

Conference Paper

Laser-based Diagnostics for Use in Ex-situ Lithium Co-deposit Analysis

E. D. Vovchenko, S. A. Krat, Yu. M. Gasparyan, A. P. Melekhov, A. Prishvitsyn, and V. A. Kurnaev

National Research Nuclear University MEPhI, Kashirskoe shosse 31, Moscow, 115409, Russia

Abstract

Laser-induced breakdown spectroscopy (LIBS) and time of flight (TOF) mass spectrometry of laser-produced ions were tested for ex-situ analysis of lithium co-deposited layers produced by plasma deposition. It was found that LIBS provides an adequate way to observe and measure lithium content in thin co-deposited layers of about 1 μm thickness. TOF mass spectrometry data of the same layers was compared with LIBS. TOF mass spectrometry provided a better resolution; however, the simplicity of LIBS setup and the rate of measurement (less than one minute per measurement) makes it more attractive. Argon was observed in the co-deposited layers, indicating that it, and likely other inert gases, can remain trapped in lithium layers even after a prolonged exposure to and chemical reaction with atmospheric air.

Corresponding Author:

S. A. Krat
sokrat@mephi.ru

Received: 22 July 2018

Accepted: 9 September 2018

Published: 8 October 2018

Publishing services provided by
Knowledge E

© E. D. Vovchenko et al. This article is distributed under the terms of the [Creative Commons Attribution License](#), which permits unrestricted use and redistribution provided that the original author and source are credited.

Selection and Peer-review under the responsibility of the Breakthrough Directions of Scientific Research at MEPhI Conference Committee.

1. Introduction

Lithium is considered as a promising material for use in plasma-facing components (PFC) of fusion devices [1–4], as a part of liquid metal first wall concept [5–7] it meant to address such issues of traditional solid PFCs as radiation damage accumulation and melting under high heat loads expected in ITER and, later in DEMO reactors. Due to its low atomic number and ionization potential, it has good compatibility with fusion plasmas [8]. It was observed that lithium injection increases plasma confinement time, mitigates plasma instabilities, and improves hydrogen recycling [5, 9–11].

Lithium is highly chemically reactive, and can accumulate a lot of hydrogen isotopes [12–17], including radioactive tritium. Hydrogen content can be as high as tens of percent in co-deposited layers. This can be problematic from the perspective of radiation safety. In addition to accumulating large quantities of hydrogen isotopes, lithium and lithium compounds expected to be observed in fusion devices also react with atmospheric gases and gases that could be present in background vacuum in case of leaks [18–20].

OPEN ACCESS

While there is a number of measurement techniques, such as thermal desorption spectroscopy (TDS) [15, 21] that can analyze the gas content in lithium compounds, measuring the amount of lithium itself is more problematic. Because of its high chemical activity, using delicate mass spectrometers to observe lithium itself is impossible due to the risk of damage *outside of studying* behavior of very thin layers [22]. Low atomic number makes the energy dispersive analysis (EDS) also impossible. Ion beam analysis techniques, such as Rutherford Backscattering, require large, complex, and expensive setups. In this light, laser-induced breakdown spectroscopy seems to be an ideal choice for analyzing lithium deposited layers both in-vacuo and ex-situ, where lithium content, which remains unchanged even after atmospheric exposure, could be measured.

In this article, first results of ex-situ measurements of lithium co-deposited layers produced by magnetron sputtering in deuterium and argon by means of LIBS and TOF mass-spectrometry are shown. Benefits and limitations of both methods are discussed for ex-situ and in-vacuo analysis.

2. Experiment

2.1. Lithium samples

Lithium layers were prepared by means of magnetron sputtering of liquid lithium cathode in deuterium plasma using MD-2 installation [15]. Layer thicknesses (measured in-situ with quartz microbalance) were about 5 μm thick. Li-D mixed layers were deposited on molybdenum substrate at temperatures varying from room temperature to about 100°C due to the lack of active cooling. For initial lithium cathode cleaning argon was used due to its lack of chemical activity with lithium.

