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Pulsed laser deposition (PLD) of multi-component oxide target for Cu_2ZnSnS_4 solar cells

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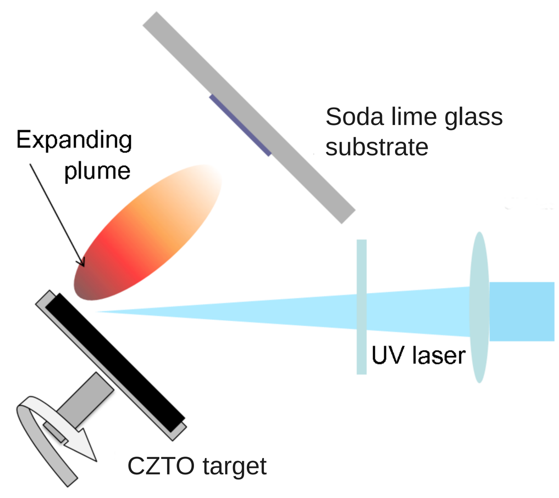
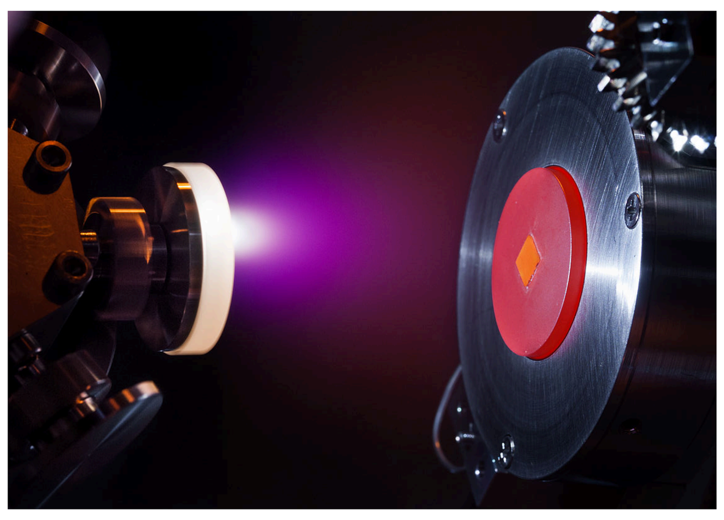
Introduction

Pulsed laser deposition (PLD) is one of the most effective methods for fabricating and controlling the composition ratio of thin films. PLD is especially appropriate for the growth of oxides, since an oxygen background can be supplied during deposition to decrease the oxygen loss[1]. In this work, we report on the fabrication of the Cu_2ZnSnS_4 thin films by pulsed laser deposition from a multi-component oxide target of CZTO in vacuum followed by annealing in a sulfur atmosphere. The laser fluence was appropriately varied for controlling the composition of the oxide thin film precursors, following a similar approach as in the case of the sulfide precursors[2].

Pulsed Laser Deposition

- The use of the laser beam enables precise control over the growth rate (sub-monolayer per pulse)
- Wide range of pressure from 10^{-7} mbar to 1 bar
- The flexibility of controlling laser beam wavelength and power density
- Deposition of multicomponent target

