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Characterization of electrodeposited nano-crystalline Sb_2Te_3 films

J.L. Lensch-Falk[1], D. Banga[1], V. Stavila[1], P. Sharma[2], D.L. Medlin[1]

[1]Sandia National Laboratories, Livermore, CA, [2]Sandia National Laboratories, Albuquerque, NM

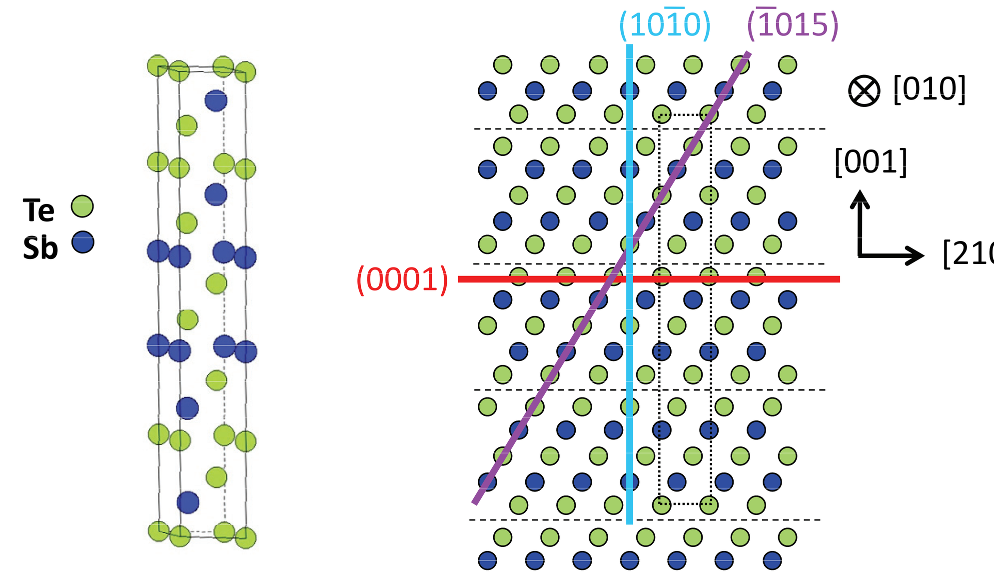
Motivation & Background

- Sb_2Te_3 based materials are of interest for thermoelectric devices. The thermoelectric properties of this material are highly anisotropic and dependent upon exact stoichiometry and doping.[1]
- Electrodeposition is a promising low-cost method to fabricate thermoelectric thin films such as Sb_2Te_3 and its alloys. However, electrodeposition of high quality, crystalline Sb_2Te_3 films without the need for additional processing and with good compositional control has presented a challenge.[2-5]
- Pulsed plating has been shown to improve the morphology, density, crystallinity, and properties in deposits.[6-7]

- ***Objective: Determine how the electrodeposition parameters affect the crystallinity, microstructure, and texture in Sb_2Te_3 thin films.***

Tetradymite

Sb_2Te_3 Hexagonal unit cell:
a = b = 4.264 Å
c = 30.458 Å



1. H. Scherrer and S. Scherrer, **CRC Handbook of Thermoelectric,** Ed. DM Rowe, Chapter 19, 1995.
2. M-Y. Kim & T-S. Oh, *Thin Solid Films*, **518**, 6550-6553, 2010.
3. C. Boulanger, *J. Electronic Materials,* **39**(9), 1818-1827, 2010.
4. Q. Huang, *et al, J. Electrochemical Society*, **155**(2) D104-D109, 2008.
5. F. Xiao, *et al*, *Electrochimica Acta*, **53**, 8103-8117, 2008.
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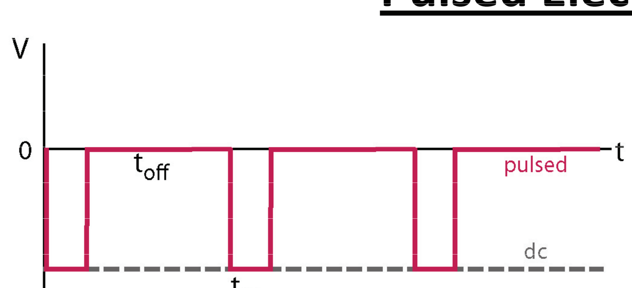
Pulsed Electrodeposition of Sb_2Te_3