Between deposition and analysis, Li layers were exposed to atmospheric air over several days, meaning that they most likely have undergone complete transformation from initial Li-D state into Li_2CO_3 .

2.2. LIBS

A schematic of the LIBS setup used in the experiments is shown in Figure 1. It consists of three main elements: a laser, a fiber optical spectrometer and an optical system. Laser pulses with energy from 90 to 110 mJ, pulse duration of 20 ns and a wavelength of 1064 nm were generated using an Nd:YAG laser operated in the so-called Q-switching

mode. Energy of the pulse was controlled using pyroelectric sensor PE50-C. A laser pulse was focused using a quartz lens ($f = 200$ mm) on the surface of a lithium target to produce a plasma. Plasma luminescence went into fiber optical spectrometer and the spectral lines of each element from laser target could be identified.

Fiber optical spectrometer AvaSpec-2048 (wavelengths interval 200–1100 nm, 1 nm resolution) with CCD Detector Array was used to record optical spectrums in PC after each laser pulse in the experiment. In the initial experiments, synchronization was not used, the integral optical spectrum was recorded from the beginning of plasma luminescence to the final stage of light attenuation.

For the effective collection of laser plasma luminescence generated on the Li target, a quartz lens ($f = 75$ mm) was used, which performed optical conjugation of the plasma (the plane of the object) with the input end of the optical fiber (the plane of the image).

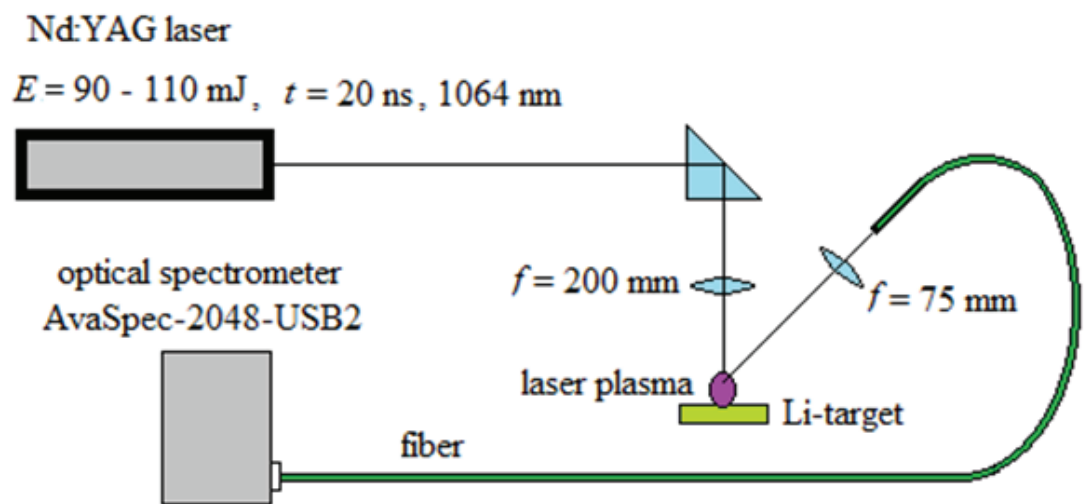


Figure 1: Principal scheme of the LIBS experimental setup.

2.3. TOF mass-spectrometry

Additionally, TOF mass-spectrometer with a sector magnet, previously used for the study of the vacuum spark [23], was also used to study the ions from laser plasma generated on Li-target. Principal diagram of the experimental setup for analysis of Li-target is shown in Figure 2. The sample was placed into a vacuum chamber pumped out to $\sim 10^{-3}$ Pa. Afterward, a laser pulse with an energy of about 30 mJ and the pulse duration of 15 ns produced by Nd:YAG laser focused on the Li-target. The ions of laser plasma generated from the Li surface were then transported through the time of flight tube 3.5 m long and separated with sector magnet.

