PULSED LASER DEPOSITION OF NOVEL SPINEL MATERIALS FOR PHOTOVOLTAIC CONVERSION

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https://doi.org/10.37904/nanocon.2024.5007

Abstract

While all traditional photovoltaic materials are covalent compounds with coordination number 4, currently the most progressive materials - hybrid halide perovskites - have coordination number 6 and are ionic. This can be the key to success, especially regarding surface electronic properties, which are essential for polycrystalline semiconductors. This motivates us to explore completely new materials - cubic lithium thiospinels - and compare them with the former. Li thiospinels are prepared from stoichiometrically mixed precursors as a pellet in a nitrogen-filled glovebox. This tablet serves as a target in Pulsed Laser Deposition (PLD) and a special chamber is constructed that avoids air exposure of the precursor tablet during the loading. Thin films of lithium thiospinels are deposited on glass substrates and they are characterized by X-ray diffraction and optically by Photothermal Deflection Spectroscopy for accurate determination of absorption edge. Results are promising and demonstrate the validity of this approach.

Keywords: Thiospinels, methodology, hybrid halide perovskites, novel material, pulsed laser deposition

1. INTRODUCTION

To meet the Paris agreement, the implementation of low carbon emission energy sources must be quick and widespread. Photovoltaics, being almost a synonym for renewable energy has not yet completely convinced the society. To do so, efficiency has to be further increased and reliability has to be maintained. For the former, the tandem solar cell is the only option [1,2]. For the latter, the technology of crystalline silicon is an obvious choice for the bottom cell, but the question about the top cell remains open as the currently mostly explored material hybrid perovskite is not stable [3] and is potentially toxic due to lead content and water solubility [4]. Among many new potential materials there are also lithium thiospinels with formula ($Li_2MSn_3S_8$) with M = Mn, Fe, Mn, Ni, Co or with formula $Li_{1.66}CuSn_{3.33}S_8$ [5]. These Li thiospinels have similarly as halide perovskites also tuneable optical band gaps between 0.91 and 2.19 eV, they are ionic crystals and have slightly indirect gap [4]. They are however less toxic and more stable in water. On the other hand, there are several challenges related to the preparation and processing of this material from powder form to thin film. These materials have so far been prepared by high temperature synthesis [5] and mechano-chemical synthesis [6]. In this work, we demonstrate the first successful preparation of Li thiospinel $Li_{1.66}CuSn_{3.33}S_8$ thin film by pulsed laser deposition (PLD). In order to avoid air exposure of the material precursors and to limit the contamination of PLD chamber, we build a small portable chamber, that can enter nitrogen-filled glove box and also fits inside PLD setup. In this way the material precursors are kept in inert atmosphere until the PLD deposition is finished.

2. EXPERIMENTAL SECTION

The material precursors were mixed into stoichiometric mixture corresponding to $Li_{1.66}CuSn_{3.33}S_8$ and milled in agate mortar and pestle. The powder was then pressed in hydraulic press Specac into small pellets of 5 mm diameter (**Figure 1a**) in a nitrogen-filled glovebox. This tablet then serves as a target in Pulsed Laser Deposition (PLD), and a special chamber (**Figure 1b**) is constructed to avoid the precursor tablet's air exposure during the loading into the PLD setup and unloading. The chamber has quartz dome cover that is transparent for PLD laser (KrF 248 nm) and is equipped with vacuum valve and vacuum flange so that it can be connected to a turbomolecular vacuum pump. The pellet together with glass substrate (2 × 2 cm) was placed inside the chamber in nitrogen-filled glovebox.

