APPLICATION OF LIBS, LA-QMS, LA-TOF-MS FOR FUSION-RELEVANT MATERIALS ANALYSIS

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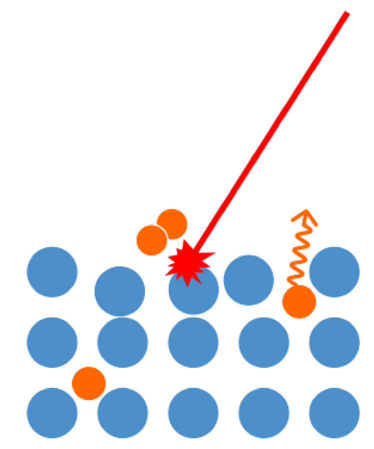
I. Motivation

The significant enhancement of plasma performance in the next-step D-T fusion reactors gives rise to several deleterious plasma–material effects. Thus, the redeposition of eroded materials leads to the formation of mixed layers, which can alter PFC's physical and chemical properties. The co-deposition leads to long-term accumulation of extensive in-vessel tritium inventories, which is a potentially severe constraint in the operation of large-scale fusion machines like ITER, as the nuclear license limits the tritium amount. In this way, there is a need for active monitoring of these processes in the fusion devices. The most promising techniques which can be applied *in situ* in tokamaks are based on laser irradiation of the surface of interest followed by mass- or optical spectroscopy.

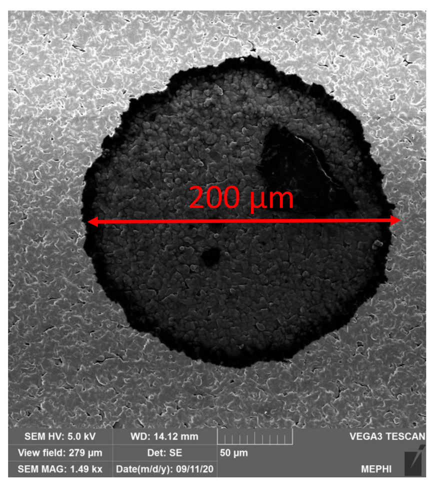
In this work, a surface analysis complex "Large mass-monochromator "MEPhI" has been upgraded to provide simultaneous studies of fusion-relevant materials by three perspective for fusion application techniques: LA-QMS, LIBS, and LA-TOF-MS. Such concurrent analysis is primarily intended for comparing the sensitivity to laser-induced hydrogen isotopes desorption. Here we present our first results of the methods comparison with Ti-D films on Mo.



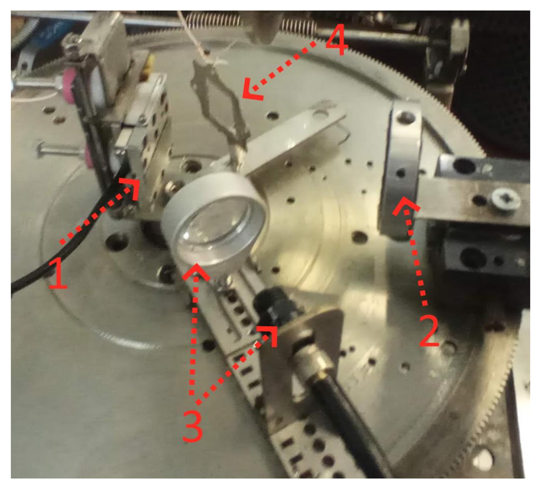
II. Experimental facility

"Large mass-monochromator "MEPhI" facility (LMM), historically intended for ion scattering spectroscopy *(Bulgadaryan D., 2016)*, has been retrofitted for implementation of laser-based diagnostics:

