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Quartz Crystal Microbalances (QMBs) for Quantitative Picosecond Laser-Material-Interaction Investigations

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Abstract

In this work Quartz Crystal Microbalances (QMBs) are used to study picosecond laser ablation of magnetron sputtered coatings. The QMBs show a linear characteristic of the sensitivity for layer thickness of different metals up to several microns. Laser pulse resolved measurements of the mass ablated from the metal layer were performed. About 400 ng of chromium was ablated during the first laser pulse while in subsequent pulses less than 220 ng were removed. This is compared with previous findings. The sensitivity for ablation of the QMBs is found to be larger than for deposition, which is explained by the radial sensitivity of the QMBs. Future refinements of the setup and the benefits of the pulse resolved mass loss measurements for laser based methods like calibration free LIBS and LIAS are discussed.

1. Introduction

Laser based material diagnostic techniques like Laser Induced Breakdown Spectroscopy (LIBS, [1-4]) and, more specifically in the context of nuclear fusion application, Laser Induced Ablation Spectroscopy (LIAS, [5] and references therein) relies on the laser ablation process. Subsequent excitation of the ablated atoms leads to line emission which is observed spectroscopically.

In case of nuclear fusion research there is an urgent need to quantify the number of released atoms solely based on spectroscopic observation [6-8]. Interpretation of observed spectra is complicated by the fact that the surfaces of Plasma Facing Components (PFCs) in nuclear fusion experiments are strongly modified during operation, thus showing changes in their material composition over time and inhomogeneity both in lateral direction and in depth. Additionally, layers formed on top

of the PFC surfaces are of high relevance for plasma wall interaction studies but have material properties dependent on the plasma processes.

We note that this challenge is not only relevant to the field of nuclear fusion but appears in different forms in different topics ranging from archaeology [9] to astrophysics [10].

As spectroscopic measurements can be performed *in situ* and measured for every single laser pulse it is highly desirable to complement spectroscopic measurements of e.g. LIBS plasmas by pulse resolved measurements of the mass ablated from the sample.

Presently, the quantitative interpretation of LIBS relies on *post mortem* analysis of the sample to determine mass removal rates. However, this only provides mass loss integrated over many laser pulses and cannot help to interpret laser pulse to laser pulse fluctuations of the observed spectroscopic signals.

In this work the exploration of the possibility of Quartz Crystal Microbalance (QMB) usage for picosecond laser-material interaction investigations has been performed.

In fact, QMBs have been used to investigate pulse resolved mass removal rate of (nanosecond excimer) laser ablation of gold in the past [11] and to study the angular distribution of the ablated material deposition [12]. However, to our knowledge this technique has not been suggested to be used for comparison with quantitative spectroscopic methods or for picosecond laser ablation.

2. Methods

2.1. Quartz Crystal Microbalances (QMBs)

QMBs are well-known and commercially available devices with broad field of application in surface science and related disciplines (e.g. [13]) for mass measurements in the nanogram range. They consist of two elements: The actual sensor made of a quartz crystal with electrode coatings and the electronic driver which can excite oscillations in the sensor and measure the resonance frequency of the sensor head. The resonance frequency of the quartz depends on its mass. Thus from measuring the change in resonance frequency the change of the quartz's mass can be deduced.

For a linear regime the relationship between the change in frequency Δf and the change in mass Δm on an area A can be described by the Sauerbrey equation [14]:

$$\Delta f = -\frac{2 f_0^2 \Delta m}{\sqrt{\rho_q \mu_q} A} \qquad (1)$$

Here f_0 is the resonance frequency of the unloaded crystal, ρ_q and μ_q denote the density and the shear modulus of the quartz, respectively. In our experiment a commercially available Inficon Q-pod Quartz Crystal Monitor was used to excite a thickness shear mode in our quartz sensor. As sensors, Inficon 6 MHz Gold Coated AT-cut Crystals were used. They consist of a ~300 µm thick Quartz layer encased by ~150 nm gold coatings on both sides. With material parameters ρ_q=2.648 g/cm^3, μ_q=2.947*10^6 N/cm^2 an expected frequency change per mass change per area of $m_{calc}=-\frac{2f_0^2}{\sqrt{\rho_q \mu_q}}$=8.15 kHz mm^2/µg is calculated.

