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Characterization of electrodeposited nano-crystalline Sb_2Te_3 films

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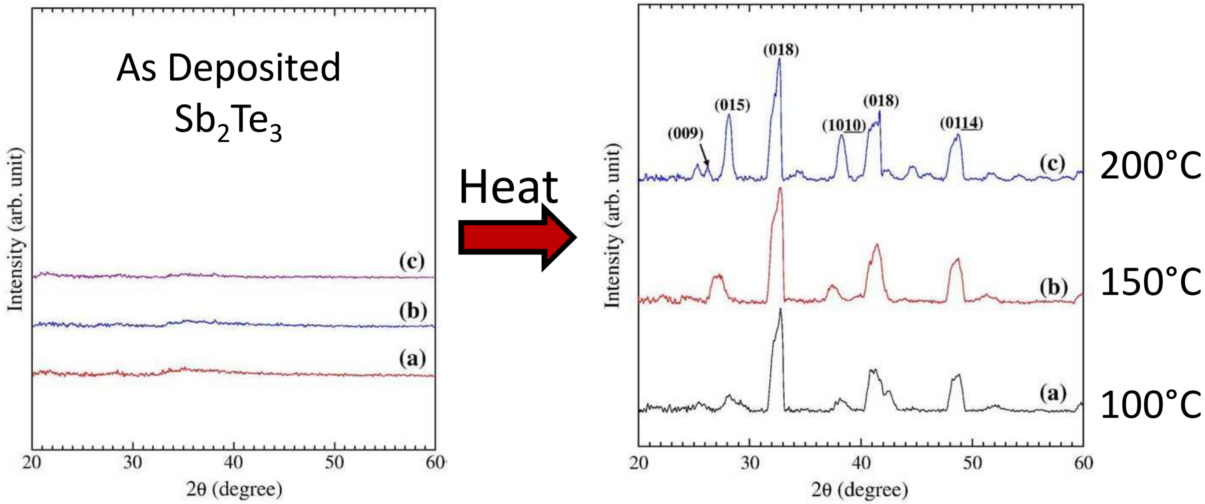
Electrodeposition of Sb_2Te_3

- Electrodeposition is promising for synthesis of thermoelectric materials such as Sb_2Te_3

Low cost **Room temperature** **Scalable** **Rapid**

Post-synthesis processing has generally been required to achieve high quality, crystalline deposits

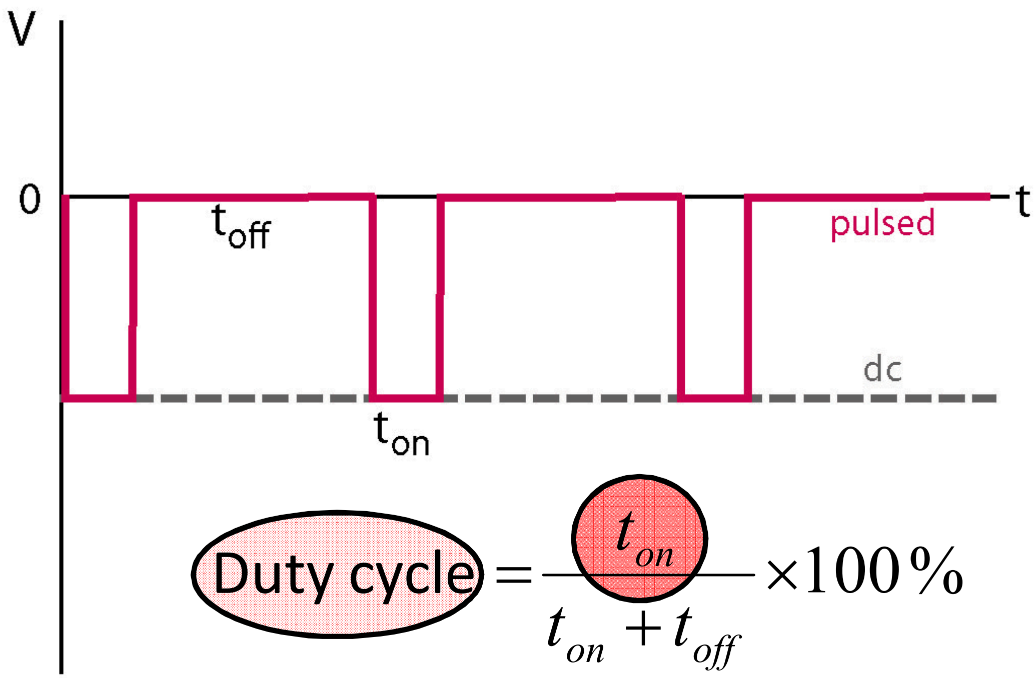


M-Y. Kim & T-S. Oh, *Thin Solid Films*, **518**, 6550-6553, 2010.

- Pulsed plating can improve **morphology**, **density**, and **crystallinity**

How do the pulsed electrodeposition parameters affect the crystallinity, microstructure, and texture in Sb_2Te_3 thin films?

