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Deuterium diffusion and retention in a tungsten–carbon multilayer system

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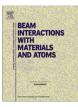[a] Max-Planck-Institut für Plasmaphysik, Boltzmannstr. 2, 85748 Garching, Germany
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ABSTRACT

A tungsten–carbon multilayer system deposited by magnetron sputtering was used as a model system to study deuterium diffusion in tungsten, carbon and related carbides. After deposition the as-deposited multilayer films were annealed at different temperatures to achieve different structures. The structural changes due to annealing were investigated by Rutherford backscattering spectrometry and X-ray diffraction. The results show that diffusion and interaction between tungsten and carbon sets in at 1150 K. Different types of tungsten carbides including WC and W_2C were formed during different heat treatments. Deuterium implantation experiments proved that deuterium diffusion in this multilayer system can be reduced substantially by formation of the tungsten carbide WC and can be almost completely suppressed by formation of the tungsten subcarbide W_2C.

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1. Introduction

In future nuclear fusion devices, such as ITER, the tritium inventory inside the vacuum vessel is one of the most important safety issues [1–5]. Due to its favourable physical properties, such as low erosion yield and high melting temperature, tungsten (W) is foreseen as plasma-facing material in the ITER divertor. Actually, a full tungsten inner wall and a full tungsten divertor have already been successful developed and tested in ASDEX Upgrade and JET, respectively [6–9]. However, until to now, only tungsten coatings were used as first-wall material in most of the so-called full-metal fusion devices, predominantly due to design limitations and cost concerns. The tungsten coatings used in these devices were deposited on graphite tiles [9]. Since first-wall materials will be subjected to intense fluxes of incident particles and thermal loading, compositional and structural changes have to be anticipated. Even in the all-tungsten ASDEX Upgrade the formation of carbon films with thickness up to 1 µm was observed. The carbon probably originated either from carbon remnants from previous campaigns, or from the bulk carbon tiles. Actually, impurities such as carbon, oxygen and nitrogen are difficult to completely remove in future fusion devices. If present, these impurities will inevitably be ionized and implanted into plasma-facing surfaces made of tungsten. There they may form mixed W:C materials which may

exhibit a different interaction behaviour with hydrogen isotopes from the boundary plasma. In particular D/T retention and hydrogen re-emission might be influenced. Consequently, the effect of changes in the microstructure within the layers as well as possible changes of the interfaces, e.g. by phase formation and interdiffusion, on fuel retention should be taken into account.

In this work, a tungsten–carbon multilayer structure deposited by magnetron sputtering was used as a model system to investigate deuterium diffusion in tungsten, carbon and related carbides. After sputter deposition the as-deposited multilayer films were annealed at different temperatures to establish different structures. The effects of these thermally induced structural changes on the deuterium diffusion and retention were investigated.

2. Experimental details

The tungsten–carbon multilayer structure was deposited onto single crystalline (100) silicon wafers using a commercial sputtering device (Discovery®18, Denton). This device comprises 3 independently controllable magnetron sputter sources. For the experiments reported here two of these sources were applied, one holding a graphite target and the other a tungsten target. The system was pumped down to a base pressure of less than 3×10^{-5} Pa and the deposition was performed in argon atmosphere at a working pressure of 5×10^{-1} Pa. A liquid N_2 cold trap was attached to the deposition chamber to reduce the water partial pressure. Amorphous carbon layers were deposited with 500 W rf

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power and tungsten layers using 300 W dc power. Prior to deposition the silicon substrates were etched by argon plasma using a bias voltage of -600 V for 2 min to remove the natural oxide layer. The deposition process of the tungsten–carbon multilayer structure was performed as following: At first a 1 μm thick tungsten film was deposited on the silicon substrate. Then two 230 nm thick amorphous carbon layers were deposited which were separated by a 250 nm thick tungsten layer. Finally, another 250 nm thick tungsten layer was deposited. The described W–C–W–C–W multilayer structure was used as model system in our experiments because a single W–C–W layer turned out to delaminate already after annealing at 900 K. In contrast the multilayer structure was stable up to the highest investigated annealing temperatures of 1200 K. In another deposition run a pure 2 μm thick tungsten film was also deposited as W reference applying the same deposition parameters. All samples were deposited on a whole 4 inch silicon wafer. After deposition they were cut to individual samples 10×10 mm^2 in size. A tactile profilometer (DEKTAK, Veeco) was applied to measure the film thickness by scanning the step height between coated and uncoated area (area covered during deposition by a thin kapton tape). In all cases no extra substrate bias and heating were applied during deposition. All the samples showed a smooth surface with RMS (root mean square) roughness below 2 nm measured by AFM, and no pinholes or cracks in the films were observed by SEM imaging before and after annealing. The bulk densities of pure W and C films deposited under identical sputtering parameters onto silicon wafers were determined by weight change and film thickness measurements. The values are 17.5 g/cm^3 for W and 1.6 g/cm^3 for C. For more details see Refs. [10,11].