Additionally to the mass dependence the resonance frequency of QMBs are known to depend on other factors as well, namely the temperature, stress and the exact position of the deposited material, e.g. [15, 16].

2.2. Experimental procedure and analysis techniques

To qualify QMBs for laser ablation studies two series of experiments were performed.

In both series the resonance frequency of the QMB was determined and the mass of the sensor was measured with a Mettler Toledo XP6U Comparator balance.

A metal coating on the front electrode of QMB was produced with a PREVAC conventional magnetron setup. Apertures were used to define the coated region on the sensor. The measurement of the mass and the resonance frequency was repeated after the coating deposition.

The sensor was placed inside a vacuum chamber with the base pressure < 10^{-6} mbar. The laser beam produced by EKSPLA PL2241 laser (λ=355 nm, $E_{p,set}$=45 mJ, τ_p=35 ps) was focused on the QMB coated surface under 45° incidence angle to a laser spot diameter D_{spot}=3.7 mm. The laser pulse energy was detected by a photodiode monitoring the pulse energy of the 1064 nm laser pulse.

After laser ablation the resonance frequency and mass of the sensor were measured again. In addition the crater area was determined by means of a confocal microscope (STIL Micromeasure 2) in the MirrorLab at Forschungszentrum Jülich [17].

Additionally, in the second series of experiments the sensor was connected to the Q-pod Quartz Crystal Monitor inside the vacuum chamber, allowing measurements during the laser ablation experiments *in situ*. The holder for the quartz crystal was based on a design described in [18] but in both cases the Q-pod device was used to measure the

resonance frequency. For the experiments reported here no temperature control of the QMB was available.

The QMB sensors at different experimental stages are shown in figure 1. Back and front side of a quartz sensor before coating deposition are shown on left part of the figure. The sensor with magnetron sputtered chromium coating is displayed on the next portion of the figure. It can be seen that the coating close to the edges created by the aperture shows some inhomogeneity due to the geometric alignment inside the magnetron vacuum chamber. Therefore, only the central part of the coating was used for ablation studies. On the right side of figure 1 a laser ablation crater is shown.

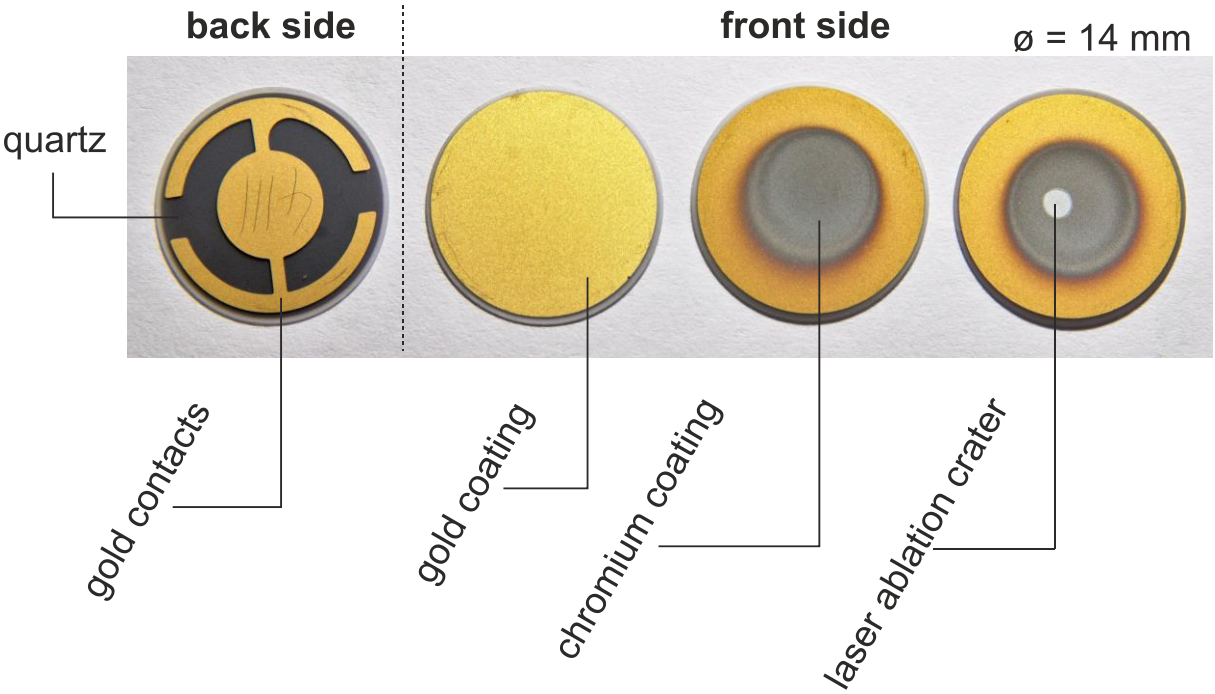

Figure 1: QMB electrodes in different stages of the experiment. From left to right: back side, front of uncoated electrode. Magnetron produced chromium coating. Laser ablation crater on the chromium coating.