Electrodeposition Conditions

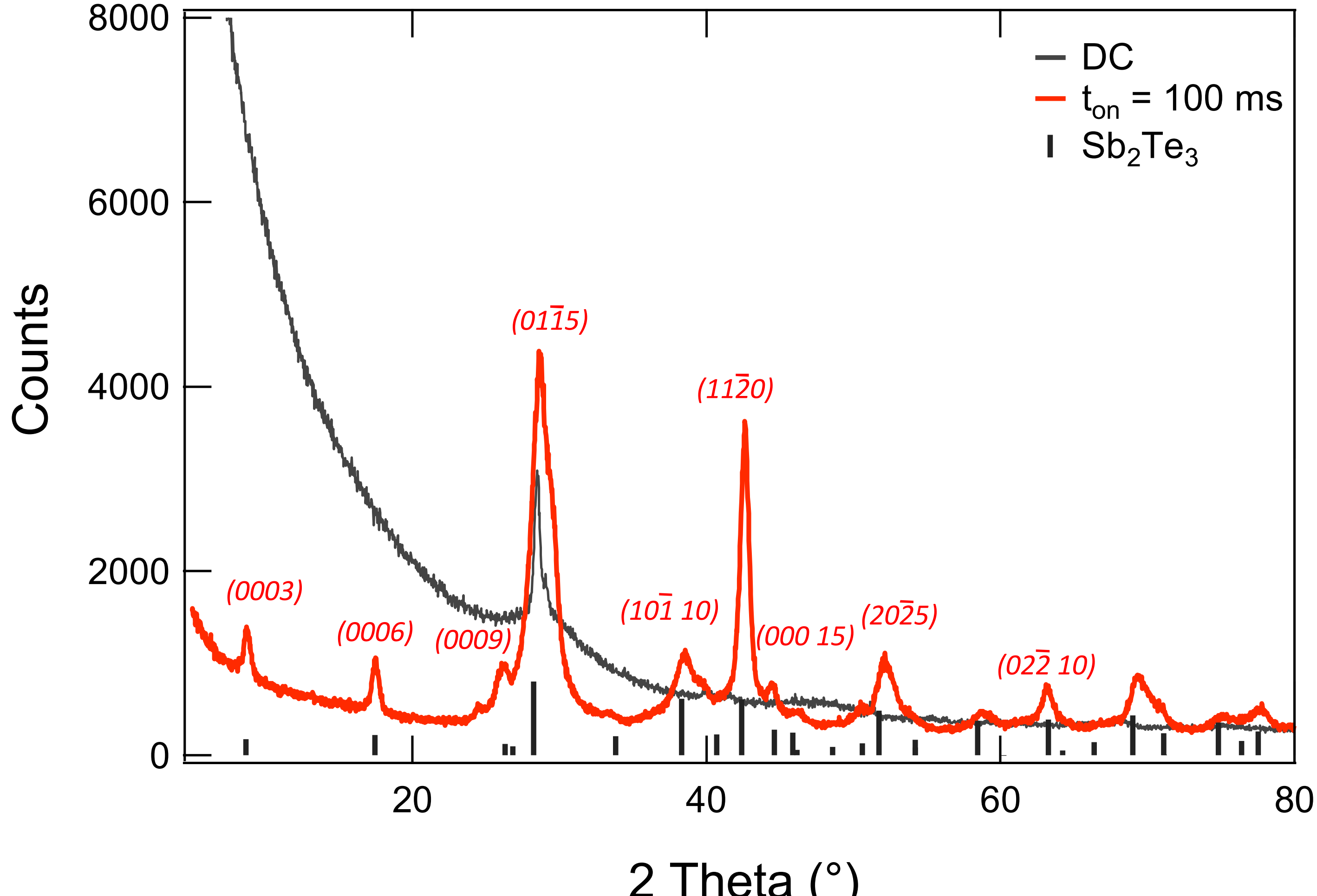


$$\text{Duty cycle} = \frac{t_{on}}{t_{on} + t_{off}} \times 100\,\%$$

Electroplating Conditions	
Bath	$HNO_3 + C_4H_6O_6 + SbO^+ + HTeO_2^+$
t_{on} for pulsed plating	25 ms – 100 ms
Duty cycle	2 % -100 % (dc plating)
Temperature	≈ 20 °C
Deposition Potential	-0.3 V

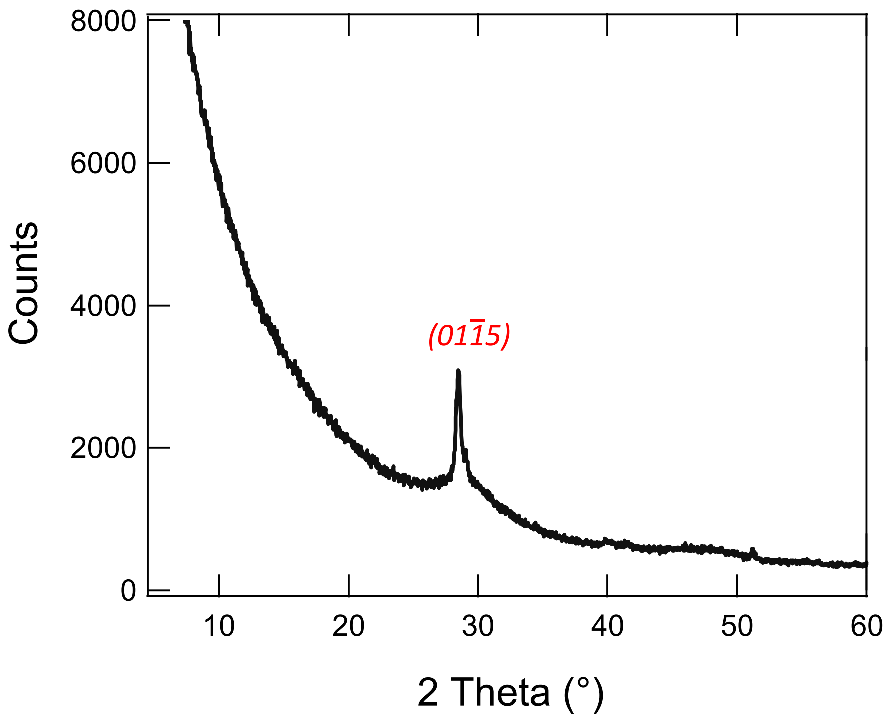
Working electrode (substrate): Au/Ti/Si; Reference electrode: Ag/AgCl; Counter electrode: Pt

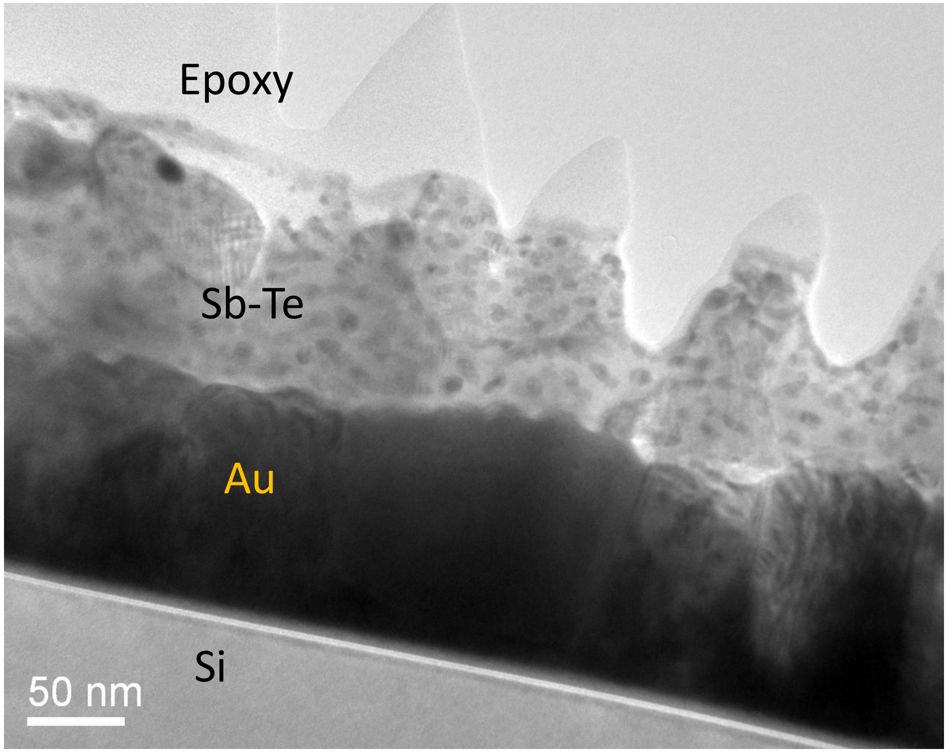
Continuous vs. pulsed electrodeposition of Sb_2Te_3