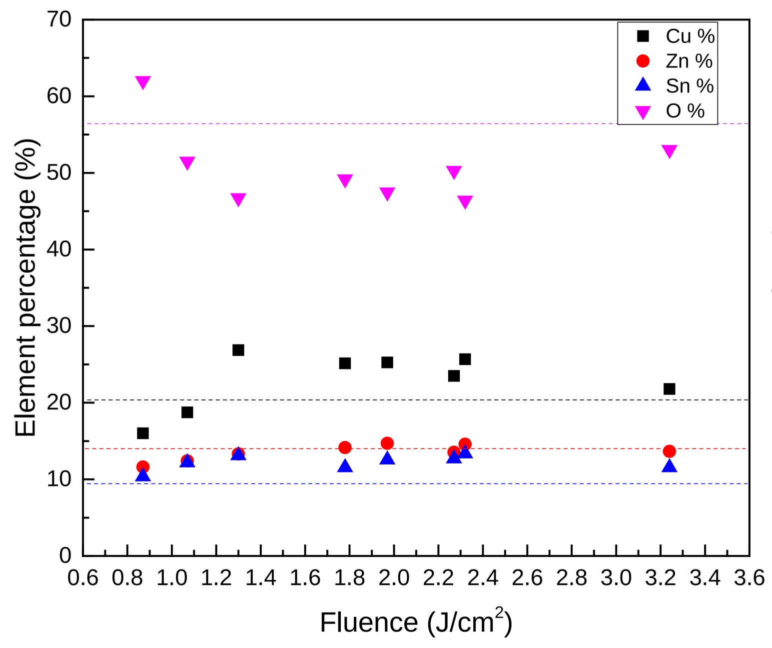


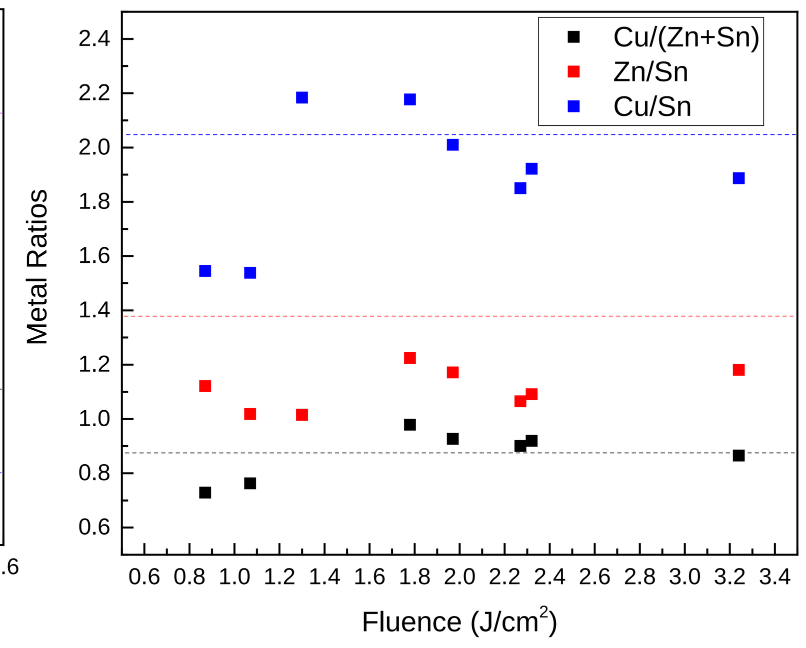


Schematic and a plume ejected from target during pulsed laser deposition.

Sample

EDX comparison with laser fluence





- EDX measurements of samples and target has been indicated with symbols and dashed lines respectively
- Possibility of controlling the Cu/(Zn+Sn), Zn/Sn and Cu/Sn ratios between 1.0-0.85, 1.0-1.2, and 2.2-1.9 at fluence higher than 1.7 J/cm².

