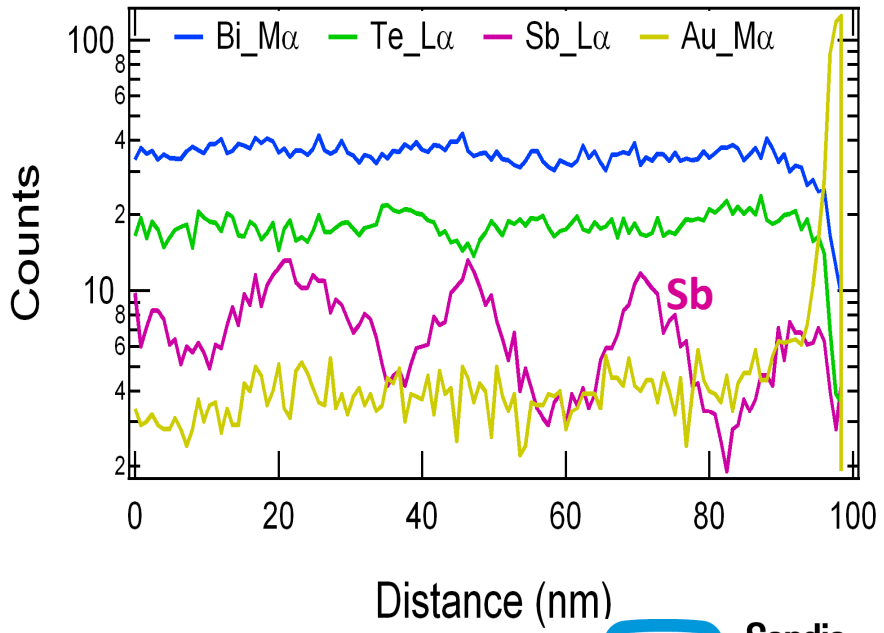
Layer Type	Potential (mV)	t_{on} (ms)	t_{off} (s)	Pulse Number
$(Bi_{1-x}Sb_x)_2Te_3$	-300	50	2.25	10
Bi_2Te_3	-100	100	4.5	26

TEM/EDS Composition
Bi_2Te_3 layers: 50 % Bi, 48 % Te
$(Bi,Sb)_2Te_3$ layers: 40 % Bi, 20 % Sb, 40 % Te

Transmission Electron Microscopy and Electron Diffraction of the Superlattice Film



EDS Linescan of 4 Periods of the Layered Film



Highly crystalline 10 (24 nm-thick) periods deposit (01-15) texture parallel to the substrate

Sandia National Laboratories

Bright Field TEM: 10 Period Superlattice Intensity Contrast

Plating Parameters

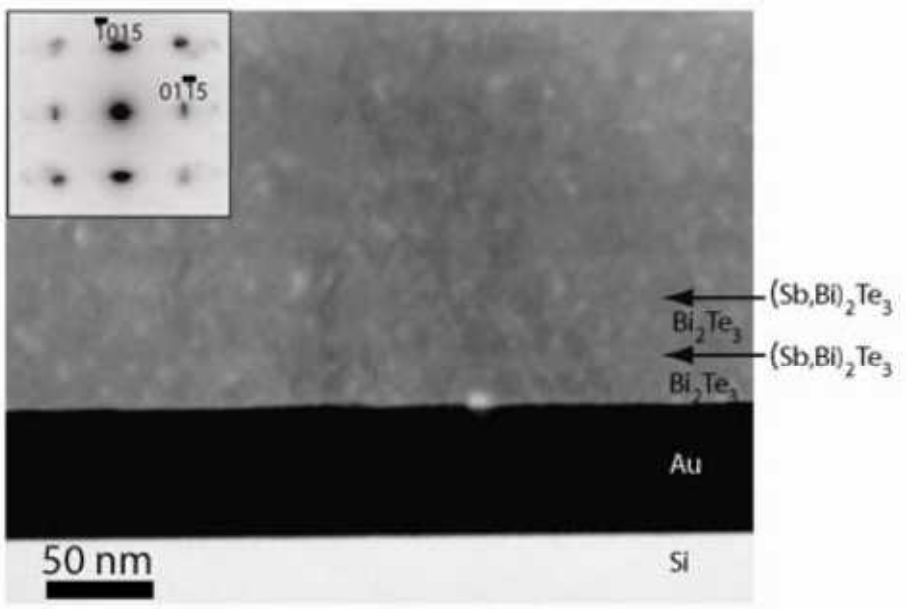
Layer Type	Potential (mV)	t_{on} (ms)	t_{off} (s)	Pulse Number
$(Bi_{1-x}Sb_x)_2Te_3$	-300	50	2.25	10
Bi_2Te_3	-100	100	4.5	26

