Analysis of hydrogen isotopes in construction materials by means of electron spectroscopy

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Abstract. The possibility of measuring hydrogen depth profiles by means of electron spectroscopy is demonstrated. In the near-surface layer with a thickness corresponding to the inelastic mean free path (IMFP) the elastic peak electron spectroscopy (EPES) is employed for this purpose. For measuring hydrogen isotope depth profiles deeper in the solid at depths corresponding to the transport mean free path (which is by several orders of magnitude larger than the IMFP) the so-called spectroscopy of reflected electrons (SRE) is used. In this work, the SRE technique is employed for the investigation of a pure beryllium sample and a beryllium sample implanted with deuterium atoms.

1. Introduction
Hydrogen isotope quantification in matter is of great interest in the field of hydrogen energy, surface analysis of plasma facing materials etc. Electron spectroscopy techniques are known to have problems with the direct hydrogen detection [1]. However, a method called the Elastic Peak Electron Spectroscopy (EPES) was recently shown to be a perspective tool for measuring the bound hydrogen [2, 3]. This method is based on sensitivity to small energy losses during elastic scattering of electrons on nucleus of atoms. Such an energy transfer between the impinging electron and the target atom is described by the energy/momentum conservation law as follows:

$$\Delta E = \frac{2m_e}{M} (1 - \cos \psi) E_0,$$

(1)

here $m_e$ is the electron mass, $M$ is the mass of the scattering atom, $E_0$ the energy of the impinging electron, and $\psi$ is the scattering angle. A typical EPES spectrum represents a set of elastic peaks with the squares being proportional to the relative concentrations of elements in the compound and with energy positions corresponding to the recoil energy losses $\Delta E$ on each element.

In [4] Vos analysed the EPES spectrum of a hydrocarbon compound where due to the significant energy resolution used in the experiment it was possible to observe the peak formed by electrons elastically scattered on hydrogen atoms. The possibility to observe elastic peaks of hydrogen isotopes
was also shown in [5], demonstrating the ability to quantify even low relative concentrations of hydrogen isotopes.

2. Methods

The EPES technique allows the analysis of near-surface layers of the solid and has a number of advantages with respect to traditional methods used for hydrogen quantification such as the Elastic Recoil Detection (ERD) and the Nuclear Reaction Analysis (NRA). The information depth depends on the inelastic mean free path (IMFP) \( l_{in} \) which is about 7 nm for the electron energy of 5 keV and increases as \( E^{0.7} \). Knowledge on quantitative amount of hydrogen in the near-surface layer is high of importance, e.g. in nuclear fusion. In order to increase the information depth a higher incident electron energy can be used. For example, for the energy of 50 keV the information depth in a beryllium target increases up to 35 nm and for the energy of 500 keV – up to 175 nm. However, the problem related to the need to increase the energy can be overcome by employing the so-called spectroscopy of reflected electrons (SRE) [6, 7].

The efficiency of the SRE technique was demonstrated in [8] for the determination of the nitrogen depth profile in niobium. The SRE method is based on analysis of the energy spectrum in the energy loss range starting from several eV up to several hundreds eV. Such an area is also called the “dome”. The SRE signal is mainly made up of reflected electrons which leave the sample from depths corresponding to the transport mean free path \( l_{tr} \). Therefore the value of \( l_{tr} \) is the information depth in SRE. For example, when a beryllium target is being irradiated by a 5 keV electron beam the information depth is about 700 nm. For the electron energy of 30 keV this value is about 15000 nm.

The SRE method opens up the possibility of hydrogen analysis at depths commensurate with those achieved in NRA and ERD methods but at the same time being implemented on incomparably cheaper equipment not requiring huge areas for placement. The disadvantage of the SRE approach is the impossibility of separating the measured profile of the hydrogen concentration by isotopic composition: the SRE spectrum is determined only by the nuclear charge. However, the EPES and SRE techniques can be implemented on the same setup, and information on the isotopic composition in the near-surface layers may be obtained from the EPES data.

Our implementation of the SRE technique was described in [5]. In this work, let us consider a beryllium sample implanted with deuterium atoms using an accelerating voltage of 5 kV and fluencies of \( 5.5 \cdot 10^{21} \text{m}^{-2} \) and \( 20.1 \cdot 10^{21} \text{m}^{-2} \). In figure 1 the SRE spectra for pure Be sample and Be sample implanted with D (fluence of \( 5.5 \cdot 10^{21} \text{m}^{-2} \)) atoms are shown.

The spectrum of BeD is clearly seen to be below the spectrum of pure Be in the range of high energy losses, since the shape of the SRE spectrum relates to the effective atomic number \( Z_{eff} \) of the sample [7]. In the range of low energy losses the experimental spectra are seen to be similar which points out that \( Z_{eff} \) is similar in the near-surface layer. Results of SRE spectra calculation based on the partial intensity approach [6] are also shown in figure 1: spectra of electrons reflected from Be samples of different thickness and from BeD\(_{n}\) compounds with different amount of D atoms. The partial intensities were calculated using the invariant embedding approach [6]. The differential inverse inelastic mean free paths (DIIMFP) were taken from [9]. The spectra were calculated for a two-layer system: a layer of beryllium on top of a BeD compound.