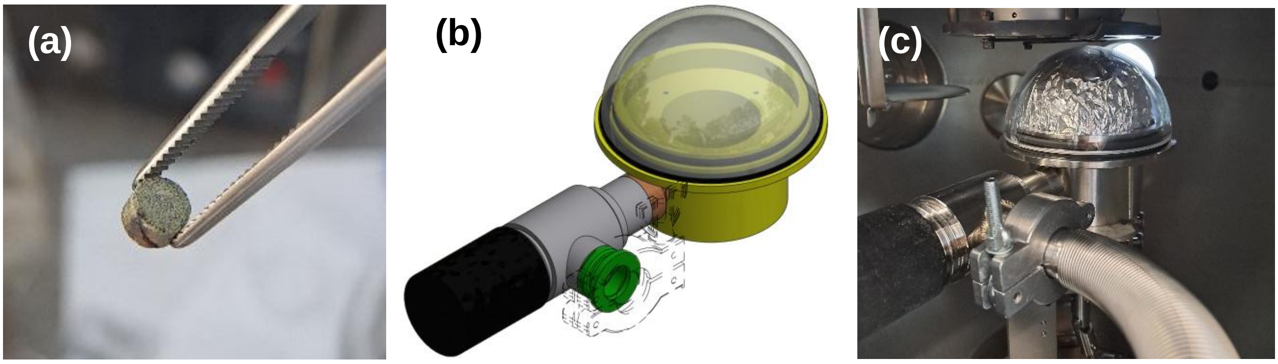


Figure 1 (a) Pellet of Li thiospinels **(b)** Special portable chamber designed **(c)** Special chamber placed inside of the original PLD chamber to avoid contamination and connected to a turbomolecular pump.

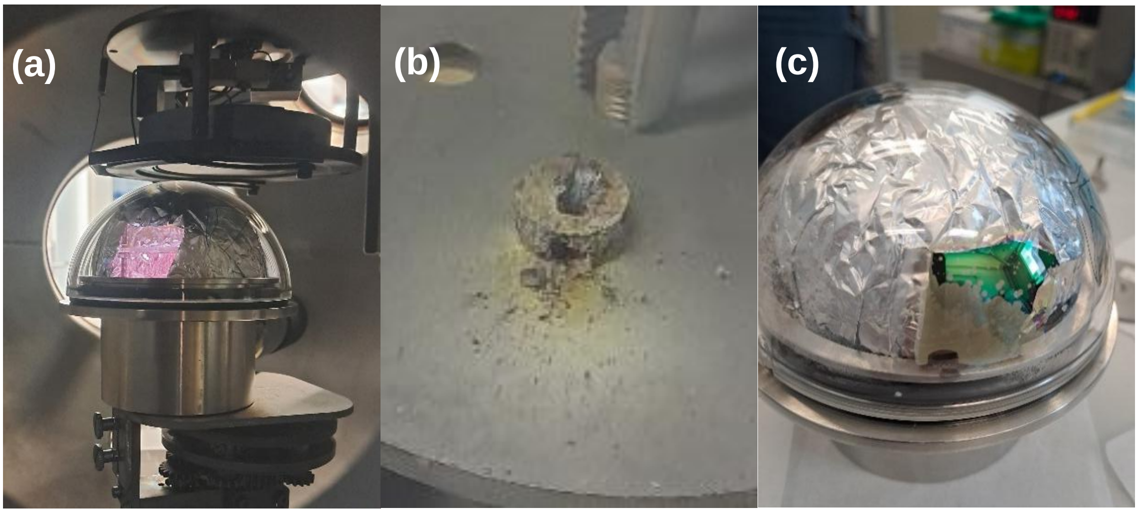


Figure 2 The violet colour of plasma plume visible at the uncovered part of the quartz dome **(a)**. Pellet of Li thiospinels after first successful deposition of thin film by PLD **(b)**. Contamination of quartz dome during deposition **(c)** of the very first thin film of Li thiospinel successfully deposited by PLD.