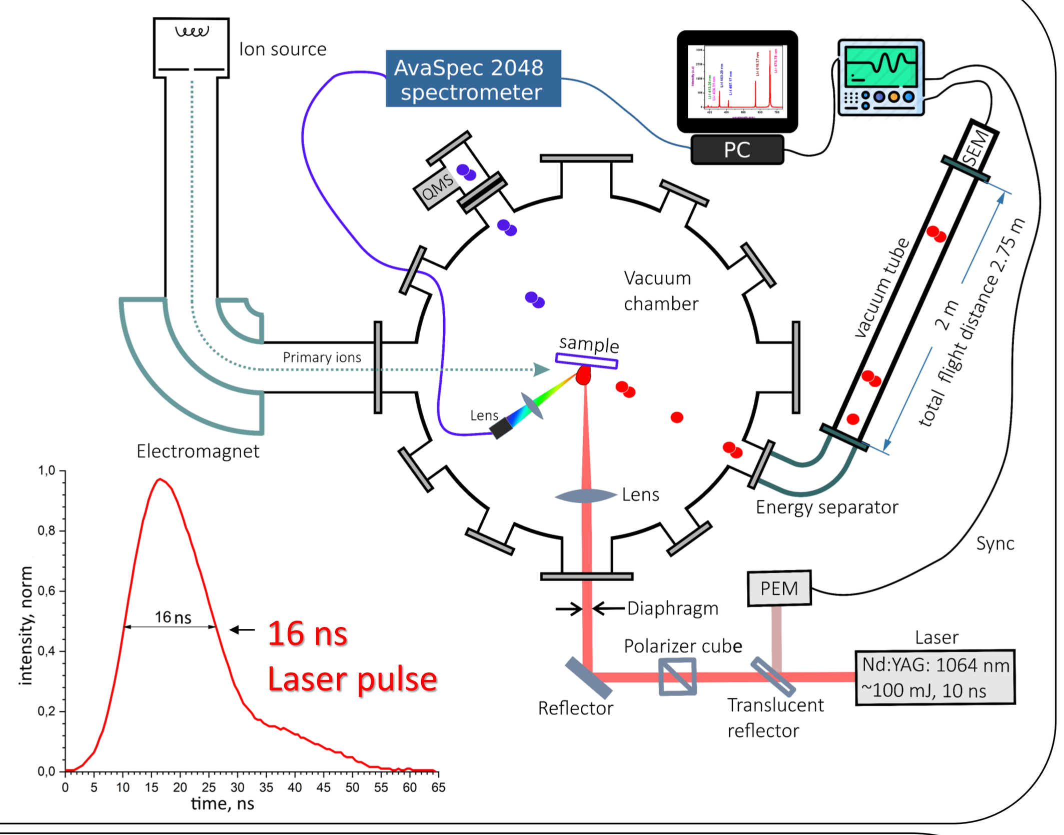
- Residual pressure ~10^{-7} mBar by TMP with S = 800 l/s and liquid nitrogen cryotrap
- Nd:YAG laser: λ = 1064 nm, τ = 10 ns, up to 40 mJ/pulse on a target with the possibility of changing the laser beam power and the spot size
- Calibrated Extorr XT100M QMS for desorption flux analysis with independent pumping system ← *LA-QMS application*
- Optical spectrometer Avantes AvaSpec 2048 (200-1100 nm) with 1 nm resolution and the possibility of changing the angle of the light emission registration ← *LIBS application*
- Electrostatic energy analyzer with 21 cm radius for the central trajectory combined with independently pumped time of flight separator ← *LA-TOF-MS application*



SEM image of a typical crater on W after the laser pulse



Vacuum chamber interior: 1 – sample on piezo motor platform; 2- laser beam lens; 3- spectrometer lenses and optical fiber; 4 – extractor for TOF