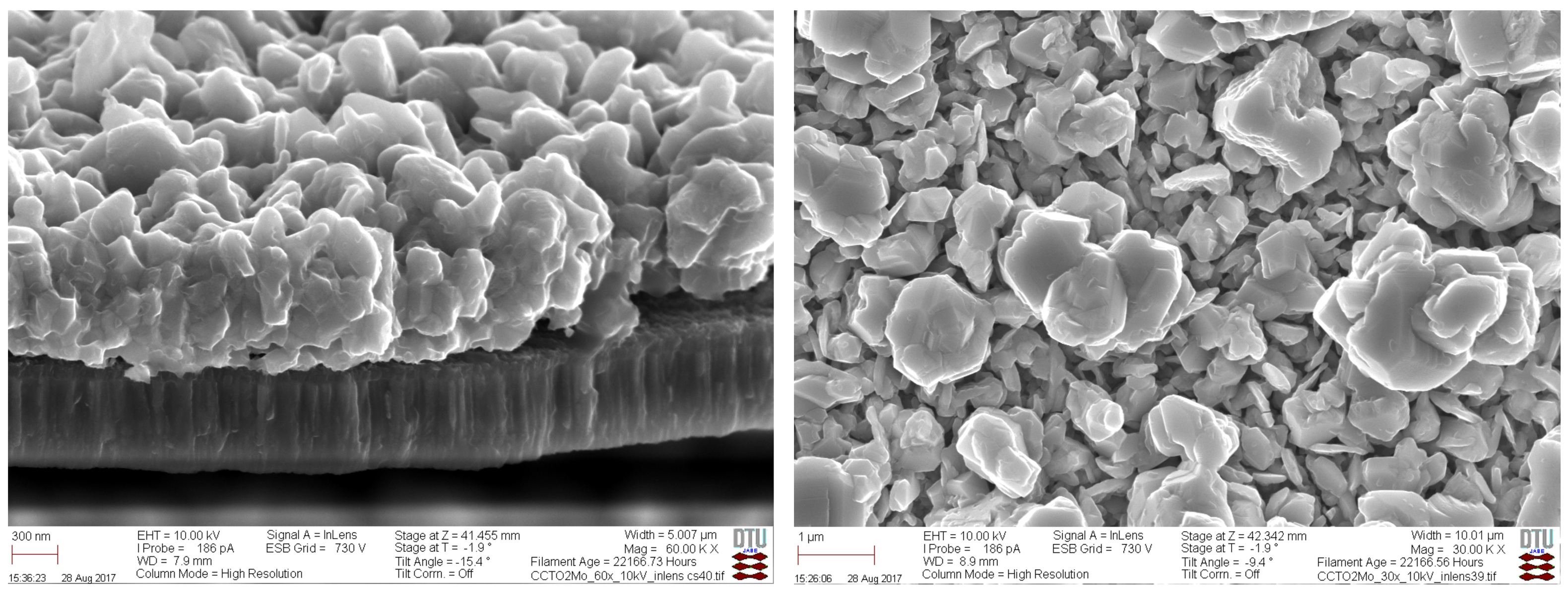
Annealing

Sample	Cu %	Zn %	Sn %	O and S %	Cu/Sn	Cu/(Zn+Sn)	Zn/Sn	Thickness (nm)
CZTO 2	25.9	14.18	12.41	47.51	2.09	0.97	1.14	691
CZTO 2 A	23.99	13.53	11.67	50.81	2.06	0.95	1.16	~1000

- Oxide films were fully sulfurized upon annealing at 100 mbar N_2 with sulfur for 10 min at 570 °C.
- Thickness increased about 45% after annealing.
- Composition ratios hasn't changed after annealing.

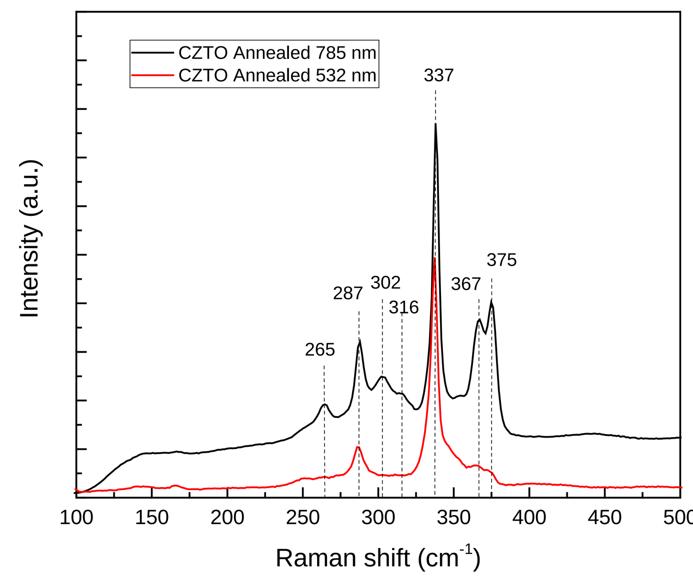
Characterization

SEM (Annealed sample)