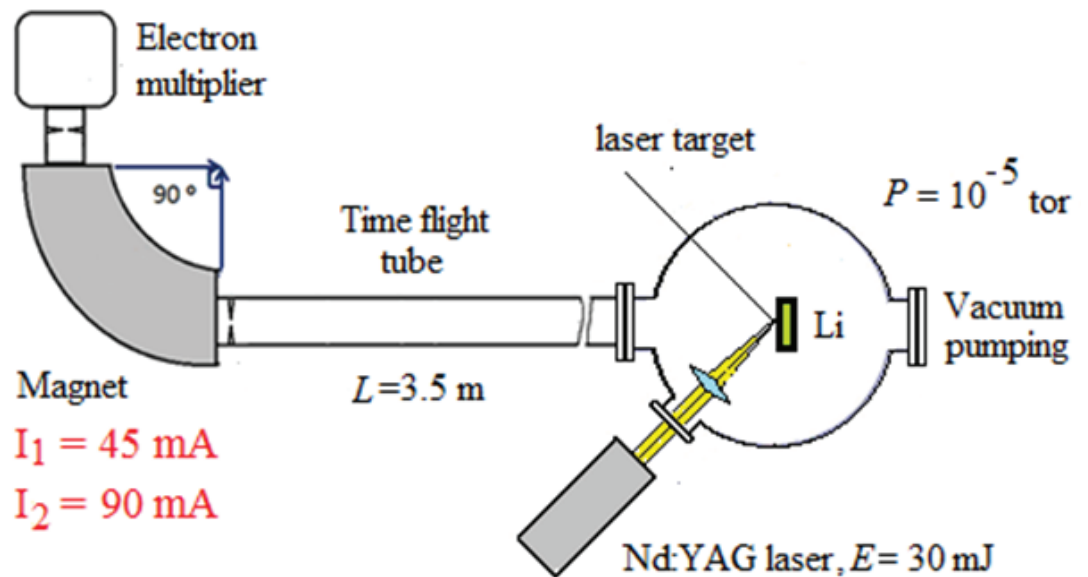


Figure 2: Principal scheme of the time of flight mass spectrometer.

3. Results and Discussion

3.1. LIBS results

LIBS spectrum of a Li layer analyzed in atmospheric air is shown in Figure 3. Li presence was observed by two characteristic lines – at 610 nm and 671 nm, corresponding to the excited Li atom. Additionally, 460 nm line corresponding to ionized lithium was observed, as well as N_2 signal, indicating the presence of lithium nitride formed due to the target contact with atmospheric air. Oxygen and carbon signals are expected to be much smaller than Li signal and can't be seen over background.

3.2. TOF mass-spectrometry results

The results of TOF mass spectrometry of Li layers at two different currents (45 mA and 90 mA) in electromagnet of mass separator are shown in Figure 4. One can see peaks of Li, C, O, N and Ar ions. No hydrogen or deuterium ions were detected, as expected [18]. As it is known in [8], on contact with atmospheric air, Li and Li-D films transform into a chemical compound of Li_2CO_3 in a slow multi-step process, with lithium nitride and lithium oxide forming in the middle stages of this process. As such, the presence of oxygen, nitrogen and carbon are to be expected. Presence of Ar atoms in the analyzed Li layer likely corresponds argon cleaning of the Li cathode. That Ar remains in the layer,

