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Full Length Article

The detection of He in tungsten following ion implantation by laser-induced breakdown spectroscopy☆

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) results are presented that provide depth-resolved identification of He implanted in polycrystalline tungsten (PC-W) targets by a 200 keV He+ ion beam, with a surface temperature of approximately 900 °C and a peak fluence of 10^{23} m^{-2}. He retention, and the influence of He on deuterium and tritium recycling, permeation, and retention in PC-W plasma facing components are important questions for the divertor and plasma facing components in a fusion reactor, yet are difficult to quantify. The purpose of this work is to demonstrate the ability of LIBS to identify helium in tungsten; to investigate the sensitivity of laser parameters including, laser energy and gate delay, that directly influence the sensitivity and depth resolution of LIBS; and to perform a proof-of-principle experiment using LIBS to measure relative He intensities as a function of depth. The results presented demonstrate the potential not only to identify helium but also to develop a methodology to quantify gaseous impurity concentration in PC-W as a function of depth.

1. Introduction

ITER, the international tokamak experimental reactor, has selected tungsten (W) as the divertor due to its high melting point, low sputtering yield, and high thermal conductivity [1,2]. The plasma conditions in the divertor, include helium (He), deuterium (D), and tritium (T) at energies ranging from 10 to 1000 eV, will induce surface and bulk modification in the plasma facing components. The PFC surface response to the plasma can include erosion, blistering and dust formation, as well as impact the recycling, retention, and permeation of the tritium fuel. The motivation for conducting these experiments is to investigate fuel retention, and more precisely, the development of new technique(s) to quantify gas retention as a function of depth, which is important because it demonstrates the total fuel retention, and provides experimental data necessary for the validation of computational models [3].

Multiple studies in the literature demonstrate the effects of He exposure on hydrogen isotope, or specifically deuterium (D), retention in PC-W [4–6]. Miyamoto et al. [7] found that the D retention with He exposure is 10% less than for samples exposed only to D plasma. They performed their experiment with simultaneous D–He plasma exposures with 1–20% He+ at ~573 K and 55 eV/ion. They observed that bubbles, presumably containing He, were formed deeper than the expected He ion range, which suggests that D retention decreases when the depth of the implanted D is less than the depth of the He bubbles. Baldwin et al. [8] showed that bubble formation decreased D permeation and hypothesized that the bubbles provide interconnected pathways from the bulk to the surface, which, in turn, reduces D retention. Their experiment involved PC-W targets at a fixed temperature ranging from ~420–1100 K that were exposed either to a D only plasma, or mixed D plasmas containing either He or argon or a D plasma following pre-exposure with a He plasma. After He-D exposure, with implanted He fluences that were greater than that of D, the D retention decreased by 2% when compared to a D-only case. Baldwin and Doerner used Nuclear Reaction Analysis (NRA) to show that D was trapped in the same area that the He bubbles were located, which suggested that

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the decrease in D retention is related the bubbles locally trapping D and limiting permeation [8]. Ueda et al. [9] found that the He and D ion stopping ranges influenced the extent to which He can block D diffusion into the bulk. In their study, experiments were performed at ~473 K with 1–1.5 keV of D only and 0.6–1.5 keV mixed He^+ and D. When the implantation depth of the He was similar to that of D, the D retention decreased when compared to D-only irradiation and blistering was suppressed. However, when the He ion range was significantly less than the H ion range, there was no decrease in D retention or blistering.

Conventional surface characterization techniques like Elastic Recoil Detection (ERD), Nuclear Reaction Analysis (NRA), Thermal Desorption Spectroscopy (TDS), and Secondary Ion Mass Spectroscopy (SIMS) are used to quantify fuel retention in the near surface regions of fusion materials [9–13]. ERD uses an energy depth relationship to determine elemental depth profiles. However, when using ERD to detect the concentration of low-Z materials as a function of depth in high-Z matrices, the resolution is directly influenced by irradiation damage, background level, and the number of counts detected [14]. NRA uses ions, such as nitrogen or ^{3}He, with energies greater than about 30 MeV to probe species of interest (usually through ion, alpha reactions) and measures the number and energy distribution of alpha particles, which can provide the concentration and depth of the species of interest respectively. While NRA is ideal for determining the magnitude of the retained gas, it is not optimal for determining concentrations as a function of implantation depth [14]. TDS heats a sample with a fixed temperature rate increase in an ultra-high vacuum and measures the resulting desorbed species in a mass spectrometer (often a high-resolution quadrupole mass spectrometer). However, in the case of detecting desorbed He, TDS is often unable to completely desorb He once it has formed large bubbles due to the lack of thermal desorption of the insoluble He from a large bubble. SIMS is a technique suitable for examining impurity (He and D) behavior in the near surface regions at high sensitivity (several ppm) and depth resolution (several nm) [15]. However, SIMS is not quantitative [16]. These surface characterization techniques are commonly used to investigate fusion material. However, the need for a suitable diagnostic technique that can perform depth profiling analysis of the near surface layers without extensive surface preparation, which is sensitive to light elements, inexpensive, and remote, is imperative for the investigation of fusion materials.