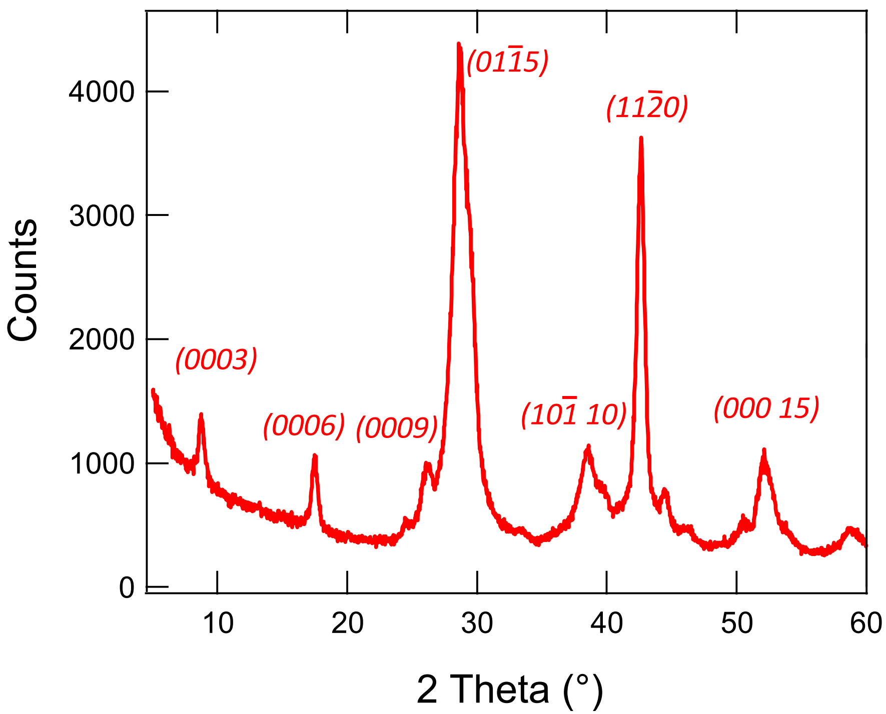
Films deposited using pulsed plating are crystalline and consistent with the Sb_2Te_3 tetradymite crystal structure

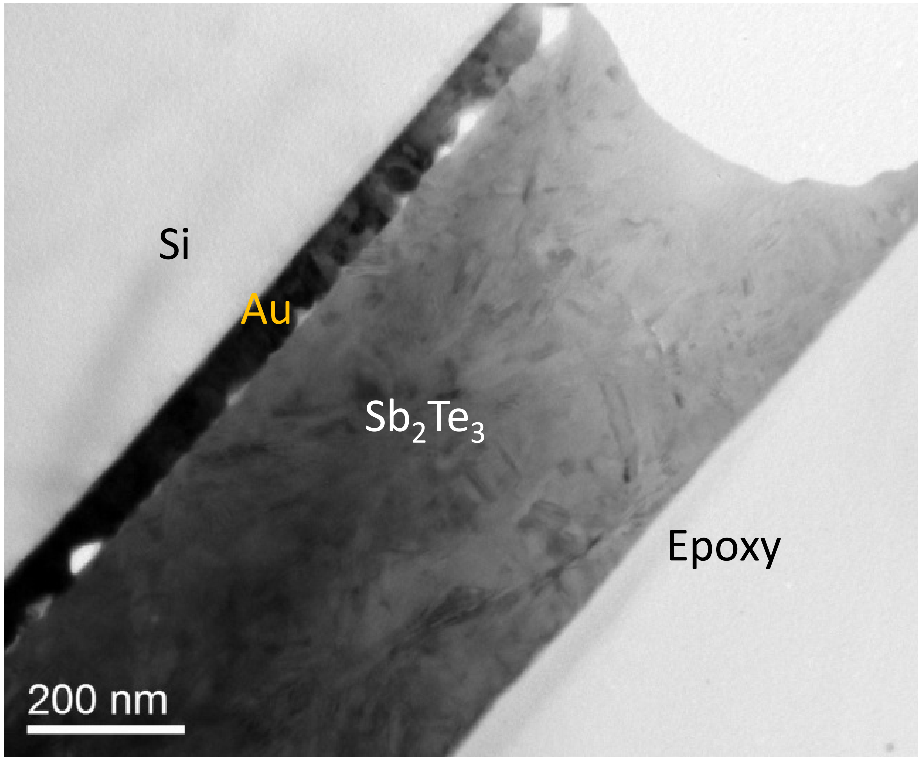
Continuous (dc) electrodeposition of Sb_2Te_3





