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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, Cu2SnS3 and a target enriched with SnS relative to Cu2SnS3 using 355 nm and 248 nm lasers.
• Cu2SnS3 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.

Deposition rate
355 nm laser: ZnS and Cu2SnS3 have similar deposition rates
248 nm laser: ZnS is deposited faster than Cu2SnS3

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 Cu2SnS3 is faster than deposition of stoichiometric Cu2SnS3. The deposition is slightly faster at room temperature than at 150-300 ° C.

Morphology
As deposited
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).

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

Morphology After annealing with S

Annealed films of Cu2SnS3 by the two lasers had similar composition and appearance.

In contrast, films of SnS-enriched Cu2SnS3 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 Cu2SnS3 film deposited at 355 nm.

Annealing was done with S-flakes by fast heating (12 °C/min) to 410 °C followed by slow heating 1 °C/min to 750 ° C.

For the deposition rate measurements at 355 nm, the spot size was 1 mm2 and the films were measured by Dektak profilometry.

For the 248 nm measurements, the spot size was 2.2 mm2 and a quartz crystal microbalance was used to monitor film growth.

*) 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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