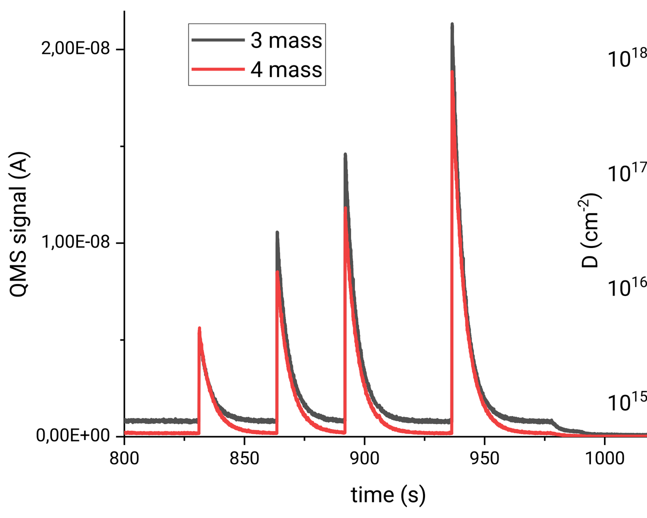


III. LA-QMS

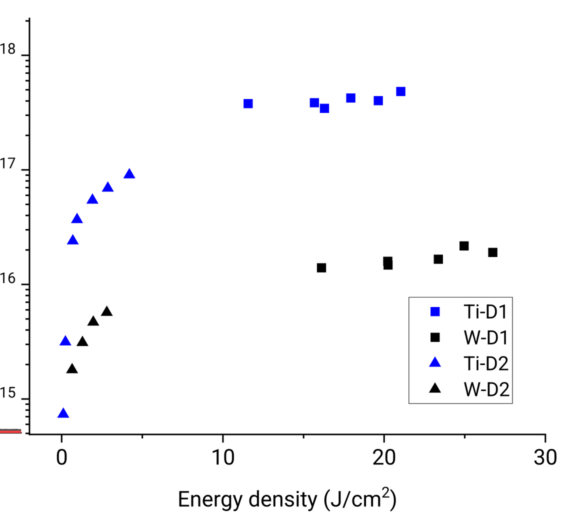
1) Key feature *(Zlobinski M., 2019)*:

- ✓ Routine calibration procedure allows reliable quantitative analysis of hydrogen isotopes desorption
- ✓ Simple instrumentation
- ✗ Only for volatile components, so composition analysis is limited
- ✗ Sensitivity is inversely proportional to a chamber volume

2) At the stage of technique's calibration release of **D from Ti and W films** for laser pulses with various power was measured (Ti-D1, W-D1 in ablation mode and Ti-D2, W-D2 in transition to desorption mode). D flux rises rapidly with increase of energy density up to ~10 J/cm². Further increase in energy density up to 30 J/cm² does not influence D release significantly. The number of D particles released per cm² in ablation mode is proportional to TDS-measured values for both materials.



Typical QMS data on D release. Each peak corresponds to one-pulse irradiation of a single spot on a target with subsequently increasing laser beam power



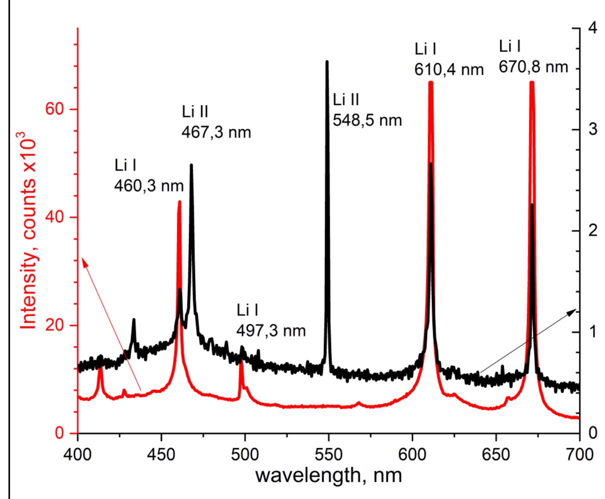
Dependence of desorbed particles amount according to QMS on the laser pulse energy density for Ti-D films

IV. LIBS

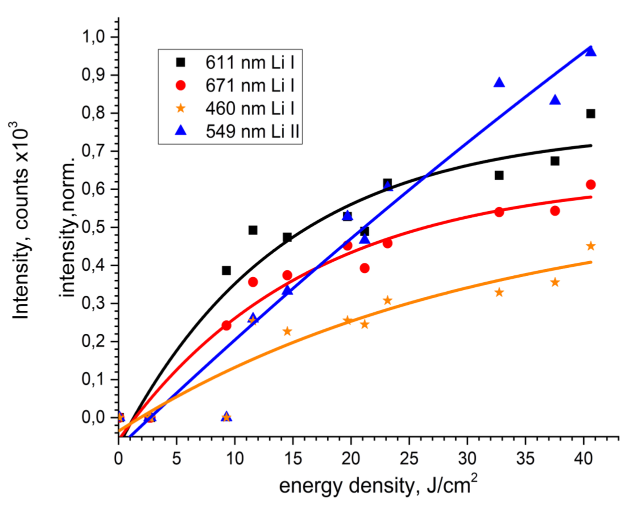
1) Key features *(Vovchenko E.D., 2018)*:

- ✓ Remote diagnostics: instrumentation can be placed outside the vacuum chamber
- ✓ Routinely utilized under atmospheric pressure
- ✓ Elemental analysis is possible
- ✗ Quantitative analysis is tricky
- ✗ Requires careful alignment of the optics with respect to the laser spot
- ✗ Needs high resolution to distinguish H (656.28 nm) and D (656.10 nm)

2) LIBS was tested on **Li sample**, since it provides very intensive emission lines. The decrease in the line's intensity of excited lithium depends nonlinearly on the power. At the same time, the decrease in the ionized lithium intensity is steeper and the corresponding lines are disappearing little bit earlier, than Li I. Overall, it is seen, that the signal-to-noise ratio is less than 10, which can be partially caused by the Bremsstrahlung and the recombination radiation. In case of laser beam energy density (42 J/cm² on the target) estimations based on the relative intensities of Li I lines (Ornstein method) give temperature of several eV (in LTE approach)



Spectra of laser induced plasma from the Li target in atmospheric conditions (RED) and in vacuum (BLACK)



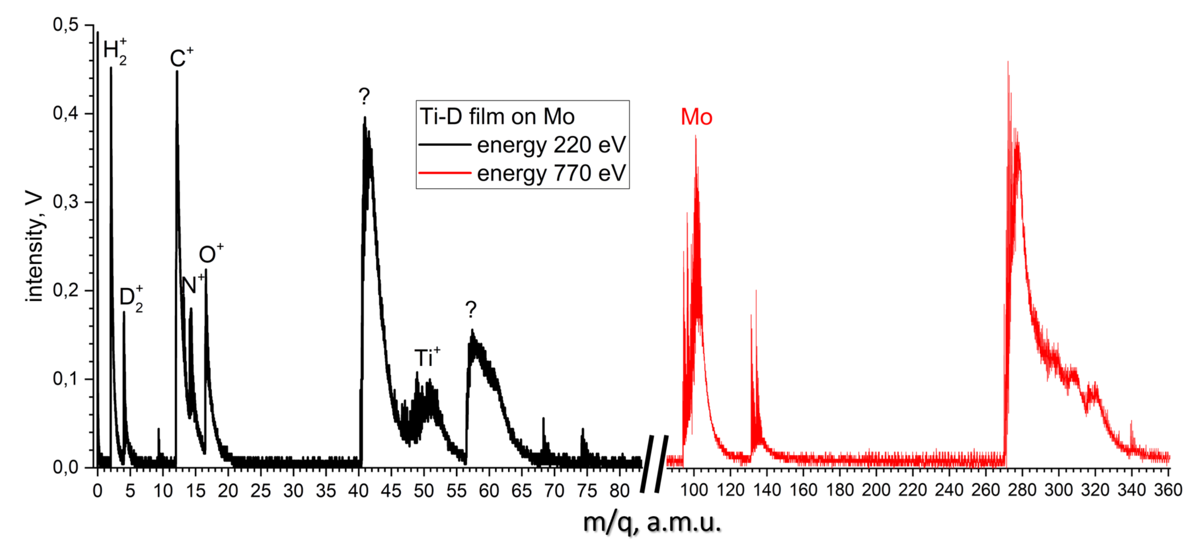
Dependencies of line's intensity on the laser pulse energy in vacuum

V. LA-TOF-MS

1) Key features *(Quan Yu, 2009)*:

- ✓ Elemental analysis in the high mass range is possible
- ✓ High mass resolution for light ions
- ✗ Instrumentation is bulky since the mass resolution is proportional to the length of a spectrometer (typical devices have 1-7 meters length)
- ✗ Quantitative analysis is tricky
- ✗ Needs ion accelerating system or energy separating system to analyze masses of the ions with the same energy

2) TOF was tested on the **Ti-D films on Mo**. An overview spectrum for energy 220 eV contains hydrogen isotopes, impurities and Ti. There are some questionable peaks, which haven't been yet recognized. It is also noticeable, that for the energy separator setting higher than ~600 eV high mass peaks (>200) appear, which may relate to clusters formation. Also, after multiple laser pulses in one spot, it is possible to see Mo peaks, wherein D_2 peak is not seen.