3. Results

3.1. QMB coatings

Different layers, namely chromium, tungsten and copper were deposited on QMB crystals with layer thicknesses ranging from 500 nm up to 4 µm. The difference between the measured resonance frequency before and after deposition is shown as a function of the mass areal density in figure 2.

The increase in mass due to the coating leads to a decrease of the resonance frequency as to be expected. It can be seen that the dataset for a wide range (up to 20 µg/mm²) is well described by a linear dependence. The slope $m_{coating}$=-8.0±.1 (kHz mm²)/µg can be used to describe the behaviour of the QMBs independent of the coating material. This shows that for these conditions a linear dependence predicted by eq. (1) is conserved. The obtained value $m_{coating}$ is very close to the theoretic prediction, m_{calc}.

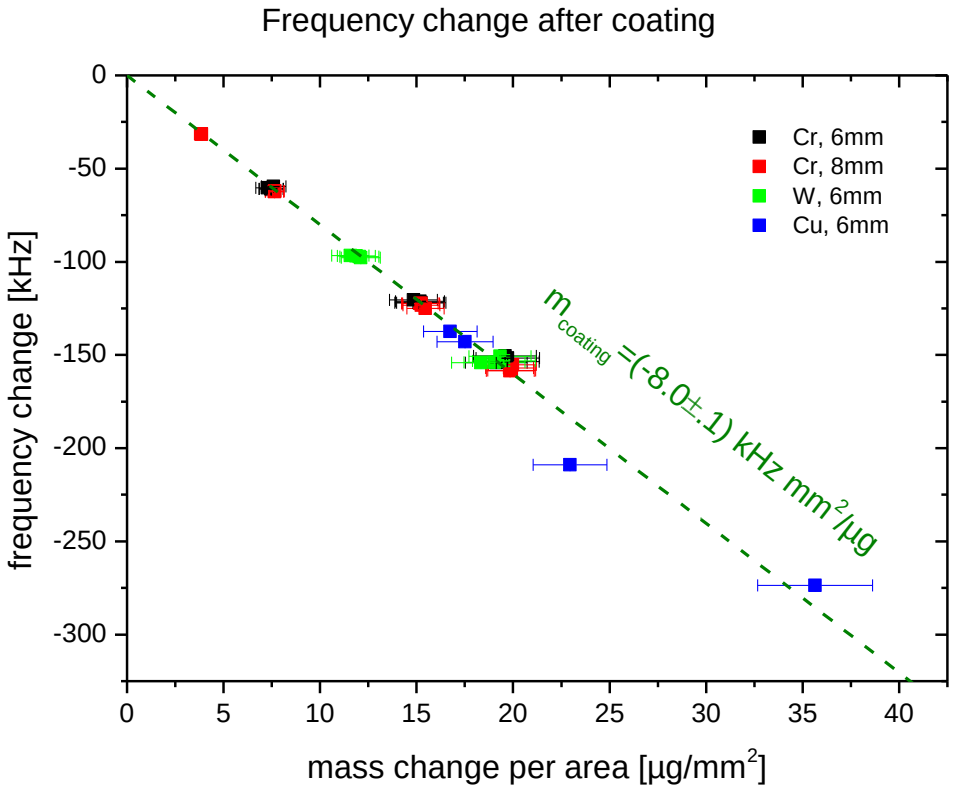

Figure 2:QMB frequency change as a function of mass areal density change by magnetron sputtered coatings.

3.2. In situ measurement of laser ablation rate by QMBs

A QMB was mounted inside the vacuum chamber to measure the frequency change for each laser pulse. The experiment was carried out with the laser conditions described in

section 2.2.