Before the deposition, the chamber was connected to an external vacuum pump and pumped to vacuum lower than 10^{-4} mbar (**Figure 1c**). Chamber was placed inside PLD setup made by TSST B.V. equipped with KrF ($\lambda = 248$ nm) excimer laser COMPex 50 with 150 mJ pulses. The laser was focused 8 times to a spot of theoretical area of ca. 2 mm^2. The alignment of the laser beam is very important because of the small size (5 mm) of the pellet. For the deposition from the Li thiospinels target, the pulse energy (measured inside the chamber) was kept at 24 mJ giving the fluence of approx. 1.2 J/cm^2. In **Figure 2a** the violet colour of plasma inside the chamber during ablation is visible. The first sample was deposited at a repetition rate of 30 Hz and the number of pulses was 5000. We observed that because of a higher repetition rate of 30 Hz and a large number of pulses, the target was fully ablated in the region of the beam hitting the target (**Figure 2b**) as no movement of the laser or the pellet was implemented and the laser was hitting always one spot. The window glass of the special chamber was also contaminated during deposition (**Figure 2c**). This contamination can be removed by ethanol. For the next experiments we reduced the number of pulses as well as the frequency in the subsequent depositions. The pellet was flipped for the next deposition. All the depositions were made at room temperature, as no substrate heating is implemented in the portable chamber. **Table 1** shows the laser frequency and number of pulses used.

Table 1 List of samples and PLD parameters

Sample no.	Frequency (Hz)	No. of pulses	Thickness (nm)
1	30	5000	51
2	20	1000	30
3	20	2000	150

3. RESULTS AND DISCUSSIONS

The deposited thin films were characterized by X-ray diffraction (**Figure 3a**) and by scanning electron microscope Tescan MAIA (**Figure 3b**). We can observe that the thin layers remain amorphous, however higher number of pulses leads to thicker layers, that eventually feature crystalline peaks. Thicker layers are unstable, likely due to poor adhesion, and tend to recrystallize. Morphology of such thicker layers is not uniform (**Figure 3b**).

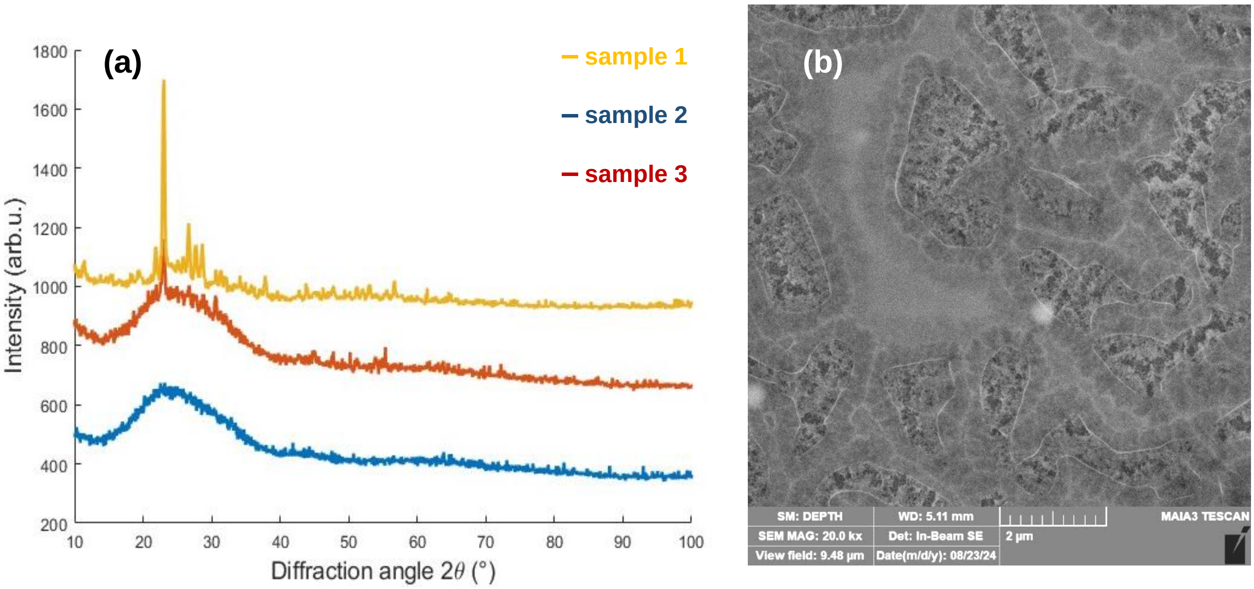
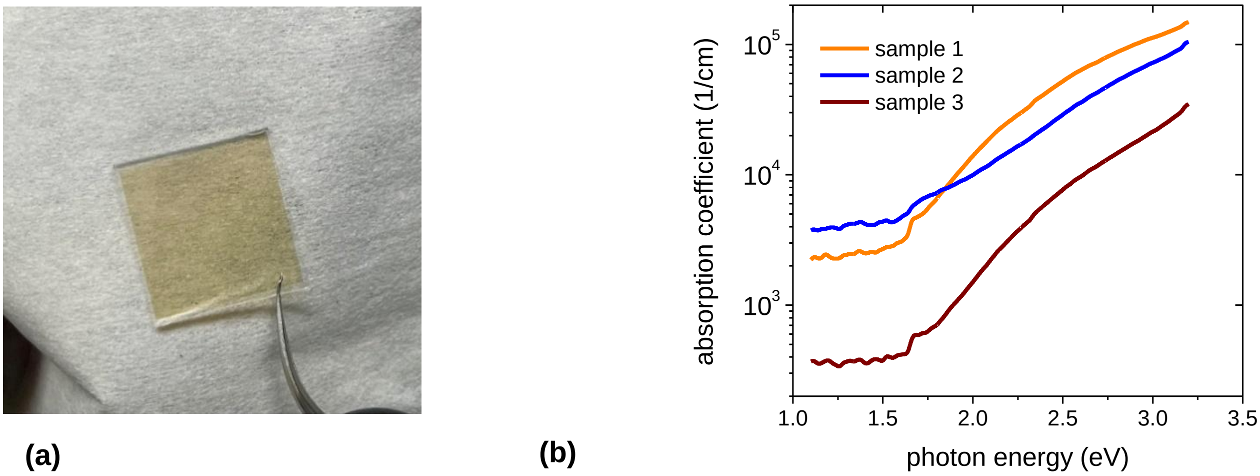


