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First GD-OES results on various deuterium ion fluences implanted in tungsten☆

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ABSTRACT

Glow discharge optical emission spectroscopy (GD-OES) was used to investigate the deep depth profile of deuterium in tungsten exposed to deuterium ions at various fluences. Deuterium was found to continue to decrease in intensity at depths 10–20 μm, even at the lowest fluences, well beyond the probing depths of conventional deuterium measurement techniques. The detection sensitivity was sufficient to allow for definite separation in spectra for all fluences used in the present experiments. The integrated deuterium signal from GD-OES measurement was compared with total deuterium content for samples implanted with deuterium with fluences ranging from 1.0×10^{20} D/m^2 to 1.0×10^{22} D/m^2. The result showed a clear trend, where the intensity scales with implanted deuterium fluence to the 0.25 power. These results motivate further experiments and calibration of the system for future absolute retention measurements using GD-OES.

1. Introduction

Understanding and predicting hydrogen isotope retention in plasma facing components is an important consideration for fusion safety and operational requirements. Thermal desorption spectroscopy (TDS) and nuclear reaction analysis (NRA) are established techniques for investigating deuterium retention. These techniques each have advantages and disadvantages. TDS is excellent for measuring total deuterium retention, however as it involves heating the sample, it would be a formidable challenge to resolve the initial spatial distribution of deuterium within the sample. Since NRA involves accelerating a probe beam to detect deuterium, depth resolution is obtained by changing the probe beam energy. The limits of accelerator beam energies determine the maximum probing depth, which in practice is around 3–8 μm. Consequently, NRA isn't able to detect deuterium that has diffused more deeply, and this has been estimated to be as much as 30–90% of the total retained deuterium in some samples [1]. Measuring deuterium in bulk tungsten and plasma facing components (PFC) is especially important when deep deuterium diffusion is expected. Some examples of this include ultra-high fluences [2,3], and samples with neutron damage [4] – both nuclear fusion reactor relevant conditions.

Glow discharge optical emission spectroscopy (GD-OES) has recently been shown to be a valuable technique for investigating the depth distribution of deuterium in tungsten [1]. The technique works by using a glow discharge plasma to physically sputter successive layers of a sample, and characterizing the optical emission from the sputtered material via an array of photomultiplier tubes, which measure the concentration of 10's of elements simultaneously. GD-OES provides a direct measurement of deuterium up to depths of 10–100's μm with nanometer depth resolution. This has potential to be particularly important for evaluating samples under fusion reactor conditions where high deuterium/tritium diffusion is expected. Relatively few studies have been performed using GD-OES to measure deuterium [5–9], and virtually none have examined the profile to significant depths.

This paper builds off of recent results [1], however emphasizes the ability to measure deuterium implanted under low flux/fluence conditions. A primary goal of this is to determine whether or not GD-OES is a suitable technique for measuring relatively small quantities of retained deuterium (i.e., low implantation fluences), and differentiating the deuterium depth profile for varying fluences. We present the deuterium depth profile results for deuterium implanted into tungsten at fluences ranging from $1.0 \times 10^{20-22}$ m^{-2}. It will be shown that despite deuterium being implanted in the near surface region (~nm), deuterium diffuses deep into the samples and is detected at depths not previously accessible with other analytical techniques. Discussion is provided on how GD-OES could be used to determine total deuterium retention by integrating the deuterium intensity signal throughout the analysis depth.

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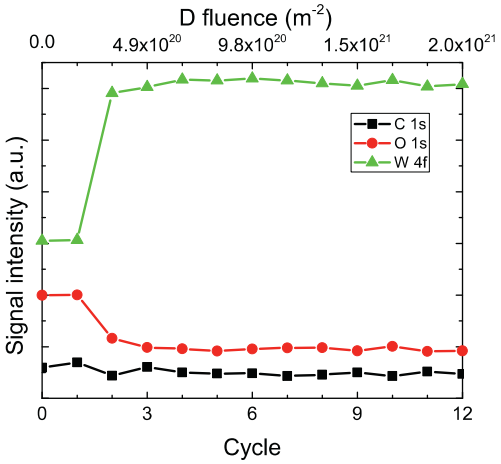

Fig. 1. XPS line intensity showing prominence and reduction of oxides on tungsten with respect to deuterium implantation.

2. Material and methods

2.1. Samples

Samples were produced by punching 16.5 mm diameter disks from a 127 μm thick polycrystalline warm rolled tungsten foil. The foil had a reported 99.95% purity. Samples were ultrasonically cleaned in acetone, ethanol, and demineralized water and then stress relieved by heating the samples at 1173 K for 1 h. The surface condition of samples was otherwise an as-manufactured technical surface, and did notably include surface oxides when examined by X-ray photoelectron spectroscopy (Mg Kα). Adventitious oxygen decreased with deuterium implantation (Fig. 1), however metal oxides (as revealed in the W 4f photoelectron peaks) were not completely eliminated due to the low sputtering yield of tungsten by deuterium. For the sake of the present study, where the primary goals relate to demonstrating the usefulness of GD-OES for measuring deuterium profile in bulk tungsten with respect to fluence, the surface condition is assumed to be of negligible importance. However, future studies will consider the relative effects of surface preparation and microstructure dependence on diffusion.