Pulsed electrodeposition of Sb_2Te_3

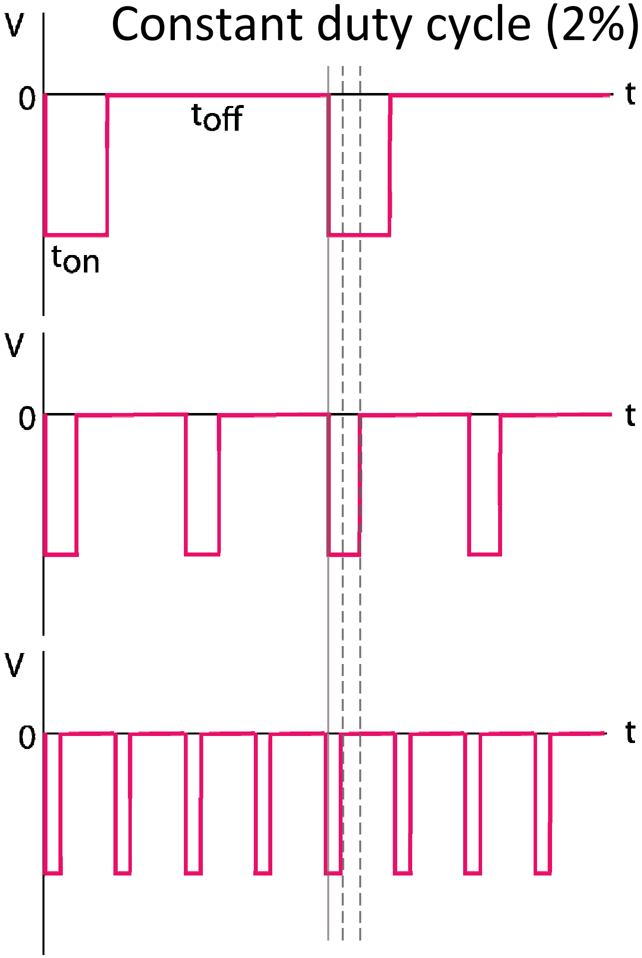




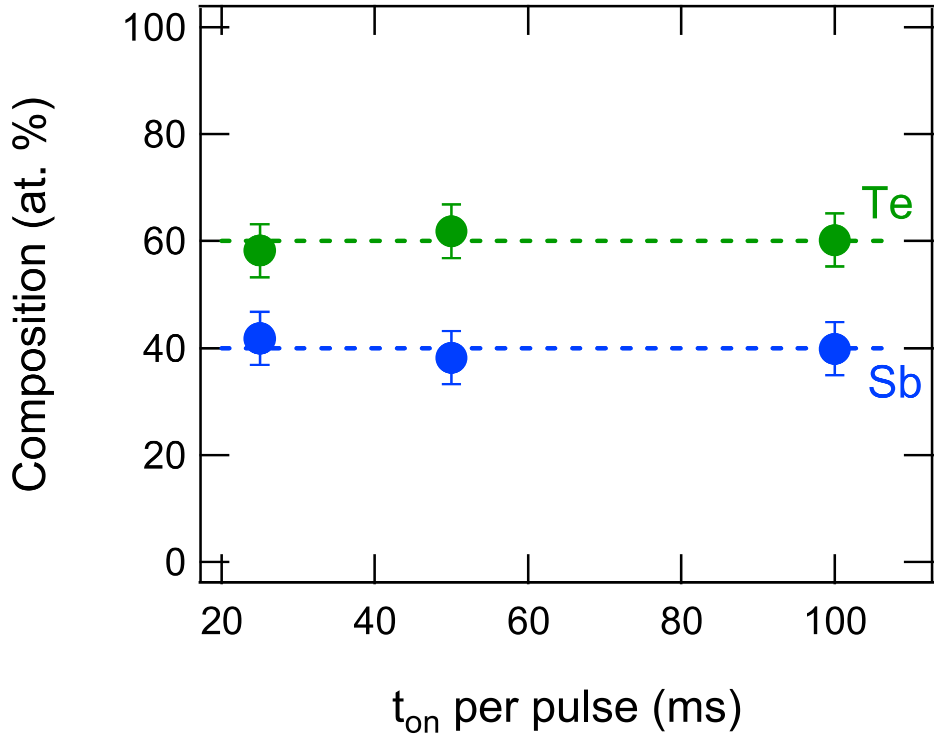
Duty cycle = 2 %, t_{on} = 100 ms

- Polycrystalline
- Stoichiometric Sb_2Te_3
- Uniform composition throughout thickness

How does the composition vary with t_{on}?



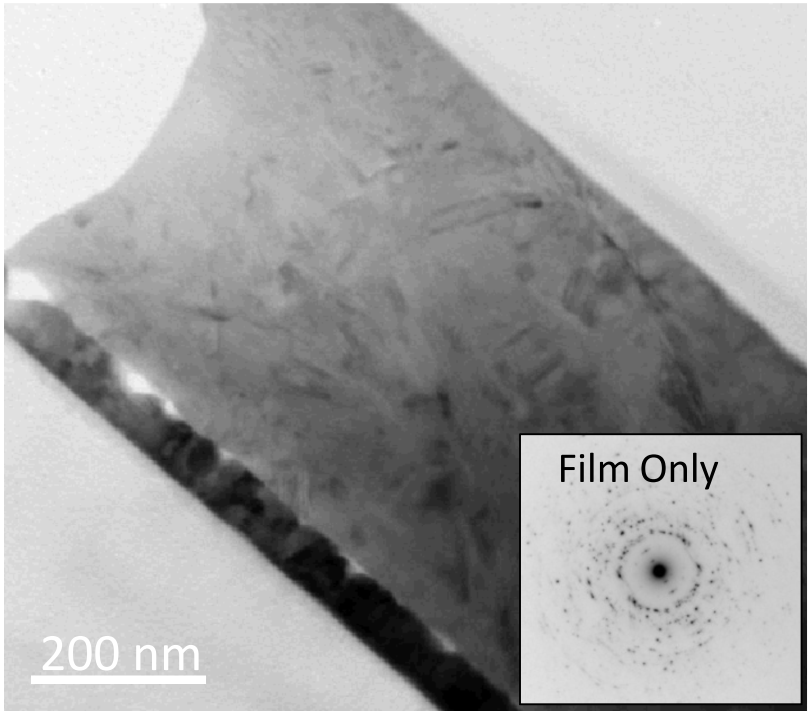
Duty cycle $= \frac{t_{on}}{t_{on} + t_{off}} \times 100\%$



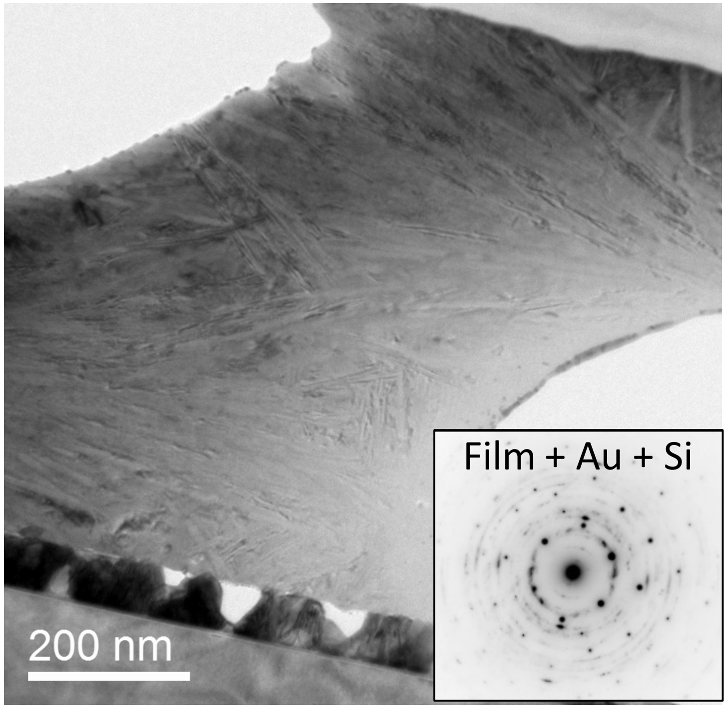
Composition is uniform and stoichiometric for pulse on times of 25-100 ms

How does the microstructure vary with t_{on}?

