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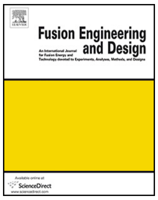

# Effects of stress-relief pre-annealing on deuterium trapping and diffusion in tungsten

Xiu-Li Zhu[a,b], Long Cheng[a,b], Gregory De Temmerman[c], Li-Qun Shi[d], Yue Yuan[a,b], Bao-Yi Wang[e], Xing-Zhong Cao[e], Er-Yang Lu[e], Ying Zhang[a,b,*], Guang-Hong Lu[a,b]

[a] *Department of Physics, Beihang University, Beijing 100191, China*
[b] *Beijing Key Laboratory of Advanced Nuclear Materials and Physics, Beihang University, Beijing 100191, China*
[c] *ITER Organization, Route de Vinon sur Verdon, CS90 046, 13067 St. Paul Lez Durance Cedex, France*
[d] *Institute of Modern Physics, Fudan University, Shanghai 200433, China*
[e] *Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China*

## HIGHLIGHTS

- The effect of residual stress on deuterium trapping and diffusion is investigated via making use of slow positron beam.
- Residual stress is found to constrain the deuterium trapping capability of vacancy-type defects.
- It is suggested that residual stress facilitates the inward diffusion of deuterium.

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## ABSTRACT

Positron annihilation Doppler broadening spectroscopy (PA-DBS) with slow positrons was utilized to characterize the change of vacancy-type defects induced by a stress-relief annealing (1273 K for 1 h in vacuum) as pre-annealing can remove not only residual stresses but also most intrinsic defects of the material. Deuterium behavior after low energy (40 eV/D) and high-flux ($10^{24}$ D/m$^2$ s) plasma exposure was analyzed by a combination of PA-DBS, elastic recoil detection analysis (ERDA) and thermal desorption spectroscopy (TDS). It is found that the vacancy defects density in tungsten is largely decreased by annealing and some intrinsic vacancies clusters to be multi-vacancies during the annealing process. With deuterium plasma exposure, a general decrease of $S$ parameter found in both non- and pre-annealed tungsten suggests the deuterium occupation of vacancy-type defects. In combination of the $S$ parameter change in the non- and pre-annealed tungsten, it is implied that deuterium trapping ability of vacancy-type defects is constrained due to the residual stresses. This confinement effect concentrates on the top surface and it becomes weaker with increasing depth. A similar deuterium distribution in the near surface of non- and pre-annealed tungsten supports this confinement effect. In addition, comparing the amount of deuterium retained in the near surface and in the bulk suggests that the residual stress facilitate deuterium to diffuse into a larger depth in tungsten.

## 1. Introduction

As one of the promising plasma-facing materials in fusion reactor, tungsten will inevitably be exposed to high-fluxes of plasma species (deuterium, tritium and helium) [1,2]. Numerous investigations have already been performed to study the deuterium behavior in tungsten in both experiments and theory [3], where deuterium-induced blistering [4,5], deuterium retention [6–10], as well as corresponding underlying physics and mechanisms [11] have been systematically analyzed. In most studies, tungsten samples with a mirror polished surface are used in the experiment. Mechanical polishing is one of the most usual method to prepare samples, and is typically followed by an annealing to remove the intrinsic defects and residual stresses which were introduced during the mechanical polishing. However, to date, no systematic analyses of the influence of residual stresses on the deuterium behavior in tungsten exist. With respect to the theory, only few simulations [12,13] were done

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* Corresponding author at: Department of Physics, Beihang University, Beijing 100191, China.
*E-mail address:* zhyi@buaa.edu.cn (Y. Zhang).

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to investigate the effects of strain on hydrogen solution and diffusion in tungsten. First principle simulations showed that under an isotropic strain, the hydrogen solution energy and diffusion barrier decrease with increasing tensile strain, but they increase with compressive strain [13]. Similarly, an increasing anisotropic strain would lower hydrogen solution energy in tungsten, and then give rise to the increase of hydrogen concentration [12].

The aim of this work is to get an insight into the effects of stress-relief annealing on deuterium behavior in tungsten. First of all, two types of tungsten samples were prepared and mechanically polished. One sample then underwent annealing (1273 K for 1 h in vacuum) while the other one remained pristine after polishing (called as "non-annealed"). As is well known, the annealing process can not only remove the residual stresses, but also remove some natural defects, such as vacancies and dislocations. So the slow positron annihilation Doppler broadening spectroscopy (PA-DBS) was utilized in this study to characterize the change in vacancy-type defects due to stress-relief annealing. Then, in combination with PA-DBS, elastic recoil detective analysis (ERDA) and thermal desorption spectra (TDS), the effects of defects change and residual stress change due to pre-annealing on the deuterium behavior is expected to be separate. Finally, the influence of residual stresses on deuterium trapping and deuterium diffusion is discussed based on excluding the inevitable effects of vacancy-type defects changes.

## 2. Experiments

In this work, investigated samples are made from warm-rolled tungsten with purity 99.95%, purchased from Advanced Technology & Materials Co. Ltd. Inc., and the sample dimensions were $8 \times 8 \times 0.8\,\mathrm{mm}^3$. Mirror-like surface was obtained after mechanically polishing. To remove the residual stresses, one group of tungsten samples was subsequently heated at temperature 1273 K for 1 h at a background pressure below $10^{-5}$ Pa. Samples, including pre-annealed and non-annealed tungsten, were sent to Pilot-PSI located at FOM Institute DIFFER [14] for deuterium plasma exposure with an incident energy of 40 eV and a flux of $\sim 1.0 \times 10^{24}\,\mathrm{D/m^2\,s}$. During exposure, the surface temperature was monitored with an infrared camera and kept around 473 K. The deuterium plasma-exposure was 100 s and the ion fluence was up to $\sim 1.0 \times 10^{26}\,\mathrm{D/m^2}$.

