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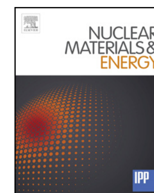

Study of the temperature-dependent nitrogen retention in tungsten surfaces using X-ray photoelectron spectroscopy

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ABSTRACT

Nitrogen is foreseen as seeding species in future magnetic confinement fusion reactors in order to reduce the power load from the plasma onto the divertor target tiles by radiative cooling. As a side effect it also gets implanted into the tungsten wall and forms tungsten nitrides (W_xN). The temperature-dependent W_xN formation was investigated in dedicated laboratory experiments. N ions of 300 eV kinetic energy were implanted into W samples under ultra-high vacuum conditions in the temperature range 300 K to 800 K. The N retention in W was monitored and quantitatively analysed by X-ray photoelectron spectroscopy (XPS). A method to calculate the statistical error of the measured data based on Bayesian statistics was developed. Argon sputter depth profiling was combined with XPS to measure N in W depth profiles which were compared with simulated N implantation profiles. Annealing of samples implanted with N at 300 K does not cause a loss of N up to 800 K. However, the retained N amount decreases linearly with increasing implantation temperature. It was found that this reduction is due to ion-irradiation-induced N release at elevated temperatures. Over the whole temperature range N diffusion into depth was not observed. N accumulation measurements showed no evidence for a phase transition in the W_xN layer. However, high resolution XPS measurements revealed that below 600 K a second photoelectron peak occurs in the N 1*s* signal which can be attributed to different local atomic arrangements of W_xN.

1. Introduction

In magnetically confined fusion plasmas, the magnetic field configuration must be chosen in a way that minimizes the interaction of the plasma with the surrounding vessel wall. In the divertor configuration the inner field lines are closed in order to confine the plasma, but the outermost magnetic field lines intersect the wall. They intentionally lead expelled plasma particles onto a small region of the vessel wall remote from the plasma, the divertor. The favoured material for the divertor tiles is tungsten (W), since its erosion and hydrogen retention is low [1]. The thermal loads onto the divertor in future fusion reactors can, however, easily exceed the power handling capabilities of tungsten [1,2]. For this reason, seeding of impurity gas in the divertor region is necessary. The seeded gas particles get ionised by the plasma particles, emit line radiation homogeneously in all directions and, therefore, reduce the power load onto the divertor target tiles. Nitrogen (N) as seeding species is a promising candidate [2]. However, the energetic nitrogen species can on the one hand increase the W sputtering of the chamber wall and on the other hand get implanted into the W tiles and form tungsten nitrides (W_xN). This might lead to a competition between W_xN formation and W erosion depending on the influxes and the impurity composition. For a better understanding of the W_xN formation and N retention in W under reactor relevant conditions, laboratory experiments employing X-ray photoelectron spectroscopy (XPS) were conducted. The obtained results are compared with findings from [3], [4] and [5], which are briefly described here: In [3] the interaction of pure N plasmas with magnetron-sputter-deposited W films was investigated. The W samples were exposed to N ions from a low-temperature plasma source with energies ranging from 20 eV to 500 eV at a temperature of about 350 K. It was found that N accumulation in W is limited at this temperature to the implantation zone. This is attributed to the low diffusivity of N in W. In an other experiment described in [3] bulk W samples were implanted with N in a plasma-immersion-ion-implantation device, applying a pulsed implantation voltage of 10 keV. The N content in W decreased with increasing implantation temperature, which ranged from 600 K to 750 K. XPS measurements of the W 4*f* signal of N-implanted W samples revealed that the W_xN peak is shifted to higher binding energies (BEs) for an implantation temperature of 800 K compared with the W_xN peak of N implantation at 300 K or 600 K. It was also found that the investigated photoelectron signal of the N 1*s* orbital consists of more than one peak, indicating different local atomic arrangements of the bound N. These observations are in

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agreement with thermodynamic calculations which predict a phase change of WN to W_2N at about 600 K [3]. On the other hand, temperature-dependent N desorption measurements of magnetron-sputtered W_xN films in [5] showed that W_xN decomposes only above 830K. The desorption spectrum consists of two release peaks with their maxima at 925 K and 960 K. In [4] W_xN layers were created by implanting N ions of 2.5 keV kinetic energy into W. The W_xN formation was followed by XPS. It was found that no measurable amount of N is lost from the surface while heating the W_xN sample up to 800 K. However, the N retention in the W sample decreased when N was implanted at 500 K and 800 K sample temperature.

The aim of this study is a more detailed evaluation of the N retention in W, i.e. the N accumulation in W and the N release from W_xN, in the temperature range 300 K to 800 K. Fluence series of N_2^+ ions impinging with 300 eV per atom on a W sample were acquired. The relative N concentration in the surface was determined by quantitative analysis of the measured XPS spectra. Additionally, a method based on Bayesian statistics was developed in order to calculate the statistical error of the measurements. Sputter depth profiles employing Ar ions of 1 keV kinetic energy were acquired and, together with SDTrimSP simulations, used to determine the N depth distributions.

2. Methods

2.1. Experimental procedure

The W samples employed in the experimental study were hot-rolled W plates with a purity of 99.97 mass percent. The samples are identical to those used in [4]. Before usage the W samples were ground, polished and annealed at 1200 K under vacuum conditions for two hours to guarantee a clean and smooth surface [6].