TEM/EDS Composition

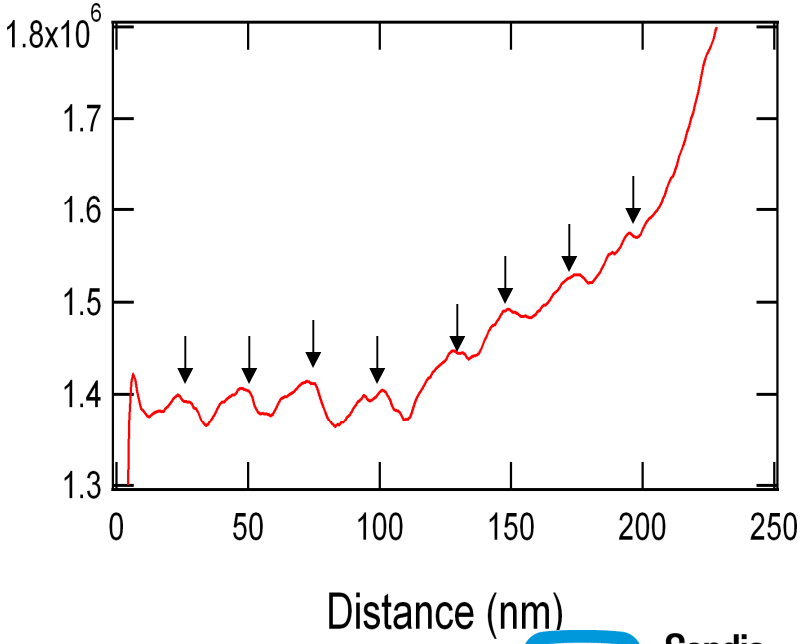
Bi_2Te_3 layers: 50 % Bi, 48 % Te

$(Bi,Sb)_2Te_3$ layers: 40 % Bi, 20 % Sb, 40 % Te

Transmission Electron Microscopy and Electron Diffraction of the Superlattice Film