Figure 3 XRD diffraction patterns collected approx. 1 month after the deposition **(a)**. SEM image of sample no 1 approximately one week after the deposition showing probably the recrystallized regions **(b)**.

Table 2 Atomic composition (without lithium).

Atom	Ideal stoichiometry (%)	Experimental - EDX (%)
S	65	73
Cu	8	1.5
Sn	27	25.5

We evaluated also the atomic composition by Energy Dispersive X-ray spectroscopy (EDX) as presented in **Table 2**. As the lithium is giving X-ray line outside of the detection limits of the EDX, we can only assess the ratio of atomic composition of sulphur, copper and tin. We see that the stoichiometry is not perfectly maintained and has to be further tuned, e.g. by laser fluence or repetition rate, or adding low amount of argon into the chamber to slow down the ions.



(a) **(b)**

Figure 4 Visual appearance of thin film (sample no 2) of Li thiospinels successfully deposited by PLD **(a)**. Spectra of absorption coefficient evaluated from PDS **(b)**.

Optically, it can be seen that the layers possess absorption edge in near infrared-to-visible spectrum, yielding typical brownish appearance (**Figure 4a**). For more accurate evaluation of absorptance Photothermal Deflection Spectroscopy (PDS) in Fluorinert FC-72 liquid (refractive index 1.25) was performed. Our PDS setup simultaneously acquires also transmittance and reflectance and allows for an absolute and more accurate evaluation of the absorption coefficient and refractive index in the range from 1.1 eV to 3.2 eV. Refractive index varied in the range from 2.1 to 2.3. Thickness variation measured optically by PDS is shown also in **Table 1**. Absorption coefficient is shown in **Figure 4b**. We can observe clear indication of bandgap, however not sufficiently sharp to yield high open circuit of solar cell [7,8]. Interestingly the absorption coefficient is varying not so much in shape, but especially in absolute value. We attribute this, as well as the variation of optical thickness, to the variable density of the material.

