Measurement of hydrogen isotopes by a nuclear microprobe

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Abstract. We here report mapping of hydrogen isotopes by elastic recoil detection analysis using heavy ions as projectiles at the Uppsala Tandem Laboratory nuclear microprobe. The system performance was evaluated by measurements on well defined samples of deuterium implanted vitreous carbon. Separation of hydrogen and deuterium as well as depth profiling was demonstrated by an appropriate choice of ion beams and recoil detection techniques. No effect was observed on the concentration profile of the implanted deuterium when a 7 MeV primary carbon ion beam was used. The hydrogen concentration near the sample surface was, however, significantly influenced by ion-induced detrapping.

1. Introduction

Investigations of hydrogen isotopes in solid matter are important for the understanding of plasma-first wall interactions in fusion reactors. Especially the tritium retention in the plasma facing walls is a key property both for safety and economy [1]. Hydrogen content and spatial distribution is also of general interest in material science, since hydrogen can influence the physical and chemical properties of a material.

Common methods to determine the hydrogen content based on Ion Beam Analysis (IBA) techniques are Elastic Recoil Detection Analysis (ERDA) and Nuclear Reaction Analysis (NRA). The main advantages of these techniques are easy sample handling, fast measurements and high sensitivity. Combined with a nuclear microprobe, 3D elemental mapping with micrometer lateral resolution is feasible [2]. Secondary Ion Mass Spectrometry (SIMS) is an alternative technique to measure the different hydrogen isotopes with an even higher sensitivity, although quantitative analysis is problematic. In contrast, quantitative analysis is straightforward with ERDA, for well known recoil cross sections [3]. NRA depends on suitable nuclear reactions and is therefore restricted to the analysis of one or a few elements at a time. ERDA, on the other hand, is not restricted to specific isotopes and several elements can be probed simultaneously.

At the Uppsala Tandem Laboratory we have previously used microprobe NRA [4] and have now started to use heavy ion beams (such as carbon) in conjunction with microprobe ERDA for mapping hydrogen isotopes. Heavy ion beams such as carbon benefit from higher cross sections and improved depth resolution compared to helium ions. When using heavy ion beams the energy deposited in the probed sample may, however, affect the original depth profile of mobile elements.

Here we present preliminary results on the performance of our nuclear microprobe for measuring hydrogen isotopes in vitreous carbon and the effect caused by the primary analyzing beam on the initial concentration of hydrogen isotopes in the sample.
2. Experimental

2.1. Experimental setup
The ERDA measurements were performed with the nuclear microprobe at the Uppsala Tandem Laboratory manufactured by Oxford Microbeams, which previously has been published as the SLIM-UP installation [5]. The carbon ions produced in a cesium sputter ion source is accelerated in a 5 MV pelletron machine and enters the microprobe setup through a collimator, defining the object dimension. The beam spot on the sample is finally defined by the focusing of three quadropole magnetic lenses adjacent to the target. The accelerator system is also equipped with two duoplasmatrons ion sources for production of hydrogen and helium ions.

Two different methods were used to determine the size of the focused beams. For larger beam spots an optical microscope was used for visual determination of the size of the beam spot by comparison to a TEM grid with known dimensions. For smaller beam spots, mapping of backscattered ions from a TEM grid were used to gain information for adjusting the scanned area and optimizing the sharpness off the beam.

Microprobe ERDA, see figure 1, was performed with 7 MeV carbon ions. A 7 µm Mylar foil was used as stopper to prevent primary ions from entering into the detector. The beam current was monitored throughout the measurements by charge integration. To suppress secondary electron from the target, a -300 V bias voltage was applied to a plate in front of the sample.

Vitreous carbon were implanted with 40-60 keV D\textsuperscript{2+} at fluences of 10\textsuperscript{16}-10\textsuperscript{17}/cm\textsuperscript{2} using a 350 keV high current implanter manufactured by Danfysik. Vitreous carbon is a form of carbon without pores and resistant to chemicals.

2.2. Hydrogen isotope separation
The relation between the energy of the primary ion before collision (E\textsubscript{primary}) and the energy of the recoiled ion after collision (E\textsubscript{recoil}) is given by

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K\text{\textsubscript{recoil}} = \frac{E\text{\textsubscript{recoil}}}{E\text{\textsubscript{primary}}} = \frac{4M\text{\textsubscript{primary}}M\text{\textsubscript{recoil}}}{(M\text{\textsubscript{primary}} + M\text{\textsubscript{recoil}})^2} \cos^2 \phi ,
\]

where \(M\text{\textsubscript{primary}}\) and \(M\text{\textsubscript{recoil}}\) is the mass of the different ions and \(\phi\) is the scattering angle [3]. For hydrogen and deuterium at the sample surface, deuterium recoils will have higher energy compared to hydrogen. Deuterium recoiled from deeper in the sample does on the other hand exhibit energy not distinguishable from hydrogen recoils at the surface. This depth depends on several parameters such as scattering angle, stopping power in the material, primary beam energy and determines the maximum depth that can be probed without isotope interference. Depending on the expected sample composition, different requirements have to be considered when optimizing an ERDA measurement.