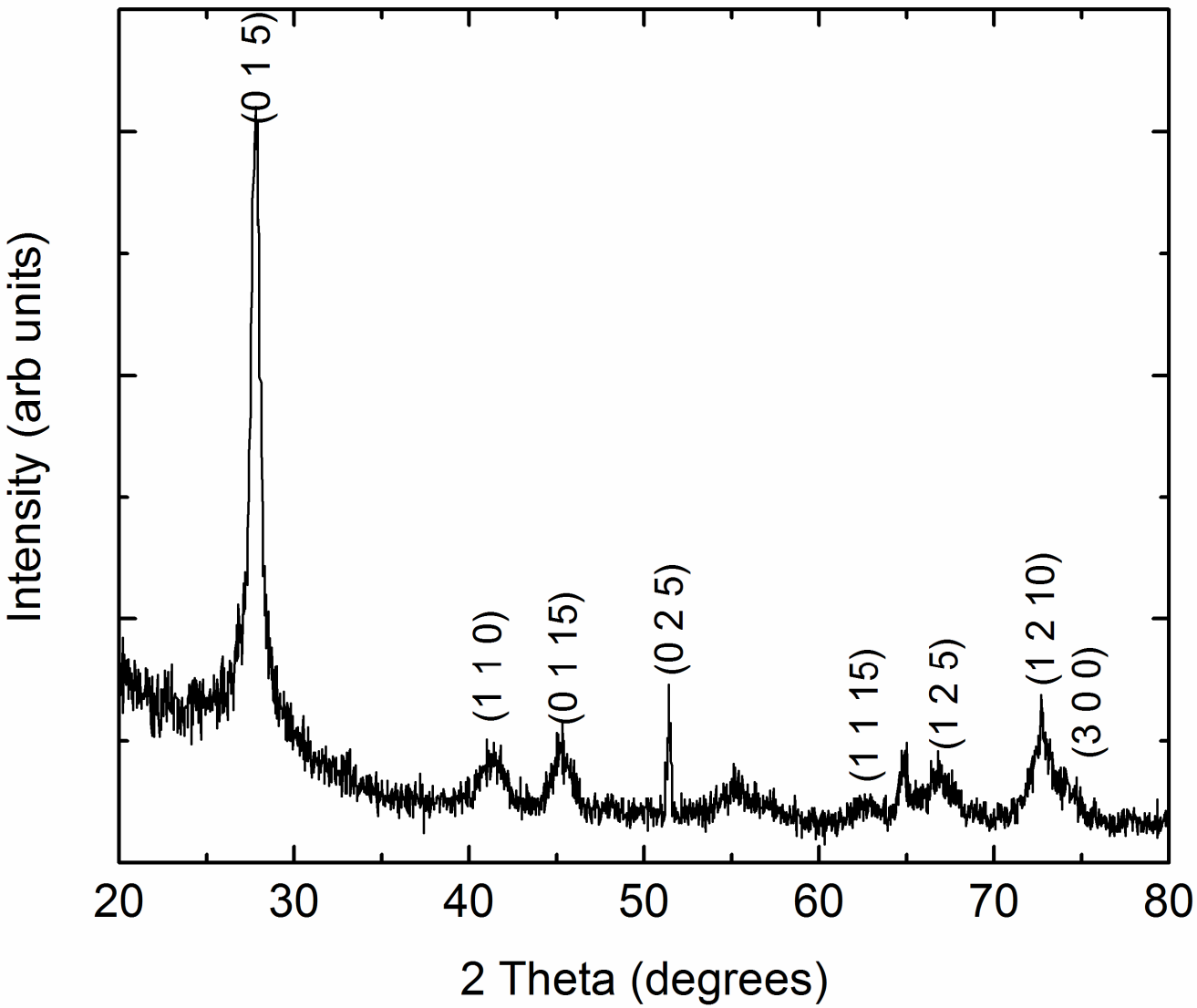
Profile of BF STEM Image Intensity of the Superlattice Film



Highly crystalline 10 (24 nm-thick) periods deposit with (01-15) texture parallel to the substrate