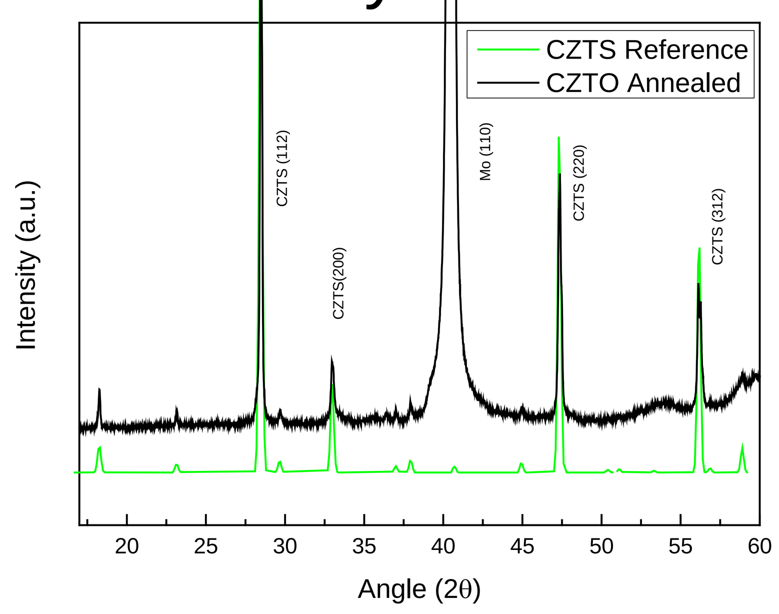


- Irregular grain size between 0.2 to 2 µm has been observed.
- Around 70 nm MoS_2 layer has been formed.
- Mo layer were partially delaminated from glass after annealing.