The development of laser-based characterization techniques can complement and expand on the capability to provide a depth profile of the gas content in fusion materials. Especially those related to questions regarding He-D interactions and gas retention. Laser Induced Breakdown Spectroscopy (LIBS) offers multi-elemental and microanalysis in the near surface with high sensitivity (ppm) and depth resolution [17–20]. LIBS is a laser ablation technique commonly used to characterize a material surface and the chemistry, specifically elemental composition. During the ablation process, the breakdown and vaporization of a small volume ($\sim 10^{-9}$ cm^3) occur, forming a plasma. In the first stage (few ns) of the plasma, the light emitted appears intense from the excitation of the material. After a few hundred nanoseconds, an intense broadband continuum of light is formed because of the bremsstrahlung process. Spectral emissions from ionized, neutral, or molecular species occur between 0.5–2 μs, 2–10 μs, and >10 μs, respectively after plasma formation. The most dominate contribution to emission lines are from the de-excitation of neutral atoms, and this occurs during the 2–10 μs spectral window. The characterization of the temporal behavior and relative intensity of the plasma light is termed Optical Emission Spectroscopy (OES) and contains information about the surface elemental composition.

LIBS is a well-establish analysis technique in many fields of research including fusion [21–29]. Farid et al. [25] investigated the laser-induced plasma parameters, electron temperature and density of W as a function of laser wavelength and irradiance. Temporal variance in the electron temperature and density as a function of laser wavelength and irradiance were also discussed. Piip et al. [26] and Paris et al. [27] investigated the depth profile of W coated molybdenum (Mo) samples exposed to a linear plasma source, Magnum-PSI. Piip et al. exposed four W coated Mo samples to a 60% D and 40% He plasma. The maximum heat flux at the center of the plasma was ~10 MW/m^2, the maximum particle flux was $\sim 1 \times 10^{24}$ m^{-2}s^{-1} and the particle fluence reached $\sim 1 \times 10^{26}$ m^{-2}. The W, D, and Mo intensities were shown as a function of depth; however, limitations such as a shot to shot fluctuation, were apparent. Mercadier et al. [28] performed LIBS on carbon fiber composite (CFC) containing hydrogen (H) and D. They performed a parametric study of laser fluence, pulse duration, and gas pressure and its influence on the H and D Balmer alpha spectral lines. The results showed that LIBS parameters could be optimized to investigate light elements such as H and D. In summary, there is an apparent need for the optimization of LIBS for fusion applications; parameters such as laser fluence, gate delay, pulse duration, limits of detection (LOD) for light elements (He, H, and D), and depth resolution need extensive investigation.

The purpose of this work is to demonstrate the ability of LIBS to identify helium in tungsten; to investigate the sensitivity of laser parameters including, laser energy and gate delay, that directly influence the sensitivity and depth resolution of LIBS; and to perform a proof-of-principle experiment using LIBS to measure relative He intensity as a function of depth. The initial section of the methodology discusses our approach to assessing the impact of LIBS experimental parameters, such as laser energy and gate delay, on the measured LIBS signal intensity. Section 3 presents initial results that demonstrate the ability to identify He, and its depth dependence by LIBS on a polycrystalline PC-W specimen following 200 keV He ion implantation at a temperature of ~900 °C to a peak fluence of 10^{23} m^{-2}. Based on these results, we discuss a procedure to perform a relative depth analysis and the dependence of the signal on laser parameters. Following an initial comparison of the measured He depth profile with the expected implantation profile, we discuss plans for additional research to compare the LIBS results to other conventional techniques.

2. Experiments

2.1. Specimens

The LIBS measurements were performed on sheet stock polycrystalline tungsten (PC-W), previously investigated by Meyer, Hijazi, and Parish et al. [30,31] using multiple surface and bulk characterizations techniques, including Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). Five PC-W specimens were cut from the sheet stock into 13 × 13 mm squares with a 0.45 mm thickness. One sample was sent to Luvak INC. to determine bulk impurity concentration by Direct Current Plasma Emission Spectroscopy (DCPES). The impurity content in the bulk W, by weight, is as follows: 0.022% Cu, 0.0002% H, <0.0005% Sulfur, 0.002% C, <0.001% N, and 0.001% O. Correspondingly, the PC-W specimen is ~99.97% pure. The remaining four specimens were cleaned and polished to a dull metal finish before the He implantation.

2.2. He implantation

As shown in Table 1, three of the four PC-W samples were exposed to a 200 keV He^+ ion beam. The first specimen in Table 1 is the control sample; it was used to determine the shot-to-shot vari-