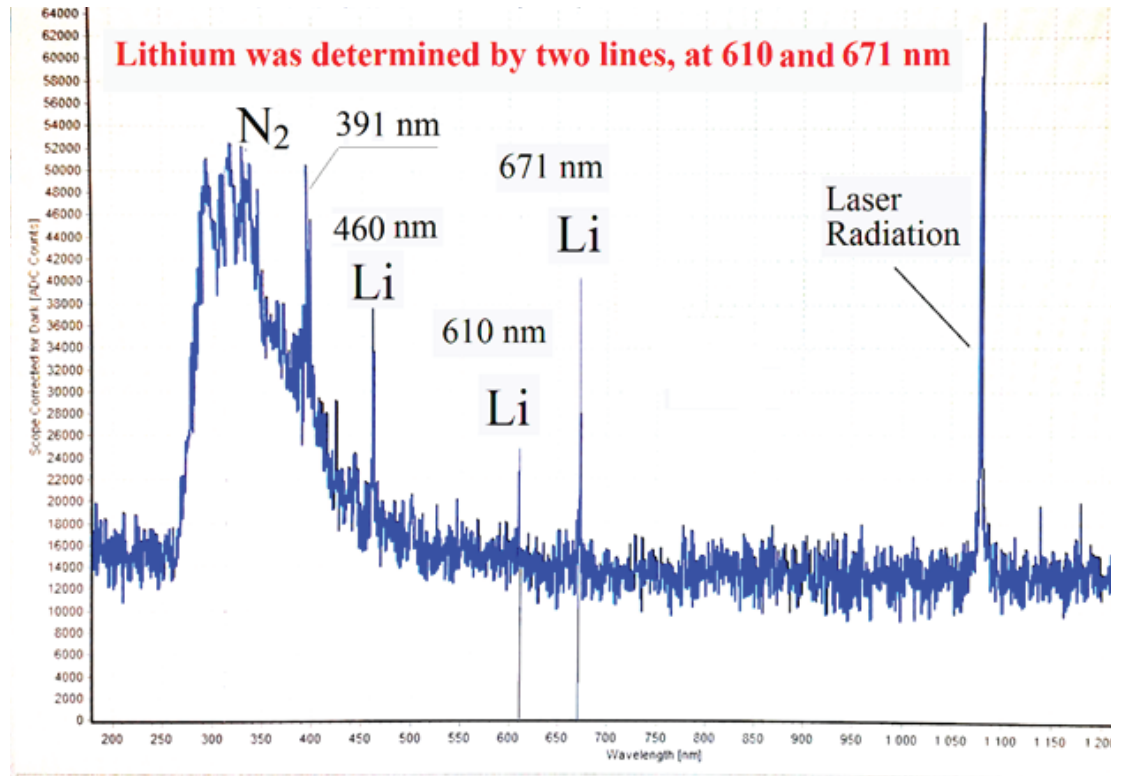


Figure 3: LIBS plasma emission spectrum of a Li layer analyzed in atmospheric air.

while hydrogen is released during chemical reactions indicating a different mechanism of inert and chemically active gases trapping.