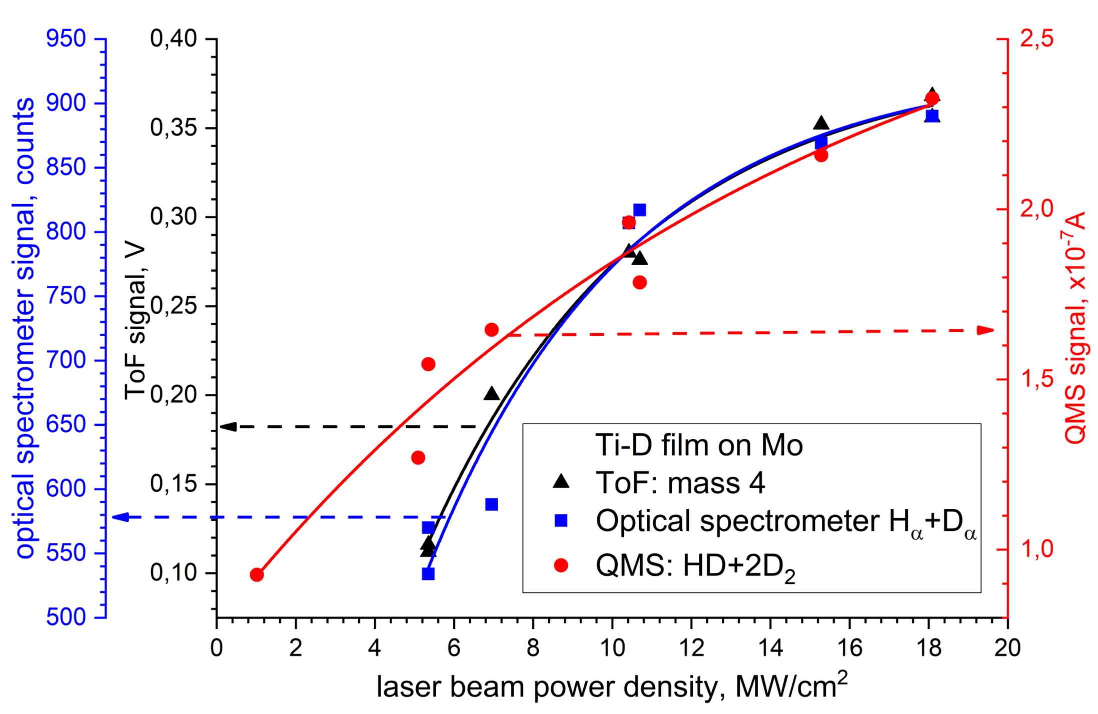


TOF mass spectra of ions from laser-induced plasma torch on Ti-D film on Mo in case of laser beam power density 18 MW/cm². Black line – for 220 eV setting on energy separator (first shot), red line – for 770 eV energy (after multiple shots)

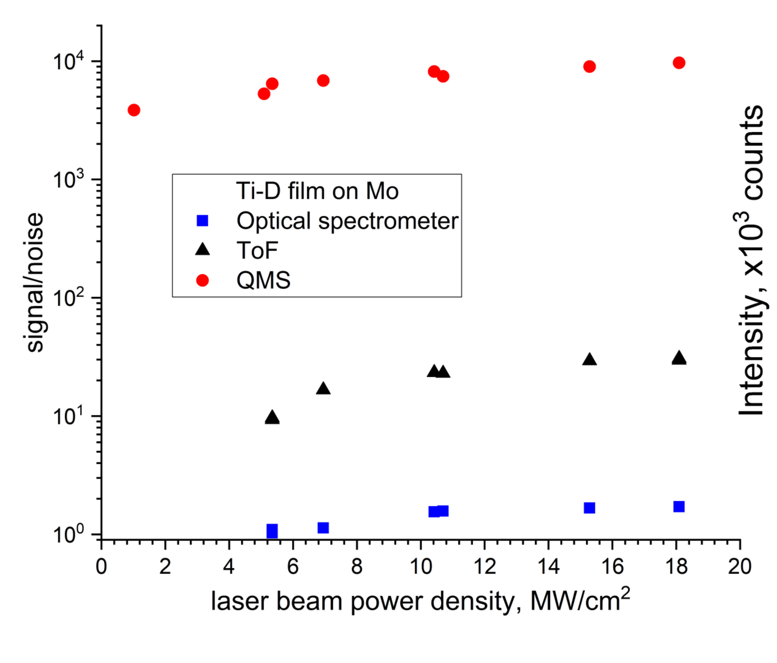
VI. Simultaneous application of LA-QMS, LIBS, LA-TOF-MS to the Ti-D films on Mo analysis

Upon completion of laser-based diagnostics implementation in LMM, a comparative analysis of the sensitivity to deuterium was carried out. A Ti film on the Mo substrate, which was prepared by magnetron sputter deposition in the MD-2 facility *(S. Krat, 2018)*, was chosen.