4. CONCLUSION

For the first time, we prepared thin films of Li thiospinels using PLD. These films were characterized using numerous methods including X-ray diffraction, Energy Dispersive X-ray spectroscopy and Photothermal deflection spectroscopy. The first attempts led to layers featuring absorption edge and medium sub-bandgap absorptance. At this point, the technology still needs optimization of deposition parameters, but the first results are very promising and served as excellent proof of the concept of the idea of preparing photosensitive thin films of novel materials by PLD. Also, we demonstrated the validity of our approach of using small portable chamber to avoid air exposure of the precursor materials including sulphides.

ACKNOWLEDGEMENTS

This work was supported by the Czech Science Foundation grant no. 23-06285S and by Czech Ministry of Education, Youth and Sports grant no. CZ.02.01.01/00/22_008/0004617 − "Energy conversion and storage" and Czech Technical University in Prague student grant no SGS24/135/OHK3/3T/13.

REFERENCES

[1] E. AYDIN, T.G. ALLEN, M. DE BASTIANI, A. RAZZAQ, L. XU, E. UGUR, J. LIU, S. De WOLF. Pathways toward commercial perovskite/silicon tandem photovoltaics. *Science*. 2024, vol. 383, eadh3849. Available from: https://doi.org/10.1126/science.adh3849.

[2] LONGi sets a new world record of 33.9% for the efficiency of crystalline silicon-perovskite tandem solar cells, (2023). Available from: https://www.longi.com/en/news/new-world-record-for-the-efficiency-of-crystalline-silicon-perovskite-tandem-solar-cells/ (accessed April 1, 2024).

[3] R. WANG, M. MUJAHID, Y. DUAN, Z. WANG, J. XUE, Y. YANG, A Review of Perovskites Solar Cell Stability. *Adv Funct Materials.* 2019, vol. 29, 1808843. Available from: https://doi.org/10.1002/adfm.201808843.

[4] C.E. TORRENCE, C.S. LIBBY, W. NIE, J.S. STEIN. Environmental and health risks of perovskite solar modules: Case for better test standards and risk mitigation solutions. *iScience*. 2023, vol. 26, 105807. Available from: https://doi.org/10.1016/j.isci.2022.105807.

[5] M.A. QUINTERO, S. HAO, S.V. PATEL, J.-K. BAO, X. ZHOU, Y.-Y. HU, C. WOLVERTON, M.G. KANATZIDIS, Lithium Thiostannate Spinels: Air-Stable Cubic Semiconductors. *Chem. Mater*. 2021, vol. 33, pp. 2080–2089. Available from: https://doi.org/10.1021/acs.chemmater.0c04651.

[6] E.M. HEPPKE, S. MAHADEVAN, M. LERCH, New compounds of the $Li_2MSn_3S_8$ type. *Zeitschrift Für Naturforschung B 75.* 2020, pp. 625–631. Available from: https://doi.org/10.1515/znb-2020-0050.

[7] U. RAU. Reciprocity relation between photovoltaic quantum efficiency and electroluminescent emission of solar cells, *Physical Review B.* 2007, vol. 76, 085303. Available from: https://doi.org/10.1103/PhysRevB.76.085303.

[8] J. HOLOVSKÝ, K. RIDZOŇOVÁ, A. PETER AMALATHAS, B. CONRAD, R.K. SHARMA, X.Y. CHIN, E. BASTOLA, K. BHANDARI, R.J. ELLINGSON, S. DE WOLF. Below the Urbach Edge: Solar Cell Loss Analysis Based on Full External Quantum Efficiency Spectra. *ACS Energy Lett*. 2023, vol. 8, pp. 3221–3227. Available from: https://doi.org/10.1021/acsenergylett.3c00951.