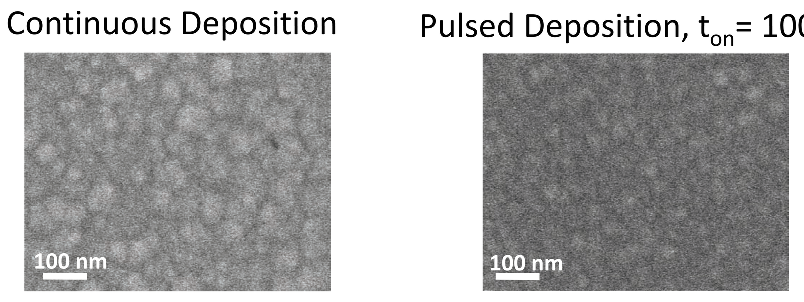
$$\text{Duty cycle} = \frac{t_{on}}{t_{on}+t_{off}} \times 100\,\%$$

Electroplating Conditions	
Bath	$HNO_3 + C_4H_6O_6 + SbO^+ + HTeO_2^+$
Working Electrode (substrate)	Au/Ti /Si substrate
Reference Electrode	Ag/AgCl
Counter Electrode	Pt
t_{on} for pulsed plating	25 ms – 100 ms
Duty cycle	2 % -100 % (dc plating)
Temperature	≈ 20 °C

- The deposition potential was varied from -0.14 to -0.5 V to determine the conditions for stoichiometric film growth
- All films shown in this work have the same total deposition "on" time (for pulse deposited films = $N_{pulses} * t_{on}$)

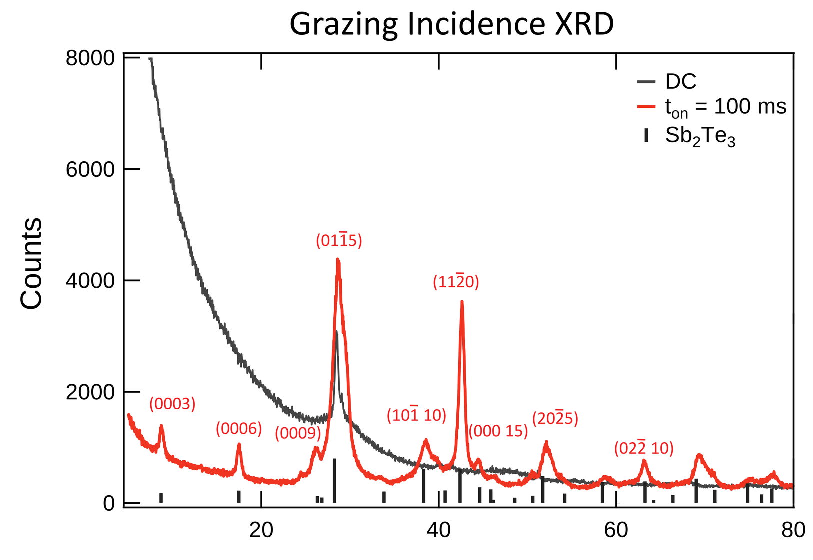
Scanning Electron Microscopy

Continuous Deposition | Pulsed Deposition, t_{on}= 100 ms



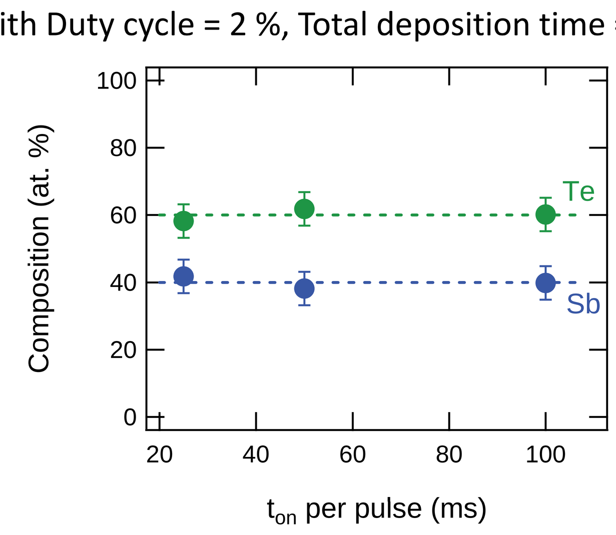
- Visual inspection of the films suggested that the continuously deposited material was cloudy indicating a rough surface
- All pulse plated films were shiny and metallic in appearance indicating a smoother film surface
- SEM images of the surfaces of these films indicates that continuous plating leaves a rougher surface than pulsed deposition