2.2. Ion irradiation

Ion irradiation was performed within a Phi 5600LS X-ray photoelectron spectroscopy (XPS) system using the sputter ion gun (model 04–303). Deuterium was used as the ion gun gas species. Deuterium implantation was conducted at 3 keV, with a flux of $\sim 9.0 \times 10^{17}$ D/m^{2}s, and at room temperature. The ion beam was not mass analyzed, and it was assumed that the beam is predominantly composed of D_2^+ ions. The ion beam was rastered to implant over a 6 × 6 mm^2 area on the sample, and the implantation area was visually verified on a SiC sample with a digital microscope. Implantation continued to one of five fluences as shown in Table 1. Some ion fluences were repeated for multiple samples in order to check repeatability of data and improve statistics. Following deuterium implantation, some surface discoloration was observed (Fig. 2), which can be attributed to the interaction with metal oxides on the technical surface. Surface discoloration was more prevalent in higher fluence samples than lower fluence samples. It is noteworthy that XPS cannot directly detect elements with atomic number Z < 3, and therefore cannot directly measure surface deuterium.

Table 1
Implantation fluences per sample.

D fluence (D/m^2)	Sample ID
Virgin	WF17_01
1.0×10^{20}	WF17_03 WF17_04 WF17_05
3.2×10^{20}	WF17_06 WF17_07
1.0×10^{21}	WF17_08 WF17_09
3.2×10^{21}	WF17_10 WF17_11 WF17_12
1.0×10^{22}	WF17_13

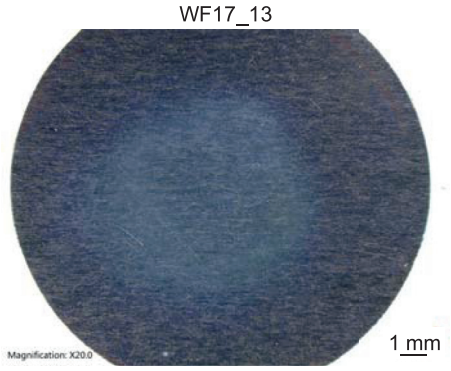

Fig. 2. Discoloration of technical tungsten surface resulted after deuterium implantation.

2.3. Depth profiling

Deuterium depth profiles in each sample were measured using a glow discharge optical emission spectrometer (GD-OES, Horiba GD-Profiler 2) approximately 6 days after ion implantation. The GD-OES uses an Ar plasma (Pressure: 700 Pa, Power: 40 W) to burn (i.e., physically sputter) a 4 mm diameter crater into a sample. The 6 × 6 mm^2 ion implantation area had to be manually and carefully centered on the 4 mm diameter anode. This careful manual positioning is susceptible to some inconsistencies, which could be translated into deviations in GD-OES signals and subsequent calculations. The ion implantation area could have been selected to be much larger than the GD-OES anode, however a reasonable balance between implantation area (and consequently implantation duration) and alignment precision had to be realized. The eroded material is momentarily integrated in the argon plasma where the electrons from the material are excited to a higher energy state and subsequently relax. This relaxation emits a spectrum of visible and ultra violet light, depending on the excitation state and element, which is separated by a diffraction grating. Photomultiplier tubes (PMT) are positioned behind a mask with slits etched to allow a portion of the diffracted light to pass. Therefore, each PMT detects the intensity of a designated wavelength corresponding to a particular element. Tens of elements can be detected simultaneously. Notably, deuterium and hydrogen are detected separately by looking at the 2nd order deuterium line (121.534 nm) and 3rd order hydrogen line (121.567 nm) [1]. The PMTs acquisition rate was 10–100 ms/measurement, which for these samples, resulted in a measured signal intensity data point every 0.1–1.2 nm. An interferometry system is integrated into the GD-OES, the differential interferometer profiling (DIP) system, and measures the real-time depth of the crater. The end result is an elemental depth profile up to 10's of μm within the sample, with nanometer depth resolution.

For the tungsten samples discussed presently, the GD-OES plasma conditions resulted in a burn rate of ~5.3 μm/min [1]. Sample analysis continued for 450 s, and the average depth for the samples in Table 1 is 39.9 ± 2.1 μm. The crater depths were independently measured using a Keyence VHX-6000 digital microscope, with 3D profilometry capabilities, and the average crater depths were measured to be 41.5 ± 1.8 μm. The results of the VHX digital microscope measurements as well as the DIP measurements are summarized in Fig. 3. Consistent crater depth measurements are important for translating the GD-OES signal intensity vs. time measurements to intensity vs. depth.