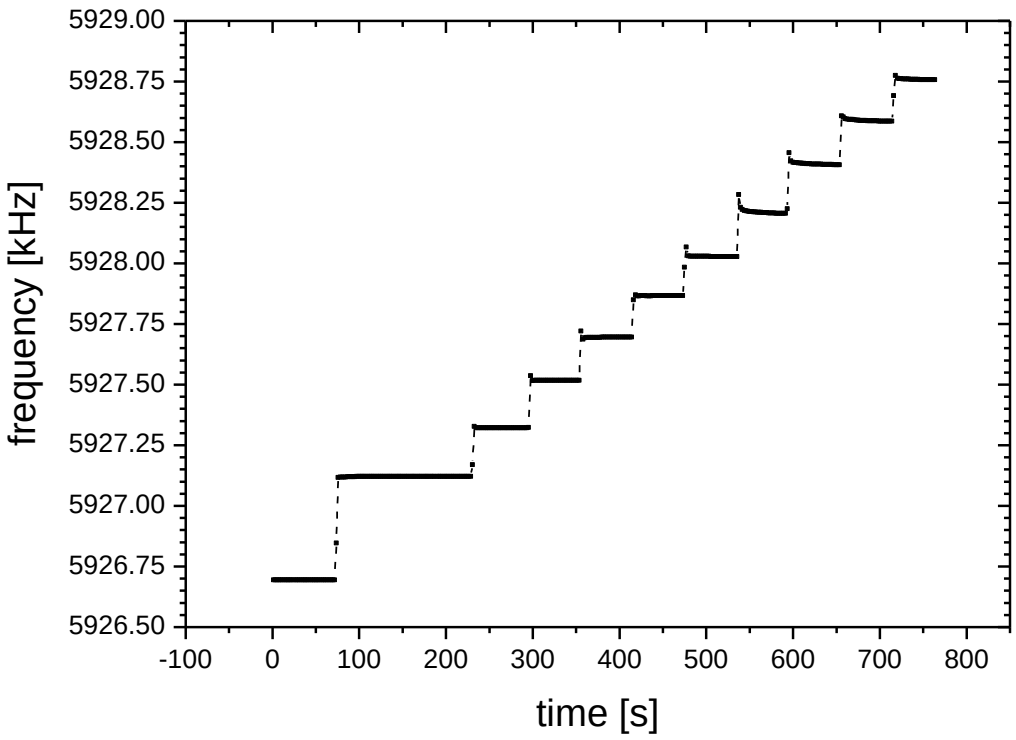

Figure 3: Measured QMB frequency as a function of time for 10 subsequent laser pulses.

The QMB frequency data recorded for the first 10 subsequent laser pulses is shown in figure 4 as a function of time. The mass removal by the laser ablation is found to lead to an increase in frequency of the QMB which is to be expected in case of mass removal. Additionally, it can be seen that the frequency shows a dynamic behaviour after the ablative pulses. Thus the difference of the averaged data before the laser pulse and after the relaxation time is used to compute the QMB frequency change resulting from the laser ablation. The results are shown in figure 3. In fig. 3a the QMB frequency change is shown for the first 10 subsequent pulses together with the laser pulse energy measured by a calibrated photodiode. In fig. 3b the mean frequency change per laser pulse averaged over 20 pulses is shown for the subsequent pulses.

The most striking feature is that the frequency change of the first laser pulse is about twice as large as for the subsequent pulses. Interestingly, the frequency change for the subsequent laser pulses shows fluctuation on the order of 25% and has no direct correlation with the fluctuation of the laser pulse energy. We attribute this to the interplay of material history effects (very obvious when comparing the first and the second pulse) and possibly uncontrolled parameters like changes in the beam intensity

profile which were not recorded at this point. We also note that this behaviour has not been observed in previous work with excimer nanosecond duration pulse experiments on gold [11].

After about 100 pulses the mean frequency change per laser pulse increases. One can attribute this to reaching the end of the chromium layer and starting ablation of the gold layer at the region of highest intensity. *Post mortem* analysis confirmed that the gold layer was reached.