Grazing Incidence XRD

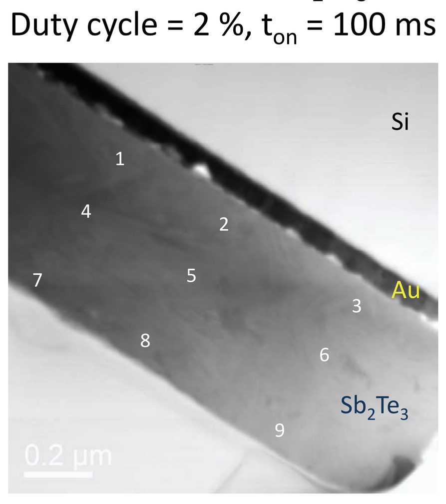


- XRD of the Sb_2Te_3 film deposited using continuous deposition was mostly amorphous with one broad peak at ~ 28° which might be attributed to a Sb-Te peak
- Films deposited using pulsed plating are crystalline and consistent with the Sb_2Te_3 tetradymite crystal structure
- GI-XRD at ω = 0.3 – 0.5° was used to minimize intensities of the substrate peaks

SEM/EDS Composition Measurements for Sb_2Te_3 films with Duty cycle = 2 %, Total deposition time = 30 min.



BF STEM Image of Sb_2Te_3 Film
Duty cycle = 2 %, t_{on} = 100 ms

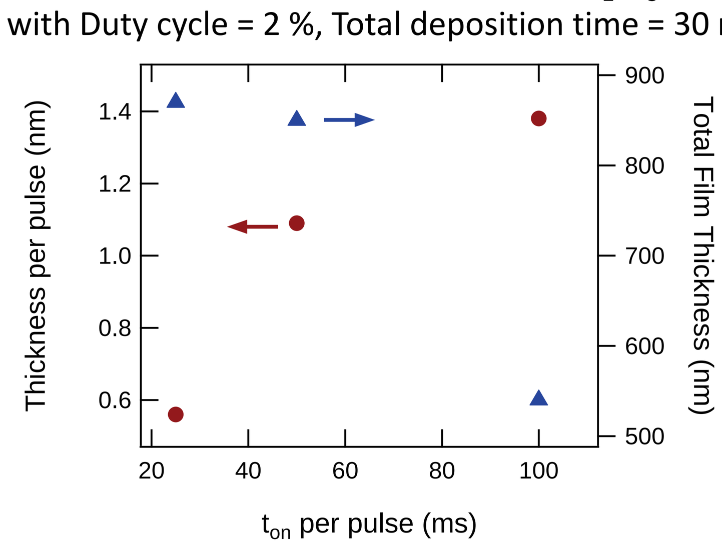


Semi-Quantitative STEM/EDS Analysis

	at. % Sb	at. % Te
1	40.0	60.0
2	38.1	61.9
3	38.3	61.7
4	39.6	60.4
5	39.5	60.5
6	37.8	62.2
7	35.8	64.2
8	39.7	60.4
9	41.7	58.3

- The composition of each film was initially measured using SEM/EDS to ensure stoichiometry with varied pulse parameters
- STEM/EDS measurements on cross-sectioned thin films indicate that the composition is uniform through the thickness of the deposit

