

# Depth-resolved sample composition analysis using laser-induced ablation-quadrupole mass spectrometry and laser-induced breakdown spectroscopy

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## ABSTRACT

Monitoring a sample's material composition became more and more important over the last years for both - industrial process control as well as for post mortem analysis in research and industrial development. Although material composition identification as well as a comparison with standard samples works fine, there is a lack of diagnostics which can provide quantitative information with depth resolution without any standard samples. We present a novel method utilizing a residual gas analysis with quadrupole mass spectrometry after picosecond laser-induced ablation and release of volatile species. In the present experiment, well characterized multilayer thin film solar cells ( $\mu\text{c-Si:H}$  and  $\text{a-Si:D}$  as p-i-n-junctions on ZnO:Al electrodes) are used as a set of well characterized material samples to demonstrate the capabilities of the new method.

The linearity of the spectrometer signal to gas pressure simplifies its calibration and reduces its uncertainties in comparison with other analysis techniques, although high vacuum conditions ( $10^{-6}$  hPa to  $10^{-7}$  hPa) are required to reach high sensitivity better than the percent-range. Moreover, the laser-ablation based sample analysis requires no preparation of the sample and is flexible regarding ablation rates. The application of a picosecond laser pulse ensures that the thermal penetration depth of the laser is in the same order of magnitude as the ablation rate, which enables to achieve depth resolutions in the order of 100 nm and avoids matrix mixing effects at the edge of the laser-induced crater in the sample.

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## 1. Introduction

The determination of the amount of hydrogen and other composites of samples is a key challenge in many research fields. In the future fusion reactor-like device ITER, the amount of retained fuel species (tritium and deuterium) in the so-called first wall, the material components closest to the fusion plasma, must be monitored to ensure reliable operation with closed fuel cycle. Not only fuel retention limits the performance of the fusion reactor by limiting the supply of self-burned tritium, but also due to safety reasons the tritium inventory in the device must be limited [1]. Currently, laser-based systems are proposed as analysis and control methods during maintenance periods in the challenging neutron-activated surrounding of the reactor device [2]. In general, laser-based post mortem and possibly in-situ analysis is suitable here, as it is preparation-free, fast, and flexible in operation.

Commonly used for process monitoring in industry [3], for example in production of photovoltaic cells [4], is the well-established technique

of Laser-Induced Breakdown Spectroscopy (LIBS). Ablation rates can be well controlled and varied over orders of magnitudes by changing the laser parameters, making it also a widely used technique in basic research as well as in challenging environmental conditions like the Mars's surface [5]. Still, LIBS is based on a highly nonlinear ablation process, which depends on the type and conditions of laser and material properties. Thus, while allowing qualitative analysis for unknown samples [6], it requires reference samples with known composition for a quantitative analysis of an unknown specimen [7]. The development of a first principle method with interpretation of the light emission for the laser-induced plasma conditions is ongoing (calibration-free LIBS: CF-LIBS [8]), but currently not available. On the other hand, the so-called calibration-free LIBS requires local thermodynamic equilibrium of the plasma and simultaneous analysis of multiple lines and is therefore challenging in real-time application.

Whereas Laser-Induced Desorption with Quadrupole Mass Spectrometry (LID-QMS) [9] can give quantitative information about sample composition, it is based on sample heating with laser-pulses of millisecond pulse duration, which gives poor depth resolution due to thermal conduction and heat diffusion and interaction with the surrounding

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material. Other ex situ post sample analysis methods e.g. Secondary Ion Mass Spectrometry (SIMS), need detailed information about the sample to give quantitative information or reference samples, which again are not always available or accessible. Further related measurement techniques like Micro Nuclear Reaction Analysis ( $\mu$ -NRA) or Thermal Desorption Spectrometry (TDS) can only provide depth resolution in the  $\mu\text{m}$  range or no depth resolved information at all of the sample composition. Moreover, NRA has only access to specific species where corresponding reactions exist, which e.g. excludes the determination of hydrogen in samples. The same holds for laser based analysis methods like Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) ([10,11]) or Laser Ablation Time-of-Flight Mass Spectrometry (LA-TOF-MS) [12], which have not demonstrated yet quantitative hydrogen isotope analysis.