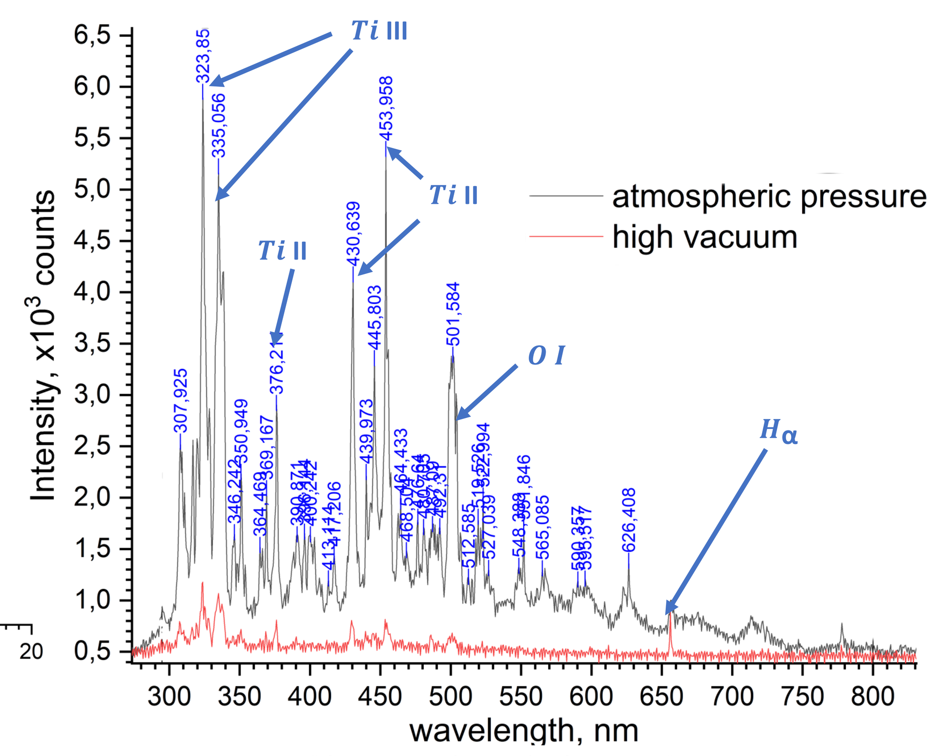
It was found that QMS shows a significantly higher dynamic range of measurements than LA-TOF-MS and LIBS, making it more suitable for hydrogen desorption measurements, which are relevant to the co-deposition problem in tokamaks. However, element analysis is unattainable for LA-QMS. In this area, the TOF analyzer shows higher certainty of results and a more straightforward interpretation than LIBS; hence some peaks on the mass spectrum remain unidentified.



Dependence of diagnostic's signal on laser beam power density for the same laser-induced plasma torches on Ti-D film



Signal-to-noise ratio for QMS, spectrometer and TOF analyzer in the identification of D in the Ti-D sample



Spectra of laser-induced plasma from TI-D on Mo target in atmospheric conditions (BLACK) and in vacuum (RED)

VII. Conclusion

LMM facility has been upgraded to provide simultaneous experiments with laser-based techniques: LA-QMS, LIBS, LA-TOF-MS. In the first experimental series, its comparison was provided with thin Ti-D films on Mo substrate. It was found that each method can reliably detect deuterium presence. Nevertheless, LA-QMS demonstrates much better sensitivity and requires lower laser beam power density (so the desorption mode is less destructive), making it more attractive for application in the tritium co-deposition control in tokamaks. Elemental analysis was possible only with LA-TOF-MS and LIBS, wherein the time-of-flight mass spectrometry demonstrates better sensitivity. Using TOF, it was possible to detect surface contaminations, Ti and Mo peaks, as well as cluster formation. In vacuum LIBS, only Ti and H_α lines were recognized, which might relate to high continuum intensity. In all, it is worth mentioning that simultaneous application of these techniques might help obtain much more extensive and reliable sample information. Further research on LMM involves increasing the sensitivity of the techniques and application to a broader class of materials.

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