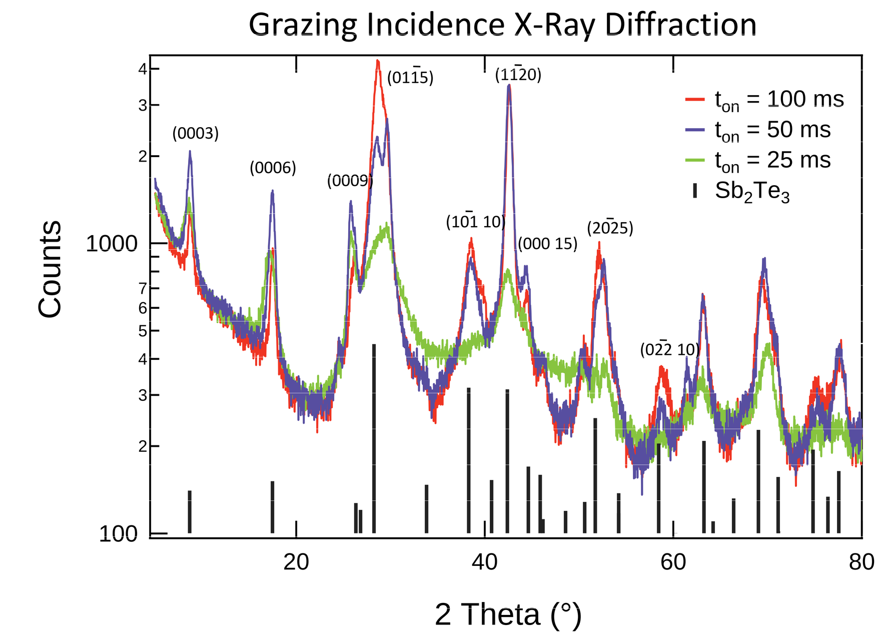
Thickness and Deposition Rates for Sb_2Te_3 films with Duty cycle = 2 %, Total deposition time = 30 min.



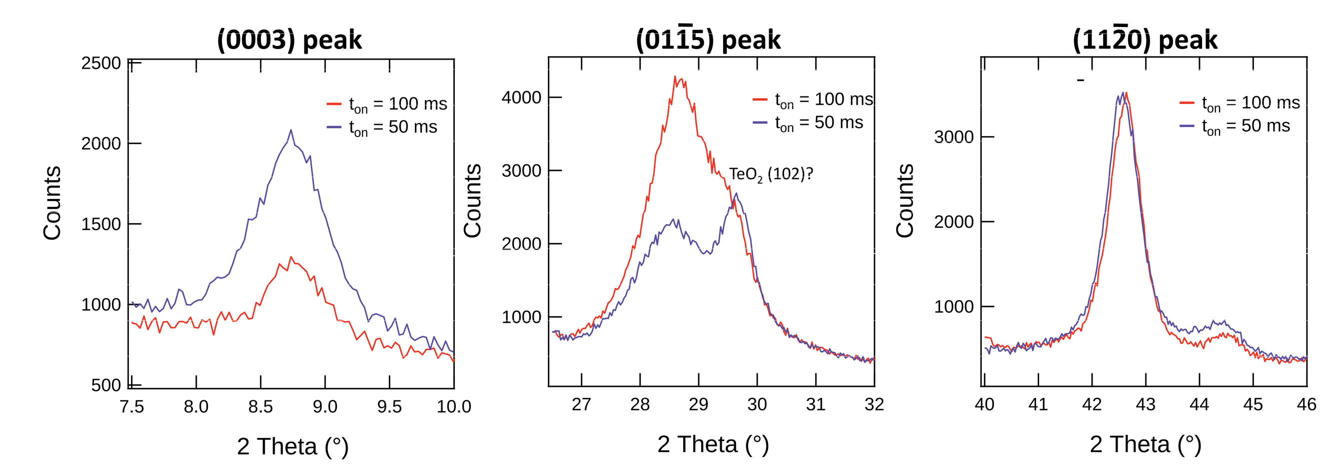
- The thickness of each film was measured on cross-sectioned TEM specimens
- Thin film thickness increased with decreasing t_{on} indicating that the deposition rate decreases over the course of each pulse