2.3. Performance
A vertical and horizontal resolution of 5 µm and 8 µm respectively was achieved for a 9 MeV \textsuperscript{12}C\textsuperscript{3+} (0.1 nA) ion beam (figure 2). The resolution can be further improved by decreasing the object collimator which limit the beam current and thus increase the data acquisition time. Mapping was performed on areas < 1x1 mm\textsuperscript{2}.

The time required to make a 3D mapping depends on several factors such as isotope concentration, the required spatial resolution and type of primary beam used. With a 8 MeV \textsuperscript{12}C\textsuperscript{3+} (1 nA) ion beam we were able to perform a acceptable mapping on a sample implanted with 2x10\textsuperscript{16} D/cm\textsuperscript{2} in approximately 6 hours. An average deuterium concentration could be obtained within one hour which also means that measuring a total concentration lower then 10\textsuperscript{16} D/cm\textsuperscript{2} is possible.
Figure 2 The yields in figure (a) are projections of the details marked in the mapping of backscattered carbon ions from a gold TEM grid in figure (b). The resolution of the focused beam is determined by the width of the edges I and II in figure (a).

3. Result and Discussion

The effect of the primary ion beam on the original hydrogen and deuterium depth profiles in the implanted samples were studied as a function of time. Different beam fluxes were obtained by varying the spot size (0.15 – 3 µA/mm²) as well as scanning the beam over a large area. The amount of deuterium and hydrogen was obtained by integrating the corresponding peak (shadowed in figure 3) in the energy spectrum. Hydrogen at the surface is mainly due to contamination and is present in most samples including vitreous carbon prior to implantation.

Total yields for the selected regions are plotted in figure 4 as a function of the ion fluence. The sample was moved slightly between runs to avoid interference between subsequent measurements. The total concentration of implanted deuterium remains unaffected for ion fluence < 2x10¹³ C ions/mm². The hydrogen close to the surface shows a decline for all different flunces and the decline is similar to that seen for thin amorphous hydrogenated carbon films [6].

The variation of the hydrogen concentration in the sample for different ion flunces exhibits the same dependency for a scanned and a stationary beam spot.

In figure 3, the profiles for the recoils in the beginning and at the end of a measurement are shown. No significant difference in the profiles of the implanted deuterium can be seen and no effects on hydrogen in the bulk of the sample. However, there is a difference in the measured hydrogen profiles at the surface. If deuterium had been present closer to the surface or at higher concentrations it would possibly have been affected, since the same type of decline has previously been observed for both hydrogen and deuterium in thin films [7].
Figure 4 The integrated yields of hydrogen and deuterium of the selected regions in figure 3 as a function of ion fluence for several beam current densities.

The implanted deuterium is found to be at depth of approximately 400 nm, which fits well with the prediction by the SRIM 2007 code [8]. This code also predicts a FWHM of about 150 nm for the implanted deuterium profile, which is slightly less than what is seen in figure 4. The measuring time can be reduced if a lower depth resolution, which comes with a larger solid detection angle, can be accepted. This is often the situation for 2D mappings were only the total lateral distribution is of interest.

4. Conclusion
We have shown that the nuclear microprobe at the Uppsala Tandem Laboratory can be used for ERDA analysis of different hydrogen isotopes making 3D elemental mapping possible. The implanted deuterium profile in vitreous carbon remained constant during the measurement but the primary beam did influence the hydrogen located at the surface of the sample. ERDA measurements of hydrogen isotopes in materials relevant for fusion research such as Be, W and other forms of carbon more suitable as plasma facing walls are in progress.

References
[1] Federici G et al. 2001 Nucl. Fusion 41 No 12 1967
[2] Grambole D, Wang T, Herrmann F and Eichhorn F 2003 Nucl. Instr. and Meth. B 210 526
[3] Tesmer J R and Nastasi M 1995 Handbook of Modern Ion Beam Materials Analysis (Pittsburgh: Materials Reasarch Society)
[4] Bergsäker H, Emmoth B, Petersson P, Possnert G, Coad J P, Likonen J and Renvall T 2007 J. Nucl. Mater. 362 215
[5] Sunde T, Nyström J and Lindh U 1991 Nucl. Instr. and Meth. B 54 80
[6] Adel M E, Amir O, Kalish R and Feldman L C 1989 J. Appl. Phys. 66 3248
[7] Grambole D, Herrmann F, Behrisch R and Hauffe W 1999 Nucl. Instr. and Meth. B 158 647
[8] Biersack J P and Haggmark L 1980 Nucl. Instr. and Meth., 174 257