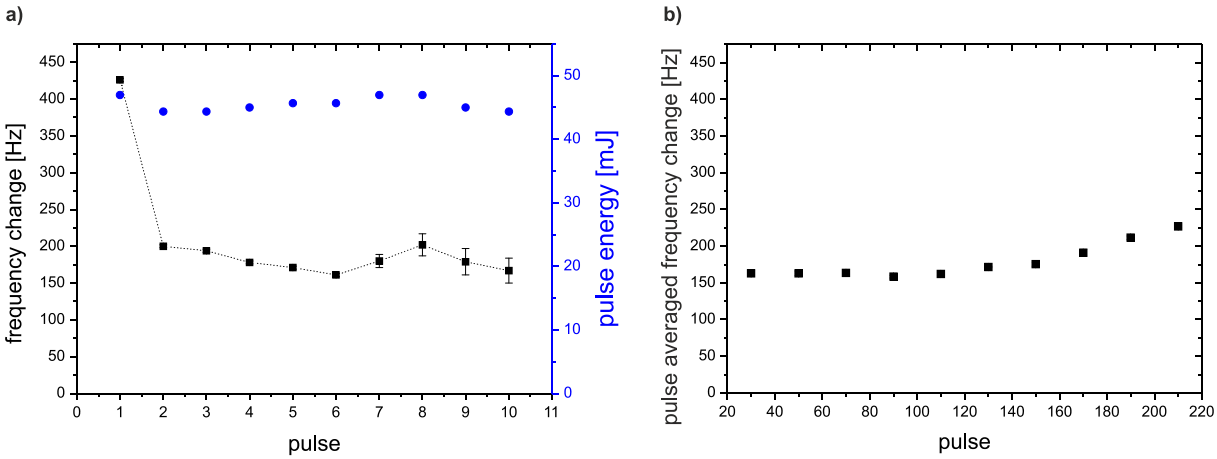

Figure 4: *In situ* measurement of QMB frequency change as a function of laser pulse number. a) frequency change for the first 10 laser subsequent pulses on the QMB (black square). The laser pulse energy is shown on the right ordinate (blue circle). b) Frequency change per pulse averaged over sets of 19 laser pulses. The data point is drawn at the number of the last laser pulse of the set.

3.3 Frequency and mass changes due to ablation

Based on five QMB experiments with chromium layers the frequency change per mass areal density change for laser ablation has been determined. The data and the resulting slope are shown in figure 5. The slope was determined to be m_{abl}=-11.3±1.1 (kHz mm^2)/µg. The value of $m_{coating}$ is shown in the graph for reference. As can be seen the slope for the ablation is up to 63.7% larger within errors than for the coating case.

For D_{spot}=3.7 mm this slope corresponds to a sensitivity of 1.02 Hz/ng, resulting in a mass removal of ~400 ng in the first pulse and 150-220 ng in the following pulses.