Changes in Sb_2Te_3 films with decreased pulse time - XRD

Grazing Incidence X-Ray Diffraction



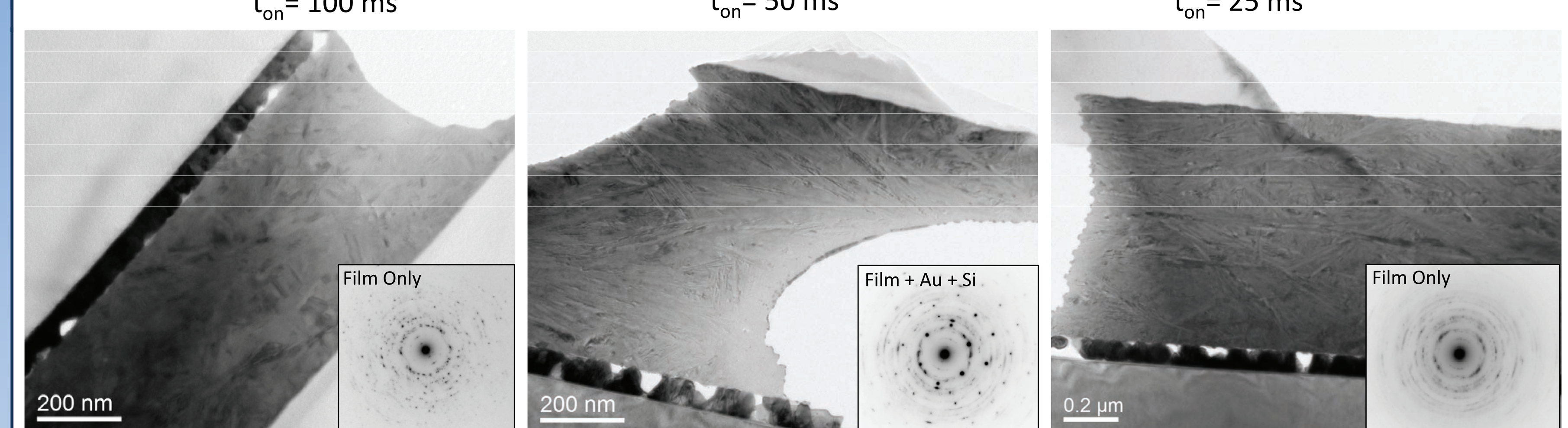
- Sb_2Te_3 films were deposited with decreasing t_{on} and duty cycle = 2 % for a total deposition time = 30 min.
- All three films were polycrystalline Sb_2Te_3 with the tetradymite structure
- The relative intensity of the (000*l*) peaks increased for decreasing t_{on} while the (01$\bar{1}$5) peak intensity decreased suggesting that deposition on (000*l*) planes was favored by depositing less material per pulse
- Some indications of oxide phases such as TeO_2 can be observed in the XRD spectra