In figure 1 the Be spectrum calculated for a semi-infinite thickness is observed to be in a perfect agreement with the experimental data of the pure Be sample, which allows us to ensure that the spectra calculated for Be for other thicknesses are reliable. Therefore from figure 1 it is clear that the thickness of a Be layer on top of a BeD compound belong to the range of 24–30 nm. The reflection function for a two-layer system can be found according to [6, 10] as follows:

\[
R_{\text{Be,BeD}}(d, \mu_0, \mu, \Delta) = R_{\text{Be}}(d, \mu_0, \mu, \Delta) + \int_0^d T(d, \mu_0, \mu, \Delta - e) R_{\text{BeD}}(\mu_0, \mu, \Delta) d\epsilon, \tag{2}
\]

\( T(d, \mu_0, \mu, \Delta - e) \) is the Landau function [11] since isotropization at the path length of \( d\left(\frac{1}{\mu_0} + \frac{1}{\mu}\right) = l_{tr} \) can be neglected. The transport mean free path for the Be sample and the electron energy of 5 keV is
The normalised DIIMFP in $T(d, \mu_0, \mu, \Delta - \epsilon)$ corresponds to pure beryllium and was taken from [9]. The normalised differential elastic scattering cross section (DECS) can be determined as follows:

$$X^{BeD_n}_{el}(\mu_0, \mu) = \frac{\omega_{el}(\mu_0, \mu) + n \omega_{el}^D(\mu_0, \mu)}{\sigma_{el}^n + n \sigma_{el}^D}$$  \hspace{1cm} (3)

with $\omega_{el}$ and $\sigma_{el}$ being the differential and the total elastic scattering cross section for each component of the compound [12], respectively. The single scattering albedo is calculated using $\sigma_{el}$ according to [12] and $l_{tr}$. The IMFP $l_{tr}$ is computed for components $BeD_2$ and $Be$ using the TPP-2M formula [13]. It is worth emphasising that the isotope composition of hydrogen in a compound of $Be$ and $H$ cannot be detected in REELS and SRE spectra. The results of calculations of the reflection function are shown in figure 2.

$$E, \text{eV}$$

**Figure 1.** The energy spectra of electrons reflected from Be and BeD samples.

The transport mean free path of an electron with energy 5 keV in beryllium is 600 nm, which means that the Be layer thickness on top of BeD is much less than $l_{tr}$. Therefore elastic scattering in the Be layer can be neglected in equation (2). The stopping power of an electron with energy 5 keV in Be is 8 eV/nm. Thus it is clear that the center of the spectrum of BeD will be shifted by 400 eV and the second term in equation (2) gives no contribution to the range of 4750–5000 eV of the spectrum of the Be/BeD system but mainly contributes to the range of 4000–4500 eV which leads to a good agreement of the calculated and measured spectra. The calculation results of the Be/BeD spectra are shown in figure 3. Figure 3 demonstrates that a good agreement of the experiment and calculation is obtained for a system with the thickness of the Be layer of 24 nm on top of the $BeD_{0.4}$ compound.

The error in estimation of the stoichiometric coefficient for the $BeD_n$ compound comes from a low quality of the experimental SRE spectrum.
Figure 2. The reflection function $R_{\text{Be}D_n}(d, \mu_0, \mu, \Delta)$ for the electron energy of 5 keV.

Figure 3. The reflection function $R_{\text{Be},\text{Be}D_n}(d, \mu_0, \mu, \Delta)$ for the electron energy of 5 keV.

3. Conclusion
The availability of experimental data on the so-called "dome" part of the energy spectrum of electrons reflected within a fixed solid angle opens up the possibility of nondestructive measurement of layer-by-layer profiles of multicomponent compounds [6, 7, 8, 10]. The method used in the present work is called the spectroscopy of reflected electrons (SRE) which is used to determine the depth profile of deuterium implanted to a Be sample. The analysis of energy spectra of pure Be and BeD (figure 3) yields that the investigated sample consists of the Be layer with a thickness of 24 nm lying on top of the $\text{BeD}_{0.4}$ compound. Since the analysis depth in the SRE technique corresponds to the transport mean free path, the information depth corresponds to the depth of 600 nm. Employing other analytical techniques such as the ERD or NRA allows to obtain only an average amount of D in the sample [3].
It should be underlined that the EPES spectra measured on the same setup allowed to obtain the hydrogen isotopes depth profile in the near-surface layer the depth of which corresponds to the average inelastic mean free path or several nm [5].

The development of the methodology presented in this work should be based on the following areas: 1. Measuring a SRE spectrum with a high energy resolution in a wide energy loss range (from a few eV up to losses corresponding to 80 % of the incident energy) which allows to decrease the error in estimation of the stoichiometric coefficient; 2. Measuring several SRE spectra for different values of the incident energy, e. g. SRE spectra acquired at 2 and 3 keV give the information about the sample at depths of 110 and 230 nm. Availability of the mentioned set of data allows to build a more detailed depth profile of hydrogen or its isotopes.

In this work, the contribution of fast secondary electrons to the “dome” area of energy spectra was not taken into account. However, this problem will be considered in future works.

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