t_{on}= 100 ms

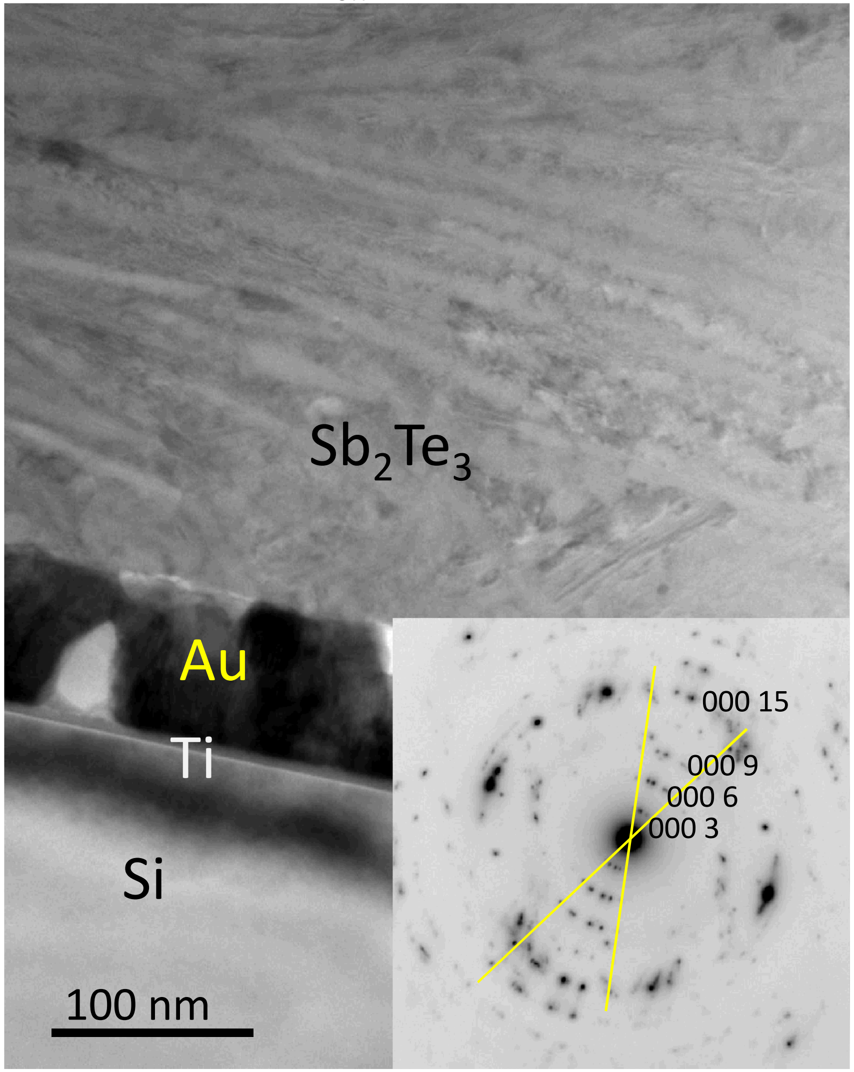


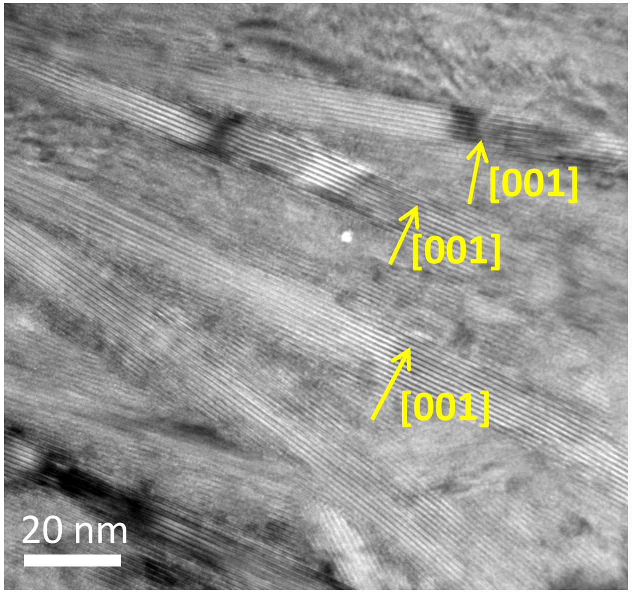
t_{on}= 50 ms



Lamellar microstructure observed at short pulse times

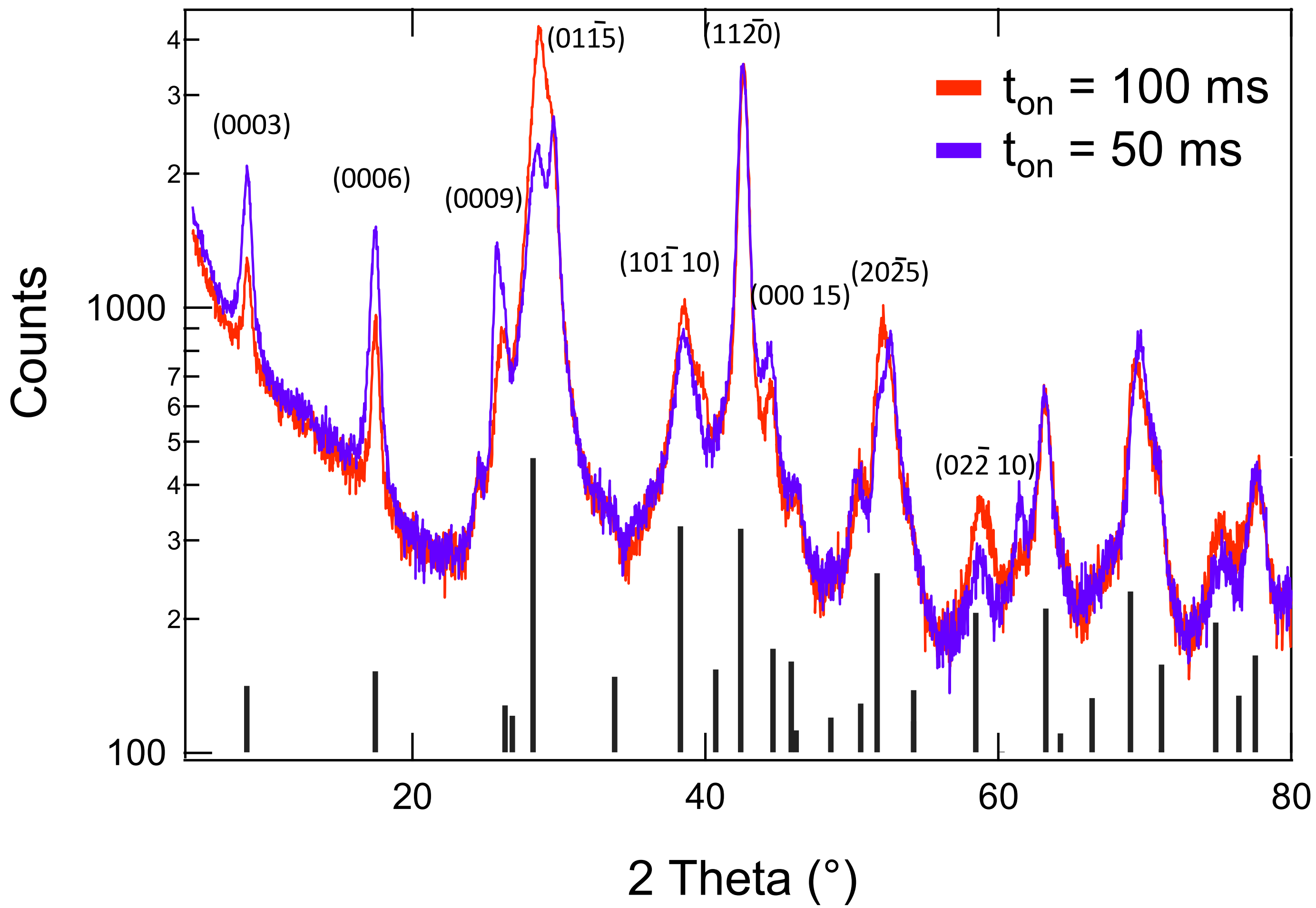
Sb-Te thin film: t_{on}= 50 ms, duty cycle = 2 %



