Laser ablation for analysis of nanoscale layers

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Abstract. Deposition of carbon layer, tungsten and carbon migration, as well as retention, co-deposition and diffusion of hydrogen isotopes are the major concerns in fusion devices. We propose laser ablation spectroscopy as an effective method of rapid qualitative and quantitative surface mapping. An average growth of the deposited carbon layer in divertor region of a tokamak is about 0.2 nm/s. Depending on the number of discharges, the thickness of a layer can reach 200-400 nm. The information about the layer must be gained within this range of thickness. Obtained results show that proposed method can be used for analysis of layers in the range of thickness of several hundreds of nanometres.

1. Introduction

A laser pulse focused to a sufficiently high irradiance can create plasma useful for spectrochemical analysis. Laser-produced plasma is of transient nature evolving through a wide range of parameters in dependence on laser irradiation conditions: laser wavelength, beam intensity, pulse width and repetition rate, ambient gas composition and pressure \cite{1-4}.

The principles of laser spark analysis are similar to those of conventional plasma-based methods of atomic emission spectroscopy (AES) \cite{1}. Several methods of investigation of samples treated by laser-induced plasma are applied, including mass spectroscopy \cite{5}, ion probes \cite{6}, laser-induced fluorescence \cite{7}, laser interferometry and fast photography \cite{8}. In comparison to these techniques, there are certain advantages of AES-based analysis being the simplicity of the method, the ability of simultaneous monitoring of all elements in plasma, and the possibility of analysis of any material irrespective of its physical state.

1.1. Physical processes in laser-induced plasma

Since the laser irradiance exceeds the ablation threshold, the laser beam evaporates and ionizes the material. The particles ejected from the surface form so-called Knudsen layer, where they collide and thermalize. The particles obtain Maxwell velocity distribution in the centre of mass coordinate system \cite{9}. When the particles leave the Knudsen layer, the further expansion is described by hydrodynamics. An adiabatic expansion of plasma occurs and the temperatures can be related to the dimensions of the plasma. The density and pressure of the ablated material are decreasing in the direction from the target surface. Initially, in direction perpendicular to the target surface particles propagate faster than in lateral direction, which explains a cigar-like shape of the plume \cite{10}. The thermal energy converts to the kinetic energy, and the plasma expands rapidly with supersonic speed. The temperature drops

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quickly in the early stages of expansion, but at later time energy is regained in the recombination of ions [11].

The interaction mechanism between laser radiation and the matter depends on the parameters of a laser beam and chemical composition and physical properties of the target material. The primary interaction is non-thermal as only optically active excitations are able to interact with light.

When the laser radiation is absorbed by the surface of the solid, the electromagnetic energy is converted into electronic excitation. In semiconductors, light can excite free charge carriers and lattice vibrations. The type of excitation depends strongly on the wavelength of laser light. Multiphoton ionization involves the absorption of the sufficient number of photons ejected from the conduction band by an electron. This process is effective for lower laser wavelength when the photon energy of laser light exceeds the band gap of a material. For infrared lasers with photon energy below the band gap, thermionic process takes place – absorption of laser radiation by free electrons.

Electrons in a laser field gain energy through electron-neutral inverse bremsstrahlung collisions. Electron energy loss is caused by elastic and inelastic collisions. Some electrons are lost by attachment. If laser irradiance is high enough, a few electrons will gain energy larger than the ionization energy. These electrons will generate new electrons by the impact ionization of the gas leading to the cascade growth [12].

The condition for initiating the electron avalanche is that the rate of increasing of electron energy exceeds the rate of electron energy loss. It was reported in [12, 13] that the cascade breakdown threshold scales as $\lambda^{-2}$, which means that minimal laser intensity required to achieve a breakdown in the metal vapour or in the ambient gas is easier to obtain with an IR laser than with UV. However, the mass ablation rate is larger using an UV laser [14]:

$$m = 110 \left( \frac{\phi_a}{10^{14}} \right)^{1/3} \lambda^{-4/3}$$

where $\phi_a$ is absorbed flux in W cm$^{-2}$.

1.2. Plasma facing components

In a fusion reactor, there are components in direct contact with the plasma. The largest surface consists of the first wall which surrounds the bulk region of the plasma torus. The plasma shape may be restricted by additional limiters to protect the vessel wall or equipment like antennas for radio-frequency heating which cannot withstand excessive heat loads. Finally, a very important part of the plasma facing components in current and future fusion devices are the divertor target plates. Divertor is a separate region in vacuum vessel to which escaping ions are exhausted along the magnetic field lines by means of auxiliary magnetic coils. In a diverted plasma configuration these plates provide the main plasma-surface interaction zone. The fraction of the fusion power carried by the produced $\alpha$-particles is coupled out to a large extent through these areas.

There are two types of plasma configurations: a limiter type and a divertor type. In a divertor configuration the distance of the plasma wetted surface areas to the confined plasma region is much larger than for limiter configurations. Due to the correspondingly lower penetration probability of eroded material, it is much easier to maintain a low impurity level in diverted plasma discharges [15].

The formation and composition of thin layers, as well as the status of near-surface layers of the plasma-facing components is important for the exploitation of materials in fusion devices [16]. Understanding the processes of plasma-wall interaction is necessary for improving of the first wall materials as well as leads to optimize plasma discharge operation conditions.