Changes in Sb_2Te_3 films with decreased pulse time - TEM

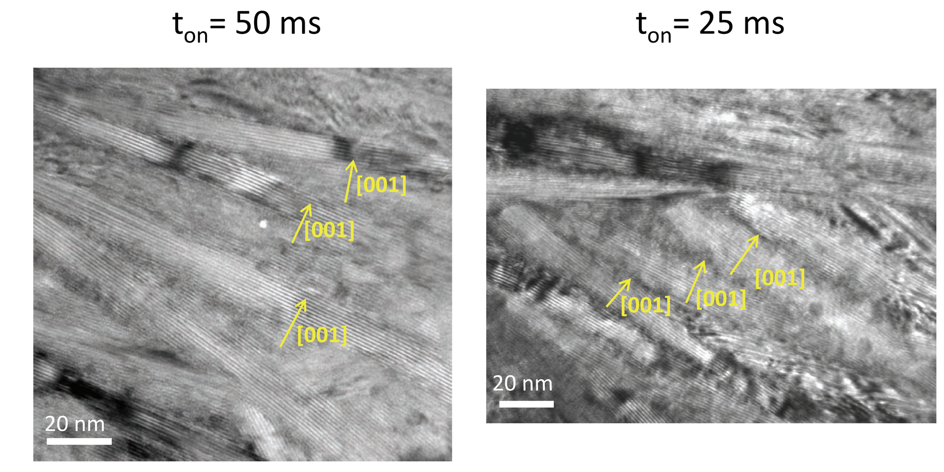
Transmission Electron Microscopy

t_{on}= 100 ms | t_{on}= 50 ms | t_{on}= 25 ms

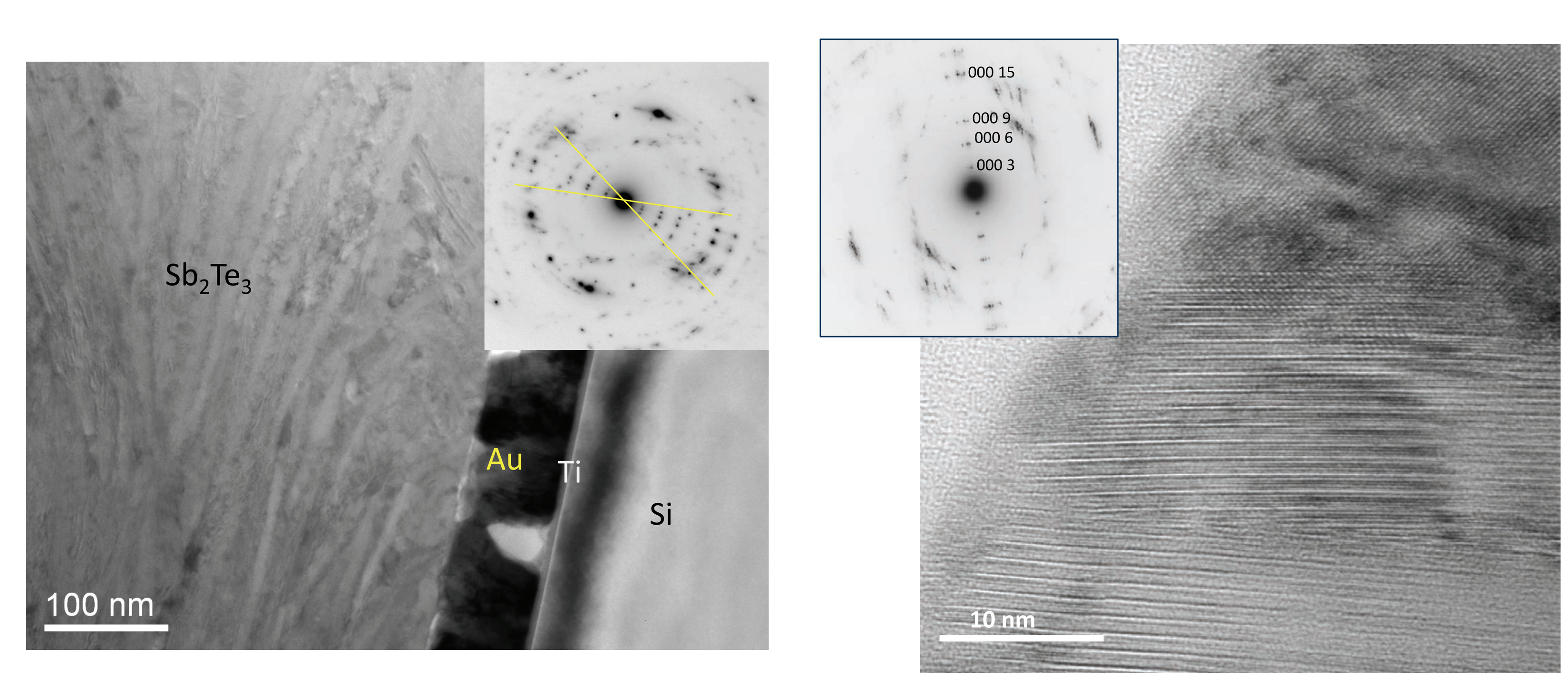


- Electron microscopy and electron diffraction confirm that all three films deposited with a 2 % duty cycle were polycrystalline Sb_2Te_3 with the tetradymite structure
- In the films deposited with $t_{on} \leq 50$ ms, lamellar features that are nearly parallel (within 20°) to the substrate are commonly observed
- These grains are up to 750 nm x 40 nm thick
  - Many pulses are necessary to deposit the material in one lamellar feature (≈ 10 - 40)
- The lamellar grains are oriented with the Sb_2Te_3 (000*l*) planes are parallel to the long axis (the [001] direction parallel to the short axis)

t_{on}= 50 ms | t_{on}= 25 ms



Sb-Te thin film, t_{on}= 50 ms, duty cycle = 2 %



Summary

- Sb_2Te_3 thin films were grown by a pulsed potentiostatic electrodeposition process
- X-ray diffraction and transmission electron microscopy indicated that these films are crystalline
- These Sb_2Te_3 films are stoichiometric and homogeneous
- XRD indicates that the films are somewhat textured with the (000*l*) planes nearly parallel to the substrate at short pulse times
- A unique microstructure with lamellar grains that measure 10-40 nm thick by up to 750 nm long present in films deposited at short pulse times (< 50 ms) was observed. Within these grains, the Sb_2Te_3 (000*l*) planes are parallel to the long axis giving the overall film a (000*l*) texture which is not observed at longer pulse times

- The ability to directly grow crystalline Sb_2Te_3 thin films by electrodeposition at room temperature without the need for high temperature anneals may lead to new opportunities for nanostructure fabrication where diffusion and coarsening must be supressed

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