All samples (annealed and non-annealed, with and without deuterium plasma exposure) were sent to the Key Laboratory of Nuclear Analysis Techniques Multi-research Center, Institute of High Energy Physics (IHEP), Chinese Academy of Sciences, for positron annihilation Doppler broadening spectrometry (PA-DBS) measurement [15,16]. It was performed at room temperature with using an energy-variable slow positron beam facility. Positrons were generated by $^{22}$Na radiation source and then moderated by tungsten to obtain slow positrons with energy ranging from 0.5 keV to 20.5 keV. The mean implantation depth of positron could be estimated with the following equation [16],

$$R = (A/\rho)E^n \tag{1}$$

in which $R$ is expressed in units of nanometer, $E$ (keV) is the incident positron energy, $\rho$ (g/cm$^3$) is the density of target material (19.35 g/cm$^3$ for tungsten), and $A$ and $n$ (*n-th* power) are constant parameters related to a given material. For tungsten, $A$ and $n$ are 40 and 1.6 respectively. In the PA-DBS measurement, diffusion effects was not considered. Two parameters, $S$ parameter and $W$ parameter, are obtained to characterize the vacancy-type defects of material. The $S$ parameter was defined as the ratio of counts in the central energy region around 511 keV (510.24–511.76 keV) to the total $\gamma$ photo counts around 504.2–517.8 keV. Correspondingly, the $W$ parameter was defined as the ratio of counts about the wing area (504.2–508.4 keV and 513.6–517.8 keV) to the total counts. Note that the $S$ parameter is sensitive to open volume defects, whereas the $W$ parameter is sensitive to the chemical surrounding of the annihilation site. In other words, a decrease of the $S$ parameter indicates a reduction of the density of vacancy-type defects. Besides, combination of the $S$ and $W$ parameters can be used to distinguish different kinds of vacancy-type defects. For a certain type of defect, the ($S$, $W$) plots would display on a line. Large deviation would indicate that positrons are annihilated in different kinds of vacancy-type defects [17]. Thus, with using PA-DBS test, the change of vacancy-type defects after pre-annealing and deuterium plasma exposure could be tracked. Taking into account the complex reactions between incident positrons and surface, annihilation data of positrons with energy below 2 keV is out of consideration in the work [18].

To determine the distribution of deuterium in the near surface, elastic recoil detective analysis (ERDA) was performed for the target with deuterium plasma exposure. The ERDA measurement was carried out in Fudan University, Shanghai, on the NEC 9SDH-2 × 3 MV pelletron tandem accelerator [19], with the base pressure of target chamber below $10^{-4}$ Pa. During the measurement, 4.5 MeV helium ion beam and 75° incident angle with respect to the sample surface normal were utilized, and a 28-μm thick Mylar foil was installed in front of the detector to absorb the scattered helium particles. The accurate determination of the dose was accomplished by placing another Au-Si surface barrier to measure the backscattering yield of the incident particles. The Au/Si surface barrier detectors for recoil and backscattering particles measurements were placed at the laboratory angles of 165°, 30° relative to the incident beam and at subtended solid angles of $1.87 \times 10^{-3}$ sr, $1.816 \times 10^{-3}$ sr, respectively. The typical current of the analyzing beam was 20 nA, and the dose for acquiring one energy spectrum was less than $1 \times 10^{12}\,\mathrm{cm}^{-2}$. The ERDA spectra was converted to a deuterium depth profile by the Alegria 1.0 codes [20]. The elastic recoil cross section used in the code for D($^4$He, D)$^4$He at a recoil angle of 30° over an incident helium energy range from 2.6 to 7.4 MeV can be found from our recent measurements [21].

Finally, thermal desorption spectroscopy (TDS) was carried out to determine the total deuterium retention. The target sample was heated up to 1273 K with a ramping rate of 1 K/s. The signal of mass 3 (HD) and mass 4 ($D_2$), as well as mass 18 ($H_2O$), mass19 (HDO) and mass 20 ($D_2O$), were recorded by a quadruple mass spectrometer (MKS Microvision Plus). Mass 4 signal was calibrated by a $D_2$ calibration leak and mass 3 signal was calibrated by averaging the calibration of mass 2 and mass 4 signals. Total deuterium retention is calculated by integrating the desorption spectra of mass 4 ($D_2$) and mass 3 (HD).

## 3. Results and discussions

### 3.1. Effect of the pre-annealing treatment

Fig. 1(a) and (b) shows the $S$ parameter and ($S$, $W$) parameter plots of samples with and without stress-relief pre-annealing, respectively. The $S$ parameter of the pre-annealed tungsten is significantly lower than the non-annealed one. This significant decrease reveals that the pre-annealing (1273 K for 1 h) leads to the removal of a significant fraction of the vacancy-type defects present in the non-annealed tungsten. In order to analyze the type change of vacancy defects, numerical fitting was performed for the ($S$, $W$) plots. As indicated in Fig. 1(b), the slopes of the ($S$, $W$) plots in the non-annealed and pre-annealed tungsten are −1.17 and −0.54, respectively. This slope change indicates that the Doppler broadening spectra of the pre-annealed tungsten becomes narrower and higher. That is, the annihilation environment of positrons becomes

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