Deposition of carbon layers, tungsten and carbon migration, as well as retention, co-deposition and diffusion of hydrogen isotopes are the major concerns in fusion devices [17 - 19]. Several methods of analyzing the surface and impurity content in the near-surface layers are applied. They involve thermal desorption spectroscopy [20], X-ray photoelectron spectroscopy [21], ion beam techniques [22], ellipsometry [23] etc. In this paper, laser ablation as a feasible method of rapid qualitative and quantitative surface mapping is proposed.
It is stated that, for example, an average growth of the deposited carbon layer in divertor region is about 0.2 nm/s. Depending on the number of discharges, the thickness of a layer can reach 200-400 nm [24]. The information about the layer must be gained within this range of thickness.

2. Experimental
The experimental set-up consists of Nd:YAG laser with an optical system in order to focus a laser beam, and laser ablation spectroscopy system.

As the laser-induced plasma source, a Q-switched Nd:YAG laser (SL-312, EKSPLA) with an emission wavelength of 1064 nm was used. It operated with pulse repetition rate of 10 Hz, pulse width of 135 ps, and tuneable pulse energy up to 250 mJ. The diameter of the output laser spot is 1 cm. The convex quartz lens with focal distance of 5 cm in the visible focused the beam onto the target. Two types of the experiment were performed. In the first case, the laser beam was focused to the surface of the target normally. In the second case, the target was placed at the distance of 2 mm in front of the focus position so that minimal amount of the material is removed from the target surface and at the same time the sufficient emission of the spectral lines was observed. The average energy of the laser beam was monitored by a power/energy meter (Ophir, model PE25BB-DIF). The target was mounted on the XYZ-translation stage. The sample was displaced in order to provide intact regions for ablation.

To record laser-induced plasma emission spectra, a spectrometer (Digikröm DK 240, CVI) with a grating of 1200 gr/mm equipped with a CCD camera was applied. A quartz lens projected the plume image of the laser-induced plasma on the entrance of the optical fibre. The fibre (core diameter 0.125 mm) was placed on the image plane of the plume and mounted on the optical table. The output of the fibre bundle was coupled to the slit of the monochromator. The maximum spectral resolution of the optical system was determined as 5 Å.

The targets prepared at the Max-Planck-Institut für Plasmaphysik were graphite R6710 substrates with 200 nm thick tungsten layer sputtered using DC magnetron sputtering technique. The samples were used as the model of the inner walls of a tokamak.

The dimensions, depth and shape of obtained craters were determined by optical microscopy and SEM.

3. Results and discussion

3.1. Depth profiling of the ablation craters
Placing the target at the distance of 2 mm in front of the actual focus of the lens, the ablation craters were obtained. A sequence of 4 pulses was applied. The energy of the laser pulse was 42 mJ. The typical ablation crater is shown in figure 1a. Figure 1b represents the crater obtained under the same conditions of laser irradiation while the laser beam was focused directly on the surface of the sample.

For obtaining the information about depth profiling by laser ablation, it is essential to achieve formation of uniform craters with perpendicular walls. However, if the depth of the craters is relatively small compared to its width, one-dimensional evaporation model is applicable to describe the process of ablation, as it was reported in [25]. This is relevant for the investigated samples supposing that the depth of the crater does not exceed the thickness of the tungsten coating. The depth of the obtained craters is several hundreds of nanometres, which is negligible compared to the craters’ diameter of several hundreds of microns.
The depth of the craters was measured by means of optical microscopy. The focus was adjusted on different levels of a calibration sample with known difference of thickness so that a micrometer screw is calibrated in respect to the depth. The thickness of layers removed by the laser pulse was then deduced reading the graduations on the screw.

As it is shown in figure 1a, defocused beam allows obtaining very shallow craters in comparison to ones acquired using focused beam under the same irradiation conditions. In the case of the defocused beam, a single laser pulse can remove about 70 nm thick layer.

3.2. Laser-induced plasma emission measurements
Reference spectrum of the pure tungsten is shown in figure 2. In the chosen spectral region, 7 intense spectral lines of tungsten were observed: W I 498.908 nm, W I 501.346 nm, W 502.125 nm, W I 505.553 nm, W I 507.173 nm, WI 522.467 nm and WI 535.661 nm.

![Figure 1 a, b. Ablation crater obtained by the sequence of 4 pulses. Laser pulse energy - 42 mJ; a) defocused beam, b) focused beam.](image1)

![Figure 2. Spectrum of the pure tungsten.](image2)
The laser-induced plasma emission spectra are represented in figure 3. The sequence of 4 pulses was applied at the same spot of the sample. Laser pulse energy was 42 mJ, the beam was defocused. The corresponding ablation crater is shown in figure 1a.

![Normalized laser-induced plasma emission spectra.](image)

Figure 3 shows the gradual decrease of the intensity of tungsten lines. At the same time, the increase of the intensity of carbon lines is observed since the tungsten layer has to be evaporated after the 3rd pulse. The presence of W I lines in the spectrum of the 4th pulse can be explained by the re-evaporation of the residues of tungsten by the laser-induced plasma [26].

4. Conclusion
Qualitative and semi-quantitative spectroscopically controlled elemental depth profiles of magnetron-sputtered tungsten coating on graphite R6710 substrate were obtained by laser ablation AES with Nd:YAG laser of the sample XYZ-translated in the plane perpendicular to the laser beam. During the “layer-after-layer” ablation process of the 200 nm tungsten coating, the thickness of an ablated layer per laser pulse was about 70 nm. Obtained results show that the proposed method can be used for the analysis of layers in the range of thickness of several hundreds nanometres.

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