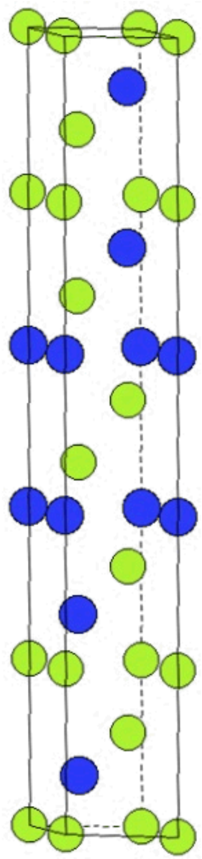


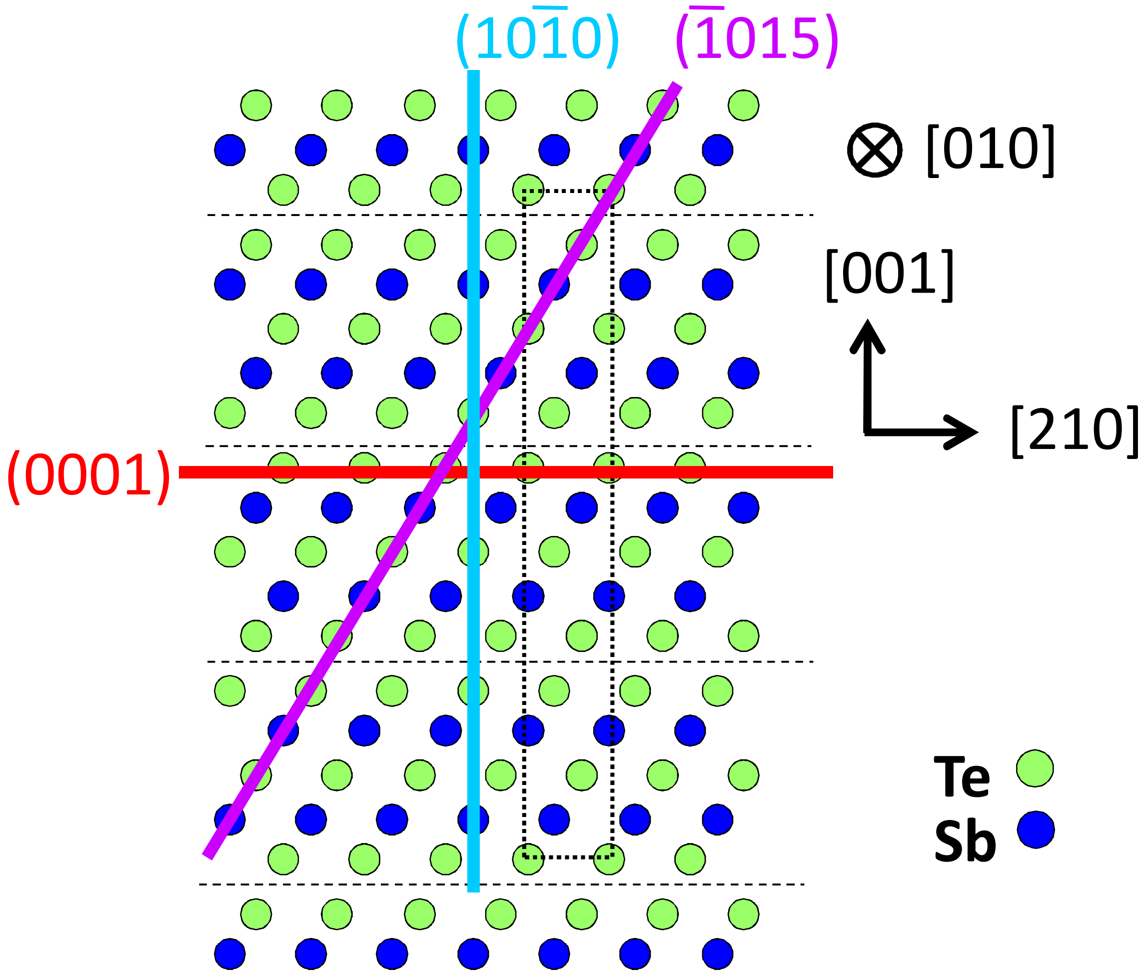
- For $t_{on} \leq$ 50 ms, lamellar features that are nearly parallel (within 20°) to the substrate are commonly observed
    - Grains are up to 750 nm x 40 nm thick
    - Many pulses (10 – 40) are necessary to deposit the material in one lamellae
- These grains are oriented with the Sb_2Te_3 (000*l*) planes parallel to the long axis (the [001] direction parallel to the short axis)