Sandia National Laboratories

XRD Pattern of the Superlattice Film



Superlattice Possesses Bi_2Te_3-type Structure

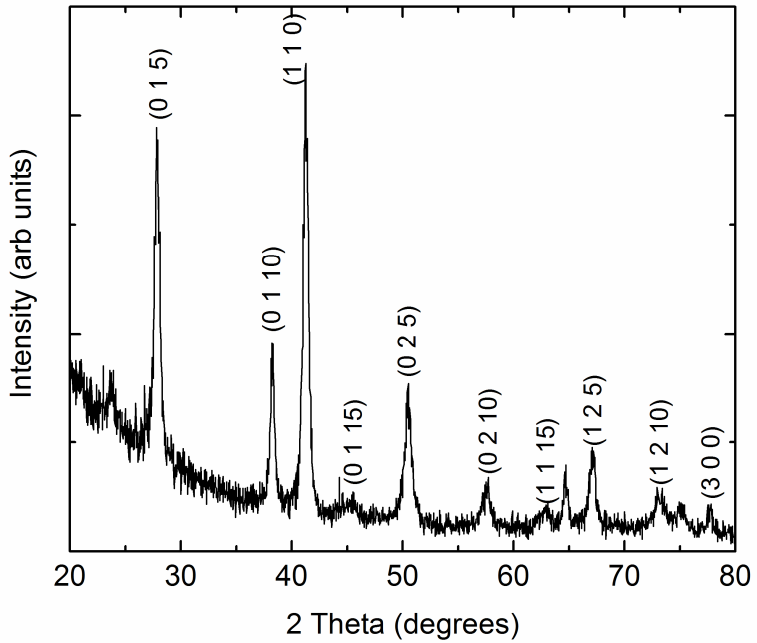
Sandia National Laboratories

Coherent Superlattice Grown Over the Entire Square Centimeter Area

Plating Parameters

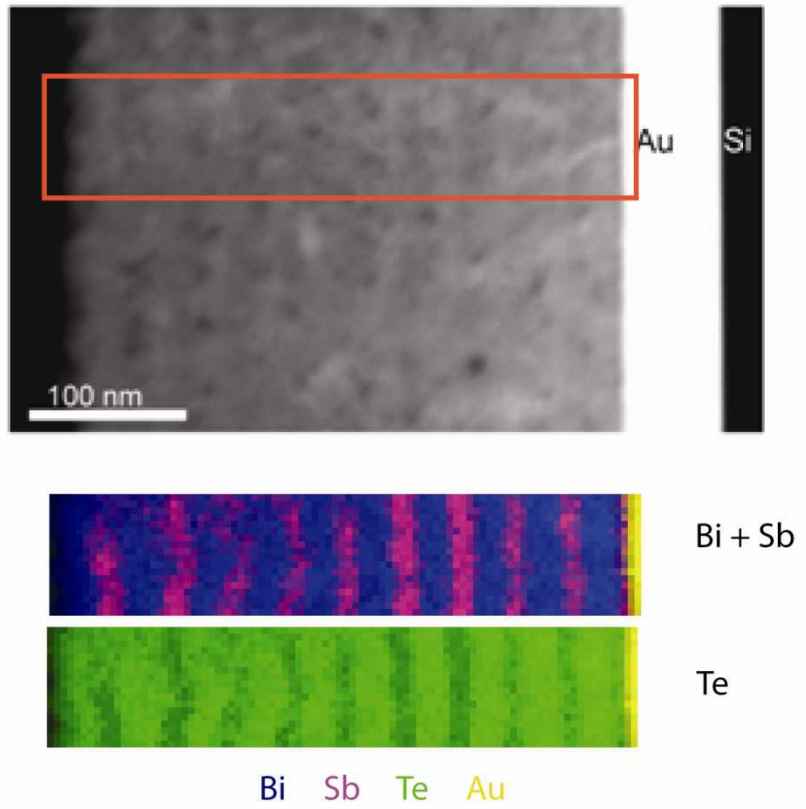
Layer Type	Potential (mV)	t_{on} (ms)	t_{off} (ms)	Pulse Number
Bi_2Te_3	-100	500	500	5
$(Bi_{1-x}Sb_x)_2Te_3$	-300	50	2000	26

XRD of the Multilayered Film



Highly crystalline 10 (17 nm-thick) periods sample with (01-15) texture parallel to the substrate