Raman

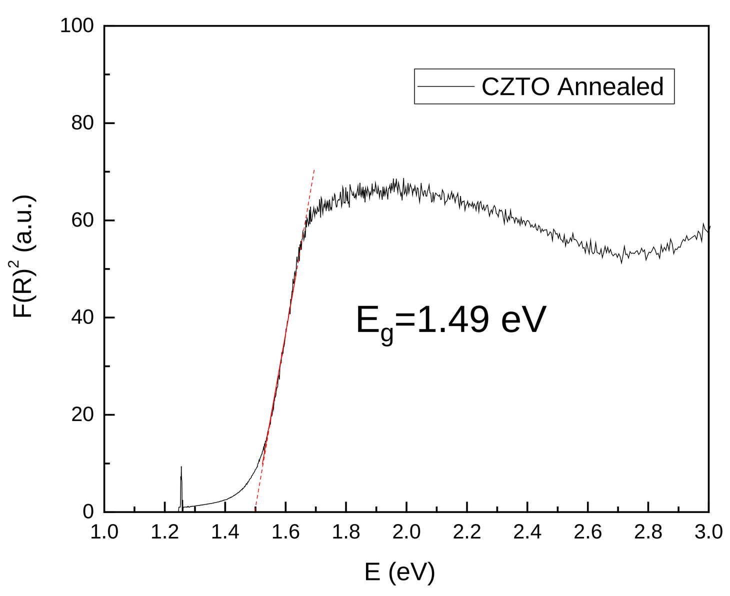


X-ray diffraction

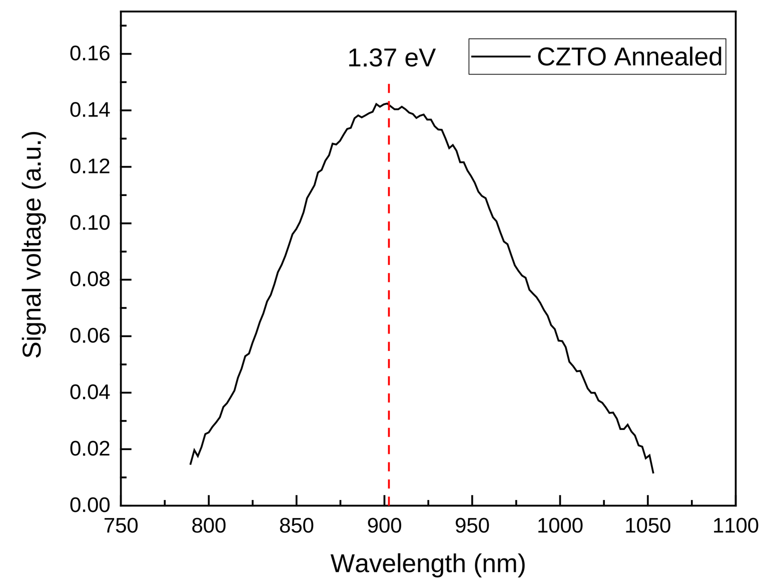


- CZTS reference peaks have been observed both in Raman and XRD without any secondary phase peaks.
- UV Raman signal was too low to detect CZTS or possible ZnS peaks.

Reflectance



Photoluminescence



- Bandgap of 1.49 eV obtained by using Kubelka-Munk method[3] for direct bandgap material
- Photoluminescence peak at 1.37 eV was comparable to previous studies with PLD deposited samples with 1.32 eV[2].

Conclusion

- Multi-component oxide precursors were fully sulfurized after annealing. More precise methods than EDX needed to quantify elements for fluence dependence sulfurization.
- Annealing conditions have to be optimized to obtain more regular grain sizes.
- Composition ratio can be slightly controlled in the Cu poor Zn rich condition
- Although grain size is irregular good CZTS crystallinity has been obtained.
- No secondary phases have been detected with XRD and Raman (532 nm, 785 nm)

References

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2. Cazzaniga, A. *et al.* Ultra-thin Cu 2 ZnSnS 4 solar cell by pulsed laser deposition. *Sol. Energy Mater. Sol. Cells* **166,** 91–99 (2017).
3. Davisdóttir, S., Dirscherl, K., Canulescu, S., Shabadi, R. & Ambat, R. Nanoscale surface potential imaging of the photocatalytic TiO 2 films on aluminum. doi:10.1039/c3ra43082k

Sample	Fluence (J/cm^2)	Cu/Sn	Cu/(Zn+Sn)	Zn/Sn	Thickness (nm)
CZTO 4	0.87	1.54	0.73	1.12	292
CZTO 1	1.07	1.54	0.76	1.02	740
CZTO 3	1.3	2.18	1.02	1.02	915
CZTO 2	1.97	2.01	0.93	1.17	691
CZTO6	2.27	1.89	1.065	1.07	
CZTO7	2.32	1.92	1.09	1.09	
CZTO 5	3.24	1.60	0.86	1.18	350

Sample	Fluence (J/cm^2)	Cu %	Zn %	Sn %	O %	Thickness (nm)
CZTO 4	0.87	16.01	11.61	10.36	62.02	292
CZTO 1	1.07	18.74	12.4	12.18	51.49	740
CZTO 3	1.3	26.85	13.32	13.12	46.72	915
CZTO 2	1.97	25.26	14.7	12.55	47.48	691
CZTO6	2.27	23.49	13.52	12.7	50.29	
CZTO7	2.32	25.67	14.57	13.36	46.4	
CZTO 5	3.24	21.79	13.64	11.55	53.02	350
CZTO 6		23.47	13.54	12.69	50.29	
CZTO 7		25.67	14.57	13.36	49.73	
CZTO 8		25.14	14.14	11.55	49.19