Effect of decreasing pulse on time: structure & texture



Crystallography of Sb_2Te_3



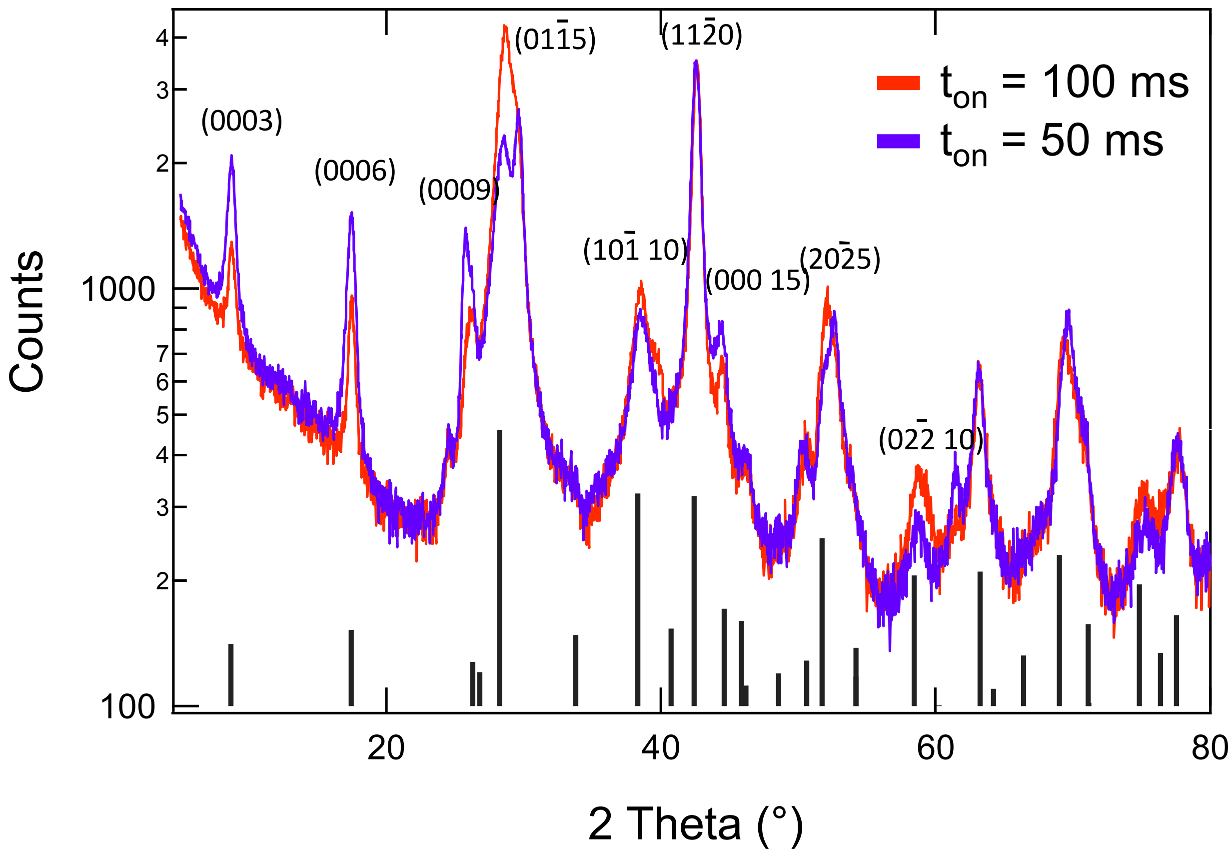


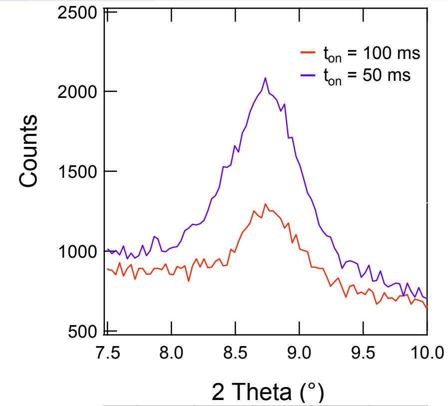
<u>Tetradymite</u>

Hexagonal unit cell:

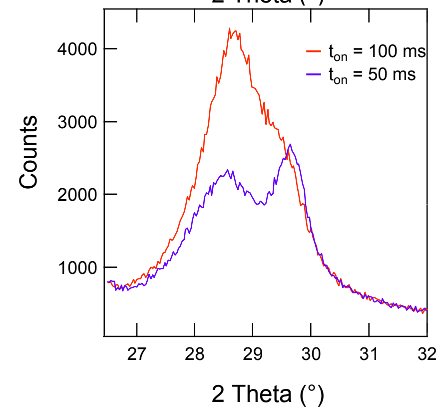
a = b = 4.264 Å, c = 30.458 Å

Changes in preferred orientation observed with decreasing t_{on}

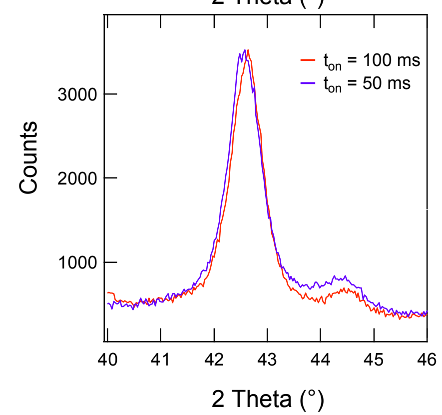




(0003)



(01$\bar{1}$5)



(11$\bar{2}$0)

- Deposition on (000*l*) planes is favored over (01$\bar{1}$5) planes at shorter pulse times

Summary

- Sb_2Te_3 thin films were grown by a pulsed potentiostatic electrodeposition process
  - For short pulse times, electron diffraction and XRD indicates that the films are somewhat textured with the (000*l*) planes nearly parallel to the substrate when deposited 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
    - Short pulses followed by off time may allow for more atoms to be in more stable configurations
    - (000*l*) are low index planes with reasonable high atomic density and are likely stable
- *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 suppressed*

