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Chalcogenide compounds made by pulsed laser deposition at 355 and 248 nm

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Summary

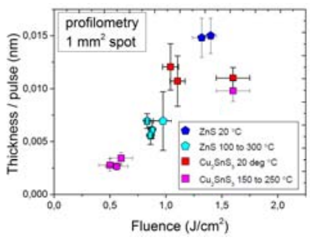
- Thin films made by pulsed laser deposition may differ depending on the laser wavelength. We compared ZnS, Cu_2SnS_3 and a target enriched with SnS relative to Cu_2SnS_3 using 355 nm and 248 nm lasers.
- Cu_2SnS_3 deposition gives a high density of droplets at 355 nm. The higher UV 248 nm laser was expected to reduce the droplets but did not.
- The SnS enriched Cu-Sn-S films had different morphology and post-annealing composition using the two lasers

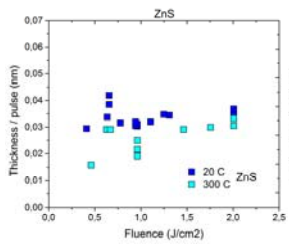
λ	355 nm	248 nm
Laser	Nd:YAG	Kr excimer
Pulse length	5-7 ns	~20 ns
Spot size	2.5 mm^2 (see note on deposition rate	2.2 mm^2
Fluence	0.4-2.3 J/cm^2	0.4-2.2 J/cm^2
Target-substrate dist	4-4.5 cm	4 cm
Pulse repetition rate	10 Hz	10 Hz
Target rotation and laser rastering in place in both setups		

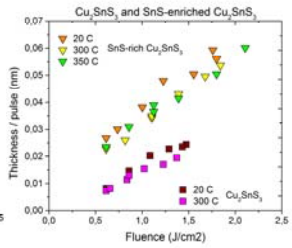
Deposition rate

355 nm laser: ZnS and Cu_2SnS_3 have similar deposition rates

248 nm laser: ZnS is deposited faster than Cu_2SnS_3







The bandgap of ZnS (3.5-3.6 eV) exceeds the 3.49 eV photon energy of the 355 nm laser, so as expected, ZnS deposition is faster using the 248 nm laser.)*

Deposition of SnS-enriched Cu_2SnS_3 is faster than deposition of stoichiometric Cu_2SnS_3
The deposition is slightly faster at room temperature than at 150-300 ° C.

For the deposition rate measurements at 355 nm, the spot size was 1 mm^2 and the films were measured by Dektak profilometry.

For the 248 nm measurements, the spot size was 2.2 mm^2 and a quartz crystal microbalance was used to monitor film growth.

Morphology

As deposited

355 nm laser | 248 nm laser

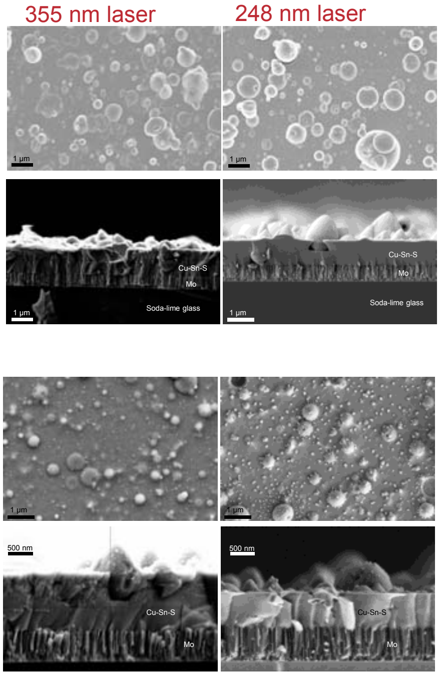
Films are covered in µm-size droplets from target

The amount and size of droplets does not change significantly with laser wavelength

The morphology of the SnS-enriched films (bottom) was quite different with the 355 nm versus the 248 nm laser. However, the stoichiometry was similar as seen on the right (under annealing).

Cu_2SnS_3

SnS-enriched Cu_2SnS_3



Depositions were done at 20-25 °C.
Substrates were Molybdenum-coated soda lime glass
Top images: SEM in-lens detector
All other images secondary electon detector

Morphology

After annealing with S

355 nm laser | 248 nm laser

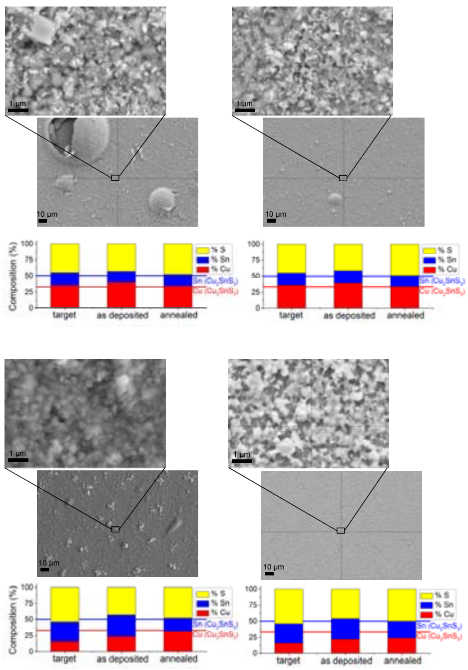
Annealed films of Cu_2SnS_3 by the two lasers had similar composition and appearance.

In contrast, films of SnS-enriched Cu_2SnS_3 by the two lasers were highly distinct. The as-deposited films had a similar atomic composition, but the annealed films differed both in composition and appearance.

All films except the SnS-enriched film deposited at 355 nm contain bubbles; large burst bubbles were seen in the Cu_2SnS_3 film deposited at 355 nm.

Cu_2SnS_3

SnS-enriched Cu_2SnS_3



Annealed films contain a mix of SnS (brighter in SEM images) and Cu_2SnS_3 (darker)
Composition was measured by Energy Dispersive X-Ray Spectroscopy at 15 keV.

Annealing was done with S-flakes by fast heating (12°C/min) to 450 °C followed by slow heating 1 °C/min) to 570 °C

*) similar data on 355 nm deposition previously shown in Ettlinger et al., 2015, App. Surf. Sci., Vol 336, pp. 385-390

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