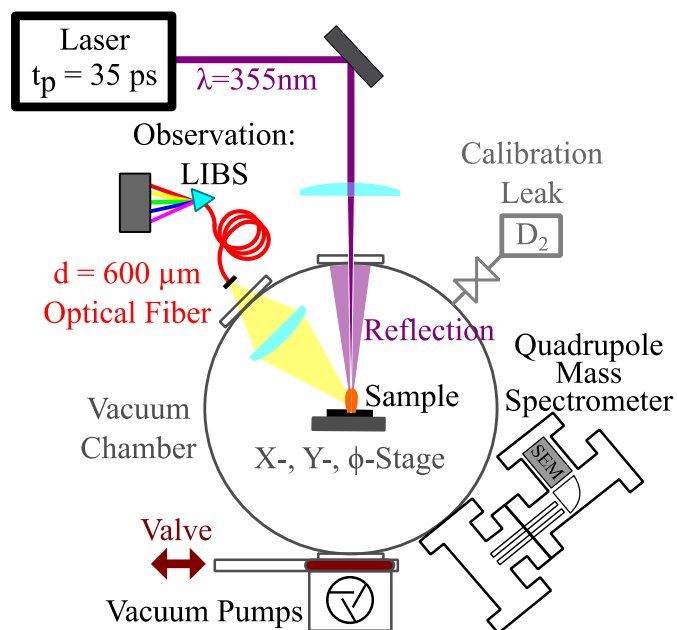
We present a setup for picosecond Laser-Induced Ablation-Quadrupole Mass Spectrometry (LIA-QMS), giving depth resolved ( $O(100\text{ nm})$ ) information of volatile sample species released during the ablation process. The recorded QMS signal of one mass/charge is proportional to the corresponding partial pressure and thus to the ablated material content which allows easy access to an absolute quantification of the material composition of the released material as long as gaseous species are produced. Moreover, in parallel to the LIA-QMS also a complementary LIBS system is embedded in the setup. This permits for the same laser-induced ablation process also a LIBS analysis. While the LIBS setups have the aforementioned drawbacks for a quantification of the sample composition, this setup allows for additional information of quantitative information of volatile sample components with LIA-QMS. Also the results of our new LIA-QMS method can be compared with an established technique. To demonstrate the method, samples from the research field of thin film photovoltaics were chosen, as they provide a stack of multiple homogenous layers, whereas samples from fusion research are inhomogeneous in general and not fully characterized yet. Thus, they are less suited to demonstrate the newly developed method.

This paper consists of six sections: The first section gives an introduction and an overview of related measurement techniques. The sections two and three introduce the experimental setup and the type of samples which were investigated. Section 4 deals in depth with the Laser-Induced Ablation-Quadrupole Mass Spectrometry technique and introduces raw signals as well as measurement and analysis techniques with the examples of hydrogen and oxygen detection. In the subsequent Section 5 first results of thin film solar cells are shown and discussed: the influence of the laser energy density is investigated, a quantitative calibration for hydrogen and deuterium is demonstrated and compared to quantitative TDS measurements. In addition, LIA-QMS results are compared with LIBS. Finally, the paper is summarized and an outlook is given.

## 2. Setup

The experimental setup for the combined LIA-QMS and LIBS consists of a laser, a motorized  $x$ -,  $y$ -,  $\phi$ -sample holder in a vacuum chamber, a quadrupole mass spectrometer, and an optical spectrometer with fiber optics coupling, schematically shown in Fig. 1.