Acknowledgements

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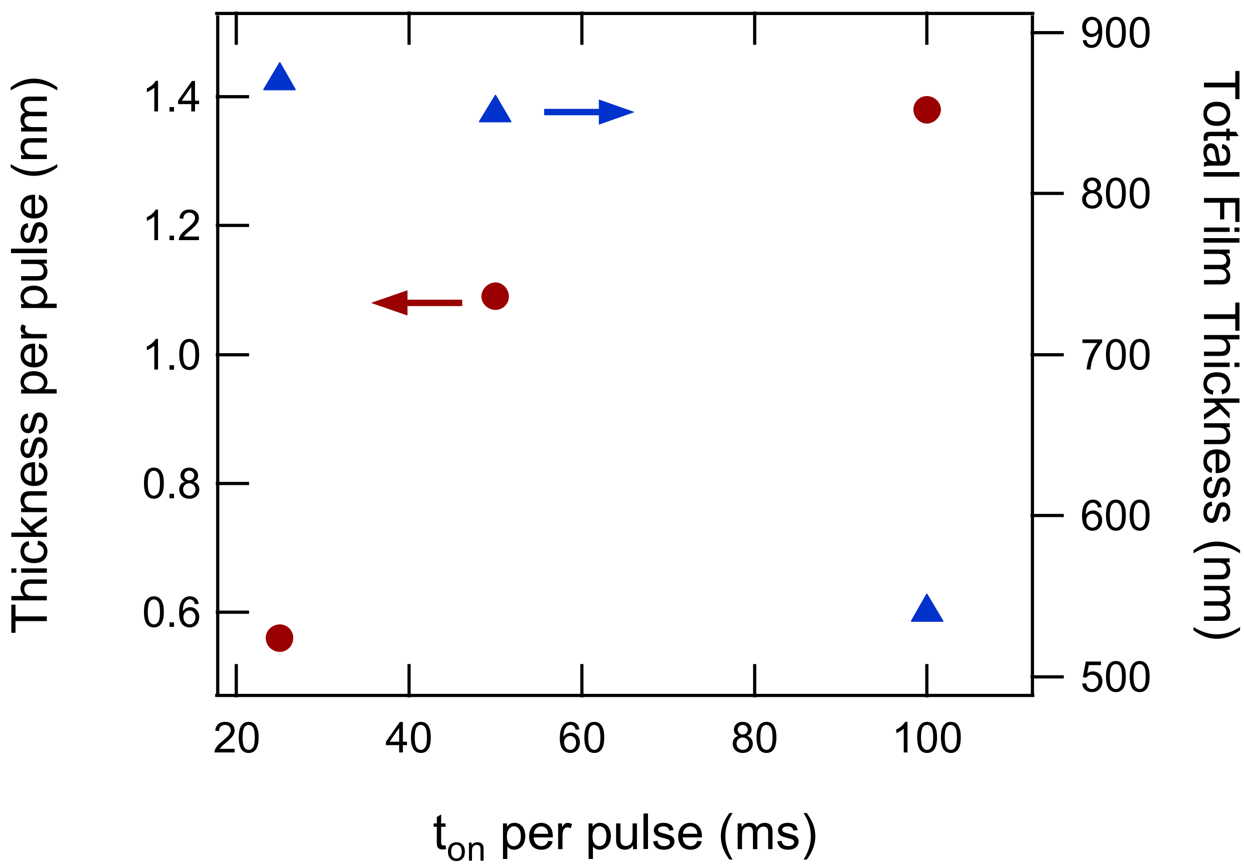
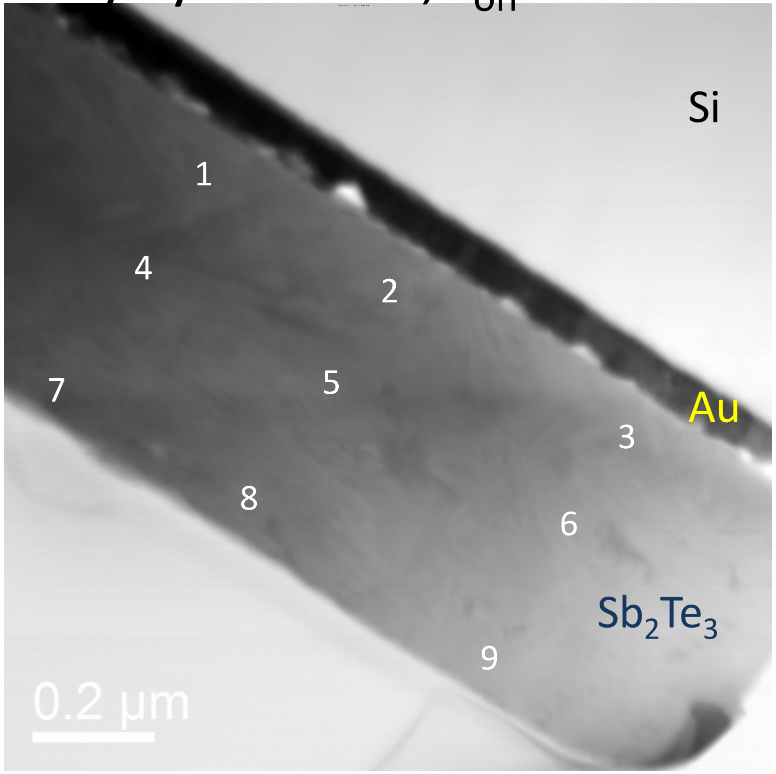
How does the film thickness vary with t_{on}?



Compositional uniformity in pulse plated Sb_2Te_3

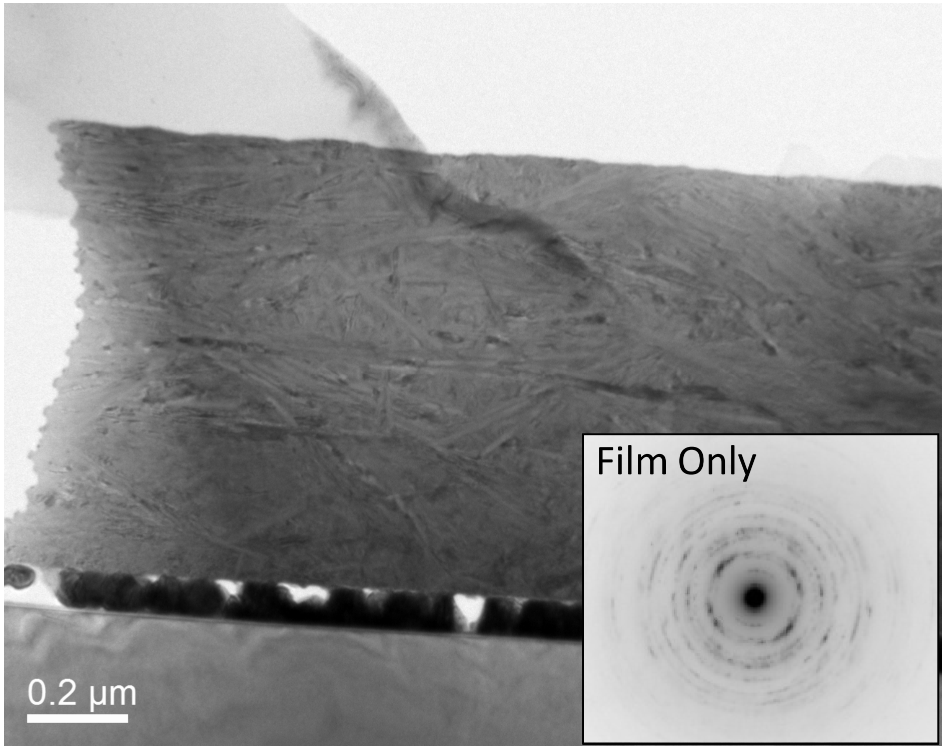
Duty cycle = 2 %, t_{on} = 100 ms



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 is uniform through the thickness of the pulse electrodeposited film at 2% duty cycle



t_{on}= 25 ms

Hypotheses for microstructural change

Shorter pulse times lead to fewer atoms deposited per pulse

Off times allow atoms in less stable positions to desorb into solution

(001) Lamellae may be a stable configuration

- Van der waals bonding between 5-layer packets
- Low index, high density planes generally stable