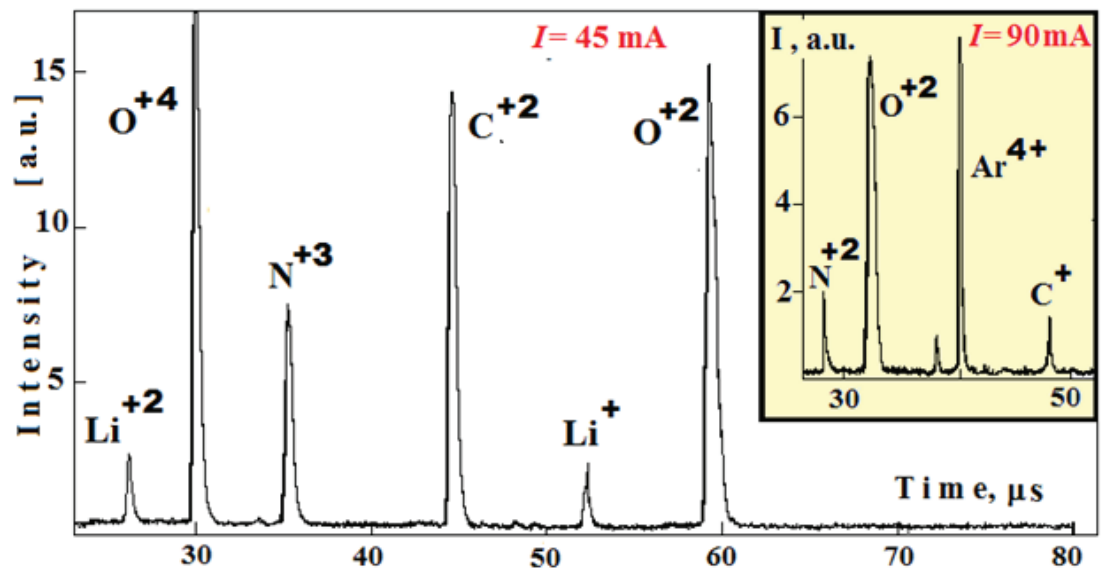


Figure 4: Time of flight mass spectrometry spectra of Li layers deposited from D plasma at different currents in separating magnet $I = 45\text{mA}$ and $I = 90\text{mA}$.

4. Conclusions

Laser-based diagnostics, such as laser-induced breakdown spectroscopy and time of flight mass spectroscopy, were used to analyze lithium co-deposits produced by deuterium plasma sputtering of liquid lithium target. It was found that each method can reliably detect lithium presence.

Of the two methods shown, time of flight mass spectroscopy demonstrated better resolution and required lower laser pulse energies as compared to optical spectroscopy. Using TOF it was possible to observe oxygen and carbon presence, which was not possible with LIBS due to high background signal. However, the need vacuum chamber for an analysis significantly increased the time required for analysis of each sample, and the large size of TOF tube made the diagnostic rather difficult to fit to compact laboratory setups.

From the point of view of usability in small laboratory setups, where space is limited, as well as in situations, where either mapping or quick analysis is required, LIBS diagnostic proved itself superior. The flexibility of the LIBS method, which can be easily integrated into diagnostic equipment, making this analysis method extremely promising.

Funding

This work was supported by Russian Science Foundation [Grant No 17-12-01575].

References

- [1] Mirnov, S. V., Lazareva, V. B., Sotnikov, S. M., et al. (2003). Li-CPS limiter in tokamak T-11M. *Fusion Engineering and Design*, vol. 65, no. 3, pp. 455-465.
- [2] Lyublinski, I., Vertkova, A., Mirnov, S., et al. (2015). Protection of tokamak plasma facing components by a capillary porous system with lithium. *Journal of Nuclear Materials*, vol. 463, pp. 1156-1159.
- [3] Fflis, P., Press, A., Xu, W., et al. (2014). Wetting properties of liquid lithium on select fusion relevant surfaces. *Fusion Engineering and Design*, vol. 89, no. 12, pp. 2827-2832.
- [4] Tabares, F. L., Hirooka, Y., Maingi, R., et al. (2016). Conference report on the 4rd International Symposium on Lithium Applications. *Nuclear Fusion*, vol. 56, no. 12, p. 127002.

