Investigation of Deuterium Implantation into Beryllium Sample by Electron Energy Loss Spectroscopy

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Abstract. Quantitative analysis of hydrogen isotopes in first wall as well as in construction materials of future fusion devices plays a crucial role to understand the evolution of those materials under operation conditions. A quantitative understanding of hydrogen in materials is also an important issue for storing energy as well as for fuel cells. A combination of Electron Energy Loss Spectroscopy (EELS) and Elastic Peak Electron Spectroscopy (EPES) is presented in this study to tackle these problems of modern material research for energy production and storage. Accurate inelastic scattering background subtraction is a key part of the presented quantitative measurement of the Be/D ratio. The differential inelastic scattering cross-section is determined by the fitting procedure. The fitting procedure is based on the iterative solution of the direct problem and minimization of the residual between computed and measured spectra. This study also takes into account the difference in electron energy loss laws for surface and bulk. The inelastic scattering cross-sections for different doses of deuterium ions in beryllium substrate (5.5 × 10²¹ m⁻² and 2.01 × 10²² m⁻²) were defined in a two-layered model. The analysis is carried out for the EELS spectra. Relative concentration of D atoms is defined.

1. Introduction
The problem of determining the material facing the plasma is one of the most complicated engineering problems for the construction of a thermonuclear reactor. Beryllium was chosen as primary first wall material in ITER (International Thermonuclear Experimental Reactor) with an area of approx 690 m². There is the problem of studying the behavior of hydrogen isotopes in beryllium, the studying of plasma sustaining and recycling problems. In the present study, the percent measurement of deuterium in beryllium will be based on the elastic peak electron spectroscopy (EPES). This technique is an analog to the Rutherford backscattering spectroscopy [1-5], but utilizes electrons instead of ions as primary projectiles. There are several advantages of this method compared to conventional RBS: on one side, there are the practical advantages. For RBS analysis accelerators are required, which are not only huge in footprint but also come with a huge price tag. EPES and EELS only require commercially
available electron sources and an electron energy analyser and can be integrated in laboratory photoelectron setups. This also enables to combine common surface analysis like e.g. X-ray photoelectron spectroscopy (XPS) with EELS allowing for valuable, well defined in-situ measurements without exposing the sample to air. By using electrons instead of ions as projectiles, ion damage to the sample is avoided.

But the most important point from a surface scientist perspective is the shallower information depth. In classic RBS the information depth is in the best case in the range of several hundred nm to µm, but most surface science techniques have an information depths in the range of nm, making it difficult to compare the results. However, with the method presented here, we are able to get the chemical information of classic methods like e.g. XPS and Auger electron spectroscopy (AES) and the quantification of hydrogen isotopes on the same length scale. The information depth is dependent on the inelastic mean free path length of electrons, which is a function of the kinetic energy which is the same order of magnitude in AES, XPS, EELS, and EPES.

2. Theoretical
The energy spectrum of electrons elastically reflected from the target can be described with good accuracy by the Gaussian function:

\[
G(\Delta, \psi) = \frac{1}{\sqrt{2\pi}\sigma_\Delta} \exp \left[ -\frac{(\Delta - \Delta_\chi(\psi))^2}{2\sigma_\Delta^2} \right],
\]

where \( \Delta = E_0 - E \) is the energy loss, \( E_0 \) is the initial electron energy, \( \Delta_\chi(\psi) \) is the peak energy shift of element “X”, \( \psi \) is the scattering angle, \( \sigma_\Delta \) is the half width at half maximum (HWHM) of the signal of elastically scattered electrons. Thus, the spectrum of elastically scattered electrons from atoms of a single type is characterized by three main parameters [6]:

1. the elastic peak shift \( \Delta_\chi(\psi) \) to lower kinetic energies with regard to the initial energy \( E_0 \). This is amount of energy which is lost by an electron in the elastic scattering event and it can be computed using the conservation laws for energy and momentum:

\[
\Delta_\chi(\psi) = \frac{2m}{M} \left(1 - \cos\psi\right) E_0,
\]

where \( m \) is the mass of the electron, \( M \) is the mass of the scattering atom;

2. the elastic peak broadening can be approximated by the Gaussian distribution [7] with HWHM given by:

\[
\sigma_\Delta = \sqrt{\sigma_D^2 + \sigma_A^2 + \sigma_E^2},
\]

where \( \sigma_D \) is the Doppler broadening, \( \sigma_A \) is the broadening due to the energy analyzer slit function, \( \sigma_E \) is the broadening of the electron beam. \( \sigma_D \) and \( \sigma_E \) are characteristics of an analytical equipment;