The laser is a Nd:YVO<sub>4</sub> laser (EKSPLA PL2241) operating at its third harmonic ( $\lambda_{3rd} = 355\text{ nm}$ ) with a pulse length of  $t_p = 35\text{ ps}$  and pulse energies up to  $E = 60\text{ mJ}$  in single shot ablation mode. The laser beam is guided through a plano-convex focusing lens ( $f = 500\text{ mm}$ ) to a sample perpendicular to its surface with a laser spot diameter on the sample of  $x_{cr} \approx 800\text{ }\mu\text{m}$ . The sample is mounted on a motorized  $x$ -,  $y$ -,  $\phi$ -stage in a vacuum chamber with a volume of  $100\text{ dm}^3$ . In contrast to LID with millisecond laser pulses, the short pulse duration of this setup in picosecond decreases the heat penetration depth  $L_{HPD} = \sqrt{2Dt_p}$  with thermal diffusivity  $D$  by several orders of magnitude [13].



**Fig. 1.** Schematic overview of the setup: Picosecond laser-induced ablation of a sample in a vacuum chamber and analysis including laser induced breakdown spectroscopy (optical measurement) and quadrupole mass spectrometer (gas composition measurement). A valve to the vacuum pumps is closed for residual gas analysis and calibration with a calibration leak.

Thus, it becomes comparable to the optical penetration depth of the laser radiation  $L_{OPD} = \alpha^{-1}$  with absorption coefficient  $\alpha$ .  $L_{HPD}$  and  $L_{OPD}$  are tabulated in Table 1 for the materials investigated. Although a completely non-thermal ablation could be achieved by femtosecond laser-induced ablation, which further increased the depth resolution, using a ps laser is preferred in this context: On the one hand, high power ps laser are in general more stable than fs laser and on the other hand light intensity of ps-LIBS light is higher than fs-LIBS intensity.

A set of thin film solar cells are used to demonstrate the developed method, as the optical properties are on the one hand well known for industrial production but also its detailed material analysis is of note to further improve the efficiency of the solar cells. Moreover, this method could be used as in-situ process controlling of a solar cell production.

After laser-induced ablation, a quadrupole mass spectrometer (Pfeiffer HiQuad QMS 700) with a mass/charge ( $m/q$ ) range of  $1\text{ u/e} - 100\text{ u/e}$  is used to determine the composition of residual gases. An ionization source (type: crossbeam) at the entrance of the quadrupole enables to measure neutral gas molecules. It can be either operated for a single mass/charge with a time resolution of  $1\text{ ms}$  or sweeping all masses/charges with a time resolution of  $0.5\text{ s}$  for the whole spectrum. A Secondary Electron Multiplier (SEM) in the spectrometer enables this time resolutions. As the sweeping is giving full information about ablated volatile species, it is used preferentially. The ionization source of the mass spectrometer is located  $50\text{ cm}$  behind the sample to minimize interaction of the SEM with scattered or reflected laser light and ablated solid particles. Notably, there is no direct line of sight from the ionization volume of the QMS to the laser ablation region. A differential

**Table 1**

Optical and heat penetration depth, calculated from absorption coefficient  $\alpha$  and thermal diffusivity  $D$  for the sample materials and laser parameters used:  $\lambda = 355\text{ nm}$ ;  $\tau_p = 35\text{ ps}$  at room temperature.

Layer	$\alpha$	$D$	$L_{OPD}$	$L_{HPD}$
a-Si:H/D	$1.1 \cdot 10^6\text{ cm}^{-1}$ [14]	$0.012\text{ cm}^2/\text{s}$ [15]	$9.4\text{ nm}$	$9.2\text{ nm}$
ZnO:Al	$9442\text{ cm}^{-1}$ [15]	$0.071\text{ cm}^2/\text{s}$ [16]	$1.1\text{ }\mu\text{m}$	$22\text{ nm}$
$\mu\text{c-Si:H}$	$6.0 \cdot 10^5\text{ cm}^{-1}$ [14]		$16.6\text{ nm}$	

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