Sample preparation and analysis was performed in a commercial XPS device, a PHI ESCA 5600. The base pressure in the main vacuum chamber was below 1.5×10^{-10}mbar. The samples can be heated up to 900 K from the bottom side using a tantalum filament mounted on the specimen holder. A thermocouple is attached to the specimen holder next to the sample in order to measure and control the sample temperature. N was implanted in situ into the W samples using a Wien-filtered SPECS IQE 12/38 ion source. It is mounted at an angle of 45° to the sample surface. The ion source was operated with an acceleration voltage of 600 V and produced a beam of N_2^+ ions. Therefore, the energy per N atom was 300 eV. This energy was chosen since it is close to the predicted upper limit of the ion impact energy with which N ions from the edge plasma collide with the chamber wall [7]. Lower N ion energies could not be used, because space-charge effects become dominant, which lead to an increase of the ion beam diameter and to a strong reduction of the local ion flux. A second SPECS IQE 12/38 ion source without Wien mass filter producing Ar ions of 1 keV kinetic energy was used for cleaning the W surface from surface oxides and adsorbates prior to N implantation. The Ar ion beam was also applied after N implantation to stepwise remove the formed W_xN surfaces for sputter depth profiling. Alternating to the sputter intervals XPS spectra were acquired to determine the N content in W as a function of the accumulated Ar fluence. The sputter yield for Ar ions impinging at an angle of 40° to the surface is about 1.3 [8]. An Ar fluence of $1 \times 10^{20}\,\mathrm{m^{-2}}$, therefore, sputters approximately 2 nm of pure W. The ion fluence was determined by measuring the sample current. Previous experiments from [4] have shown that under the present implantation conditions secondary electrons account for about 10% of the measured current. This amount was subtracted from the sample current.

To attain homogeneous ion irradiation on the sample the N ion beam was rastered over an area of 5 mm × 5 mm and the Ar beam over 4.5 mm × 4.5 mm. Both ion beams have a Gaussian profile with a full width at half maximum (FWHM) of 0.8 mm for the N beam and 1.5 mm for the Ar beam. The actually irradiated area was determined to be 33 $\mathrm{mm^2}$ for the N and 36 $\mathrm{mm^2}$ for the Ar beam. This leads to a mean N ion flux of about $3.6 \times 10^{16}\,\mathrm{s^{-1}m^{-2}}$ and to a mean Ar flux of $9.5 \times 10^{16}\,\mathrm{s^{-1}m^{-2}}$ on the target.

During the acquisition of XPS spectra the ion bombardment was stopped, while the heating of the sample, if applied, was continued. Since residual gas may adsorb on the surface during acquisition, the acquisition time of the XPS spectra was chosen as short as possible. To still have a high count number, the acquisition was restricted to the N 1*s*, W 4*f*, carbon and oxygen photoelectron peaks. This led to an acquisition time of 5 to 15 min, depending on the quality of the N 1*s* photoelectron signal. The acquisition time was increased to 30 min for high-resolution spectra. Monochromatic X-rays were produced with an aluminium (Al) anode X-ray source plus monochromator. This radiation has an energy of 1486.7 eV and a FWHM of 0.50 eV. Due to technical problems the X-ray source with monochromator could not be used for all measurements. The Al K_α-line of a dual-anode source was used instead, which has a FWHM of 0.85 eV. A N implantation experiment at 300 K employing both sources showed that the use of the non-monochromated X-ray radiation does not change the intensity ratio of the measured N 1*s* to W 4*f* peaks.

The emerging photoelectrons entered the analyser with multichannel detector via an OmniFocus III lens system. The lens system decelerates the electrons to the pass energy of the analyser. The hemispherical energy analyser is positioned at 45° to the sample surface and at 90° to the monochromatic X-ray source. The angle between the analyser and the dual-anode X-ray source is 54.7°. The pass energy of the analyser was constant and chosen to 93.9 eV in order to have a high count rate. For high resolution measurements the pass energy was set to 11.75 eV with a reduction of the lens system's aperture from 1.1 mm to 0.6 mm.

2.2. Quantitative analysis of XPS spectra

Quantitative analysis of XPS spectra means to determine the depth-dependent particle density $n_A(z)$ of element A within the depth of three to five electron's inelastic mean free paths. The XPS signal is an exponentially weighted average over this depth [9]. The area I_A under the photoelectron peak of element A can be calculated to

$$I_A = \sigma_A\, L_A\, T(E)\, \Gamma_{\mathrm{phot}}\, t \int_0^\infty n_A(z) \exp\left(- \int_0^z \frac{1}{\lambda(z')\cos\alpha} \mathrm{d}z' \right) \mathrm{d}z, \tag{1}$$

with σ_A, the total cross section, L_A, the angular asymmetry of the studied orbital, $T(E)$, the transmission function of the analyser, which also depends on the photoelectron's energy E, Γ_{phot}, the incoming photon flux, t, the acquisition time, $\lambda(z')$, the electron's inelastic mean free path in the depth z', and α, the angle between detector and sample normal [4,10].

The background which was subtracted from each photoelectron peak consists of a constant part s^0 and a contribution which arises due to inelastic scattering of the photoelectrons. To account for the latter, the commonly used Shirley background was calculated [11]. If s_i is the actual photoelectron signal, i.e. the background subtracted signal of channel i, then the Shirley background of s_i is $k\sum_{j=1}^{i-1} s_j$ with the fit parameter $k \in [0, 1]$. The Shirley background was calculated for the measured N 1*s* and W 4*f* signals using the XPS data processing program MultiPak version 9.0. The integration limits were set to 393 eV and 405 eV for the N 1*s* peak and to 26 eV and 44 eV for the W 4*f* peak. To determine the N 1*s* to W 4*f* intensity ratio, the background-subtracted photoelectron peak signals were integrated over the full measured range and divided. The intensity ratio is a quantity which is independent of set-up-dependent factors as, e.g., the incoming photon flux. For comparison of the measured intensity ratios with simulations not the Shirley background, but the Tougaard background has to be calculated. The Tougaard background is based on a physical model employing a universal cross section for inelastic scattering instead of the fit parameter k [10]. According to [4] the calculated N 1*s* to W 4*f*

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