3. the electron signal intensity or the area under the peak of elastically scattered electrons from a layer is determined by the reflection function:

\[
R_\psi(\Delta, \mu, \mu_0, \varphi) = R_{0D}(\Delta, \mu, \mu_0, \varphi) + R_{0B}(\Delta, \mu, \mu_0, \varphi).
\]

The reflection function \( R_0 \) determines the flux of electrons elastically scattered from D and Be nuclei. To calculate \( R_0 \) we use the small angle scattering theory [8]. To evaluate this function, we can use the approximation, which ignores the contortion of the trajectories in inward and outward direction:
\[ R_0(\Delta, \mu, \mu_0, \varphi) = \lambda \frac{1}{\mu + \mu_0} \left\{ \frac{l_{ID}}{l_{ID}} x_{elD}(\mu, \mu_0, \varphi) G_{el}(\Delta, \psi) + \left[ l_{el} - x_{elBe}(\mu, \mu_0, \varphi) G_{elBe}(\Delta, \psi) \right] \right\}, \]

where \( \mu_0, \mu \) are cosines of the incident polar angle \( \theta_0 \) and detection polar angle \( \theta \), respectively, with regard to the surface normal, \( \lambda = \frac{l_m}{l_s + l_m} \) is the single scattering albedo, \( l_s = \frac{l_{Be} l_{elD}}{l_{Be} + l_{elD}} \) is the elastic mean free path, \( l_m = \frac{l_{elBe} l_{elD}}{l_{elBe} + l_{elD}} \) is the inelastic mean free path.

The more accurate calculation is being performed by using the theory presented in [8]. Eq. 4 determines only elastically scattered electrons. However, to obtain the peak area formed by electrons elastically scattered from D we need to subtract inelastic background. For this purpose, we use the partial intensity approach [9, 10], so reflection function is given by:

\[ R(\Delta, \mu, \mu_0, \varphi) = \sum_{k=0}^{\infty} R_k(\mu, \mu_0, \varphi) x_{elD}(\Delta), \]

where \( R_k(\mu, \mu_0, \varphi) \) determines the contribution of \( k \) inelastically scattered electrons to the reflection function and \( x_{elD}(\Delta) \) determines the energy loss spectrum after \( k \) inelastically scattering events. As we have REELS spectra of Be-D, measured in two different geometries of experiments:

- “normal”: \( \theta_0 = 30^\circ, \theta = 30^\circ \);
- “glancing”: \( \theta_0 = 60^\circ, \theta = 60^\circ \).

3. The experiment technique

A polished, quadratic beryllium sample with a side length of 10 mm is used as base material for the experiments. The average roughness Ra of the samples is below 0.1 \( \mu \)m. The samples are supplied by MaTecK and have a bulk purity of at least 99.8 \% Be.

All experiments are conducted in a multi-chamber UHV-setup with a base pressure of 1.10\(^{-8}\) Pa from Prevac. The system is equipped with the hemi-spherical analyser (HSA) R4000 and a monochromatic Al K\( \alpha \) X-ray source MX 650 for X-ray photoelectron spectroscopy (XPS) both from Scienta-Omicron. Two electron sources EM-802 from Staib serve as excitation sources for electron energy loss spectroscopy (EELS). The angle between the first electron source and the HSA is 60\(^\circ\) (“normal” geometry) and between the second source and the HSA 120\(^\circ\) (“glancing” geometry). The sample is located at a 4-axis manipulator with heating capabilities up to 1370 K and can be rotated towards the electron sources. For sample cleaning and the implantation of the hydrogen isotope deuterium, a Prevac ion source IS 40E1 is used.

The sample is cleaned by annealing at 900 K and sputtering with Ar\(^+\) ions with a kinetic energy of 5 keV. The cleaning steps are repeated cyclically until no surface contamination is visible in the XPS survey spectrum. There is no beryllium oxide detectable in the high resolution XP spectrum of the Be 1s core level. Thus, the sample surface is atomically clean. After the cleaning process D-ions are implanted with an acceleration voltage of 3 kV and a fluence of 5.5.10\(^{11}\) m\(^{-2}\). After the implantation a XPS survey scan shows no contamination of the sample. No beryllium oxide is visible in the Be 1s core level spectrum.

After the cleaning procedure and after the implantation, EELS spectra are recorded at three different primary electron energies \( E_E \): 1500 eV, 3000 eV and 5000 eV. Each spectrum is recorded two times: in “normal” and “glancing” geometries.