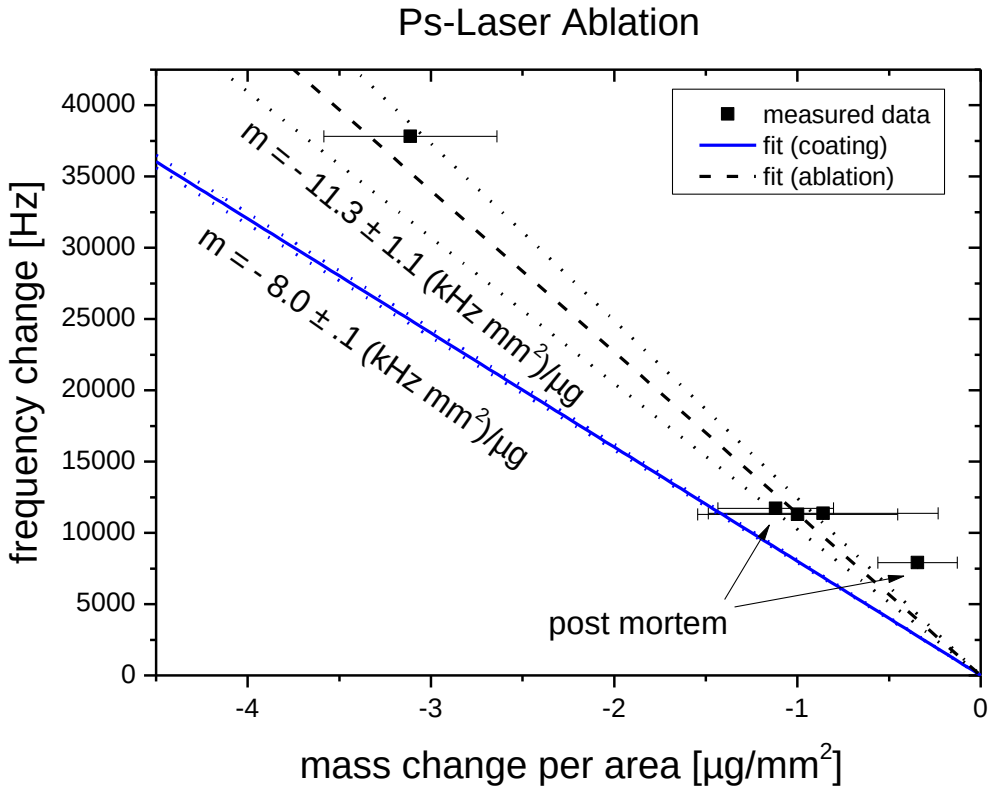

Figure 5: Frequency change vs. mass areal density change for laser ablation. The slope determined for coatings is shown for reference.

4. Discussion and Conclusion

In this work *in situ* shot resolved measurements of laser ablation by picosecond laser pulses have been performed. It was demonstrated that QMBs can be applied in vacuum for the pulse resolved study of laser ablation processes, making them a useful tool for direct comparison with (also pulse resolved) optical emission spectroscopy and mass spectroscopic measurements and being able to measure mass loss in the nanogram range.

The Inficon QMB sensors showed a linear behaviour for layers of different metals up to several micron thickness, making them suited for laser ablation studies. *In situ* measurement of laser ablation rate of these layers was demonstrated. In the first pulse 400 ng were ablated while in all following pulses less than 250 nanograms per laser pulse were ablated. This is highly relevant for the local plasma perturbation due to the LIAS method [19] and requires additional studies. It seems unlikely that a water film on the substrate can explain the observation, as a) the mass loss excess compared to the following pulses would require a diameter of 10 mm to be desorbed due to the laser pulse and b) even for $1.0*10^{-7}$ mbar the monolayer formation time should be < 30 seconds, but we do not see a subsequent increase in mass. We notice that this observation is consistent with our spectroscopic measurements in

previous experiments [20] where a much stronger signal during the first laser pulse on layer deposits than in the subsequent pulses was observed. In figure 1 it can be observed that the laser crater looks more metallic while the coating looks dull. So possibly there is an oxidation layer on top of our sample. In the future this will be addressed be joint investigation by optical emission- and mass spectroscopic analysis of the ablation from layers deposit on QMB sensor.

Even if the first pulse is excluded from analysis no correlation between fluctuation of the laser pulse energy and the mass removal per laser pulse was found. Material history effects and/or laser beam profile instability can be responsible for these fluctuations. Additionally, a fixed conversion efficiency from the fundamental pulse energy, which was measured by a photodiode, to the third harmonic, which was used for ablation, was assumed. Modifications of the optical parameters of the material occur during the ablation process which one can see in figure 1 as changed reflectivity of the laser crater. Therefore, the correlation between the mass change per pulse and parameters like the optical properties of the sample as well as additional laser beam parameters should be further investigated in future work.

From the measured data shown in figure 3 it can be seen that the frequency after the laser pulse is not stable but shows an asymptotic behaviour of the frequency after the laser pulse on a time scale τ~20 s. We note that this is indicative of stress forming in the QMB and/or the layer. As we cannot ensure that the relaxation is complete this is a source of uncertainty for our measurement. In future work it is desirable to actively control the QMB temperature and select sensors which have the least influence by stress caused due to temperature gradients [13], as well as monitoring the temperature distribution of the film by thermography.

The obtained sensitivities for coating deposition and laser ablation are different within their errors, with increased sensitivity for the latter. The ablation could lead to residual stress in the remaining coating film and/or it could be an effect of the location dependent sensitivity of the QMB which is known to have a maximum in the center and decreases with increased radius, as well as exhibiting poloidal dependence. To clarify which of the effects is causing the observed effect, work to evaluate radial and poloidal sensitivity of the QMB adapting the procedures first described in [11, 15] is ongoing.

In summary it could be demonstrated that QMBs can be used for *in situ* monitoring of the picosecond laser ablation process on magnetron coated materials. Such a setup can provide important pulse resolved information to improve the understanding of laser based quantitative methods like calibration free LIBS and LIAS, where the knowledge of the removed material amount per pulse is highly desirable for the interpretation of signals.

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