STEM/EDS Spectrum Image of the Film



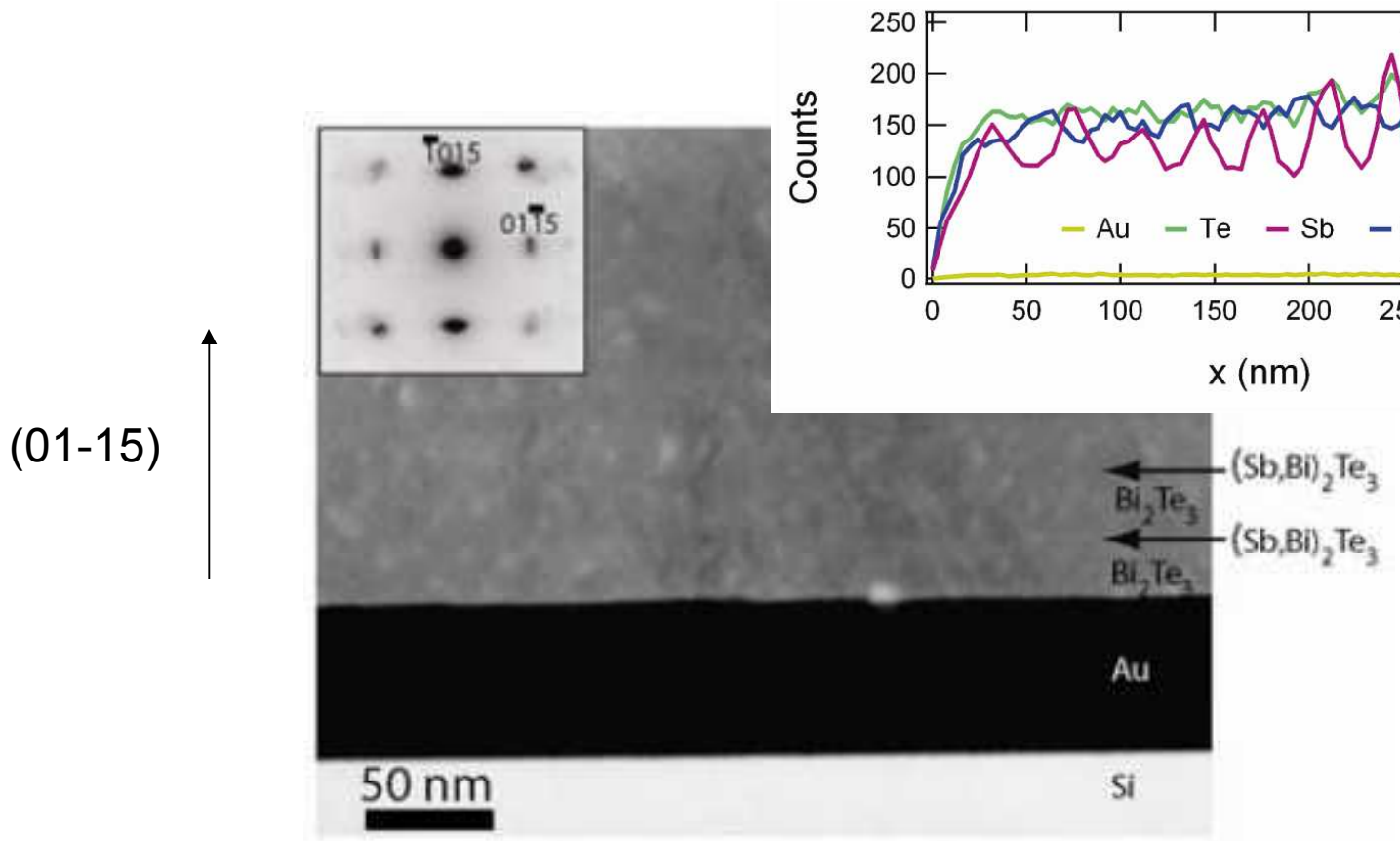
TEM/EDS Composition

Bi_2Te_3 layers: 44 % Bi, 56 % Te

$(Bi,Sb)_2Te_3$ layers: 32 % Bi, 24 % Sb, 46 % Te

Sandia National Laboratories

Large Area, Oriented Bi_2Te_3-Sb_2Te_3 Superlattices through Electrodeposition



We are working on: improving stoichiometry, shorter periods, scale up

Sandia National Laboratories