In between the recording of the EELS spectra the sample is analysed by XPS to check for surface oxidation during the experiments. No BeO is detectable in the high resolution spectra of the Be 1s.
region. The difference in the spectra of the clean reference measurements and the measurements of the implanted sample therefore can all be assigned to the implantation of deuterium.

Figure 1. REELS spectra with $E_0 \sim 5$ keV: a) “normal” geometry; b) “glancing” geometry.

4. Results and discussion

The differential inverse inelastic mean free path (DIIMFP) is retrieved from the experimental spectra [11]. We use different energy loss laws for the near-surface and the bulk region. The cross sections reconstructed from the Be-D spectra with a fluence of $5.5 \cdot 10^{21}$ m$^{-2}$ at $E_0 \sim 5$ keV satisfactorily describe the spectra taken with different geometries. The result is shown in Fig. 1. A similar situation is observed for the Be-D spectra with a fluence of $20.1 \cdot 10^{21}$ m$^{-2}$.

The calculated as well as the experimental REELS spectra are shown in Fig. 2. Calculated REELS spectra without taking into account the EPES deuterium peak with the DIIMFPs reconstructed as a result of the fitting procedure are presented in Fig. 2 by green lines. The discrepancy between the calculation and the experiment (red circles) in the energy loss region of 2-5 eV is due to presence of the EPES deuterium peak. In order to take it into account, according to formulas (1) - (3), an elastic peak of deuterium was calculated and the area under this peak $S_D$ was determined (black dash-line). The result of the complete calculation with D is shown as blue lines in Fig. 2. The area under the elastic peak of beryllium $S_{Be}$ was also determined. Knowing the areas and electron elastic cross sections for D and Be, the relative concentrations were determined.

From these results it is followed that the concentrations ratio $n_D/n_{Be}$ in the very surface layer with thickness $l_m \sim 9.2$ nm is $0.12 \pm 0.02$ at dose of $5.5 \cdot 10^{21}$ m$^{-2}$ and $0.15 \pm 0.03$ at dose of $20.1 \cdot 10^{21}$ m$^{-2}$.

The EELS experimental data measured at initial energies 1500 and 3000 eV give the opportunity of energy scanning or determination of an average D concentration in layers with thickness $l_m \sim 3.4$ nm (1500 eV) and $l_m \sim 6.0$ nm (3000 eV). For these electron beam energies, energy shifts between the peaks of electrons elastically scattered from Be and D are 1.0 and 1.9 eV. In this situation, these shifts won't allow to split elastic peaks from Be and D.
Figure 2. Energy loss spectra of electrons reflected Be substrate with deuterium ions dose of a) $5.5 \times 10^{21}$ m$^{-2}$, b) $20.1 \times 10^{21}$ m$^{-2}$.

5. Summary
The possibility of quantitative analysis of hydrogen isotopes by EPES method was demonstrated in a number of works [2-4]. The studies were carried out with the following materials: H$_2$O, D$_2$O, CH$_2$. The concentration of H-atoms in these materials is 66.7%. In [12, 13] hydrocarbon films were studied in which an approximate ratio of carbon to hydrogen of 1:1 is observed. We have shown in our study, that it is also possible to quantify to H content in a sample, where H is the minority species by an order of magnitude.

Figure 3. Angular distributions elastic scattering electrons with different incident polar angles $E_0 \sim 5$ keV.

To determine the area under the elastic peak it is necessary to subtract inelastic background from the total energy loss signal. In the work, a technique is developed that allows the most accurate implementation of the background subtraction procedure based on the EELS spectra measured on implanted targets in two geometries: scattering by 120 degrees, scattering by 60 degrees. The impurities control was carried out in-situ by XPS. To determine the inelastic background the
differential inverse inelastic mean free paths $\lambda_{in}(\Delta)$, $\lambda_{out}(\Delta)$ were retrieved in a two-layer model for both Be-implanted by deuterium.

In conclusion, we have shown the feasibility of EPES for the determination of hydrogen in metals with D-concentrations down to 11% This method has great potential to address recent problems in material research for nuclear fusion, energy storage and fuel cells. Classic methods of surface science like e.g. XPS and AES will greatly benefit if paired with EPES and EELS for hydrogen detection in situ.

In Fig. 1 EELS spectra measured in geometries described above are presented. One can clearly see a higher error in measuring the flux of reflected electrons in the case of normal probing of the target, rather than in scattering at glancing angles. The answer to this question there is in Fig. 3 which illustrates the reflected signals intensity in the indicated geometries. If during planning EPES experiments we take into account the fact that the measurement error of the reflected electron current is inversely proportional to the signal intensity, it is possible to significantly reduce the measurement errors of the hydrogen isotope content, which in the present paper is about 20%.

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