- [5] Mirnov, S. (2009). Plasma-wall interactions and plasma behaviour in fusion devices with liquid lithium plasma facing components. *Journal of Nuclear Materials*, vol. 390–391, no. 1, pp. 876–885.
- [6] Kaita, R., Berzak, L., Boyle, D., et al. (2010). Experiments with liquid metal walls: Status of the lithium tokamak experiment. *Fusion Engineering and Design*, vol. 85, no. 6, pp. 874–881.
- [7] Nygren, R. E. and Tabarés, F. L. (2016). Liquid surfaces for fusion plasma facing components—A critical review. Part I: Physics and PSI. *Nuclear Materials and Energy*, vol. 9, pp. 6–21.
- [8] Lyublinsky, I. E., Vertkov, A. V., and Evtihin, V. A. (2007). Physical–chemical basis of lithium use in liquid metal systems of fusion reactor. *Problems of Atomic Science and Technology, Series. Thermonuclear Fusion*, vol. 30, no. 4, pp. 13–44 (in Russian).
- [9] Mazzitelli, G., Hirooka, Y., Hu, J. S., et al. (2015). Conference report on the 3rd International Symposium on Lithium Application for Fusion Devices. *Nuclear Fusion*, vol. 55, no. 2, p. 27001.
- [10] Vertkov A. V., Lyublinskia, E., Tabares, F., et al. (2012). Status and prospect of the development of liquid lithium limiters for stellarator TJ-II. *Fusion Engineering and Design*, vol. 87, no. 10, pp. 1755–1759.
- [11] Antonov, N. V., Belanb, V. G., Evtihin, V. A., et al. (1997). Experimental and calculated basis of the lithium capillary system as divertor material. *Journal of Nuclear Materials*, vol. 241–243, pp. 1190–1196.
- [12] Stubbers, R., Olczak, W., Nieto, M., et al. (2005). Measurement of hydrogen absorption in flowing liquid lithium in the flowing lithium retention experiment (FLIRE). *Journal of Nuclear Materials*, vol. 337–339, no. 1–3, pp. 1033–1037.
- [13] Martín-Rojo, A. B., Oyarzabal, E., and Tabarés, F. L. (2014). Laboratory studies of H retention and LiH formation in liquid lithium. *Fusion Engineering and Design*, vol. 89, no. 12, pp. 2915–2918.
- [14] Oyarzabal, E., Martín-Rojo, A. B., and Tabarés, F. L. (2015). Laboratory experiments of uptake and release of hydrogen isotopes in liquid lithium. *Journal of Nuclear Materials*, vol. 463, pp. 1173–1176.
- [15] Krat, S. A., Gasparyan, Yu. M., Popkov, A. S., et al. (2014). Deuterium release from lithium–deuterium films, deposited in the magnetron discharge. *Vacuum*, vol. 105, pp. 111–114.
- [16] Shcherbak, A. N., Mirnov, S. V., Dzhurik, A. S., et al. (2017). Investigation of dependence of lithium and hydrogen collection by collector target on temperature of target surface in emitter-collector system on T-11m tokamak, in V. A. Kurnaev, Y.

- M. Gasparyan, and S. A. Krat (eds.) The Book of Abstracts and Scientific Programme of the 5th International Symposium on Liquid Metal Applications for Fusion, p. 29. Moscow: NRNU MEPhI.
- [17] de Castro, A., Sepetys, A., González, M., et al. (2018). Temperature dependence of liquid lithium film formation and deuterium retention on hot W samples studied by LID-QMS. Implications for future fusion reactors. *Nuclear Fusion*, vol. 58, no. 4, p. 46003.
- [18] Gasparyan, Yu. M., Popkova, A. S., Krat, S. A., et al. (2017). Deuterium release from Li-D films exposed to atmospheric gases. *Fusion Engineering and Design*, vol. 117, pp. 163–167.
- [19] Popkov, A. S., Krat, S. A., Gasparyan, Yu. M., et al. (2015). Interaction of Li-D films with water vapor. *Physics Procedia*, vol. 71, pp. 88–92.
- [20] Krat, S. A., Gasparyan, Yu. M., Popkov, A. S., et al. (2017). Time-resolved studies of deuterium release from lithium films exposed to water vapor. *Fusion Engineering and Design*, vol. 124.
- [21] Rusinov, A. A., Gasparyan, Yu. M., Pereygin, S. F., et al. (2009). A setup for thermodesorption measurements. *Instruments and Experimental Techniques*, vol. 52, no. 6, pp. 871–876.
- [22] Capece, A. M., Roszell, J. P., Skinner, C. H., et al. (2015). Effects of temperature and surface contamination on D retention in ultrathin Li films on TZM. *Journal of Nuclear Materials*, vol. 463, pp. 1177–1180.
- [23] Alkhimova, M. A., Vovchenko, E. D., Melekhov, A. P., et al. (2015). The source of X-rays and high-charged ions based on moderate power vacuum discharge with laser triggering. *Nukleonika*, vol. 60, no. 2, pp. 221–227.