To change the initial structure of the as-deposited tungsten–carbon multilayer, different annealing treatments were carried out in a vacuum oven (MOMO). MOMO has a base pressure of about 2×10^{-5} Pa and at the maximum annealing temperature of about 1250 K the working pressure increases to about 2×10^{-4} Pa. The temperature of the heated substrate holder can be increased from room temperature to 1250 K using a tungsten filament as heating element. Sample temperatures are measured by thermocouples attached to the surface of the sample holder.

Composition and crystallographic phases of the samples were investigated by Rutherford backscattering spectrometry (RBS) and X-ray diffraction (XRD), respectively. RBS was applied to measure the depth-resolved stoichiometry of the samples before and after heating treatment. A beam of 4.0 MeV ^{4}He was used at a scattering angle of 165°, and a charge of 15 μC was usually accumulated for one RBS spectrum. The depth resolution is good enough to clearly distinguish the carbon interlayers. The crystallographic phase formed in W films was determined by XRD (Seifert XRD 3003 PTS) using Cu Kα source (0.154 nm). Diffractograms were acquired from 20° to 90°.

Deuterium implantation was carried out in the laboratory plasma experiment PlaQ. A basic description of PlaQ is given in [12–14]. In short, PlaQ consists of a stainless steel chamber and is equipped with a remote electron cyclotron resonance (ECR) plasma source. Microwaves (2.45 GHz) are coupled into the vacuum vessel from the high B-field side through a waveguide terminated by a quartz window. The magnetic field is created by a single magnetic coil. To decouple the plasma from the substrate, the plasma is confined in a metallic cage 150 mm in height and 140 mm in diameter. Particles can leave the cage in an axial direction through a hole in the bottom plate with a diameter of 55 mm. A diverging plasma beam impinges perpendicularly onto the substrates which are located 100 mm below the cage exit. The energy of the ions impinging on the substrates can be varied by applying a dc or rf bias to the substrate electrode. In the experiments described here a dc bias was used. The sample holder and its support structure

are made of copper and a boron nitride insulator is used in order to maximize the heat conductivity between the sample and the heat sink. The temperature of the sample holder is stabilized using an open circuit thermostat with silicon oil. Sample temperatures are measured by a thermocouple attached to the sample holder and by an infrared camera observing the sample surface.

To ensure identical conditions in all implantation processes, the microwave output power for the ECR plasma was set to 144 W with a constant D$_2$ gas pressure prior to plasma ignition of 1 Pa (gas flow 50 sccm). At floating potential, the total deuteron flux in the form of ions is 5.6×10^{19} D m^{-2} s^{-1}, the flux consists dominantly of D$_3^+$ ions (97% of the impinging deuterons) with minor contributions of D$_2^+$ (2%) and D$^+$ (1%) [14]. The ion flux increases while the ion flux composition does not change with increasing substrate bias voltage [14]. In this article we refer to the energy per deuterium atom of the dominant molecular ion species as the ion energy. Most deuterium implantations described here were performed at a dc substrate bias of -100 V. This produces, together with the plasma potential (-15 V [14]), ions with an energy of about 115 eV corresponding to a mean energy of about 38 eV per deuteron for the dominant D$_3^+$ ions. The deuteron flux was 9×10^{19} D m^{-2} s^{-1} [14]. Some other experiments were carried out with a substrate bias voltage of -75 V corresponding to ions with energy of about 90 or 30 eV/D, respectively. The flux is approximately the same.

The amount of D retained in the samples was measured by nuclear reaction analysis (NRA) by means of the D(^{3}He,α)p nuclear reaction 2 month after implantation. The D concentration within the near-surface layer (at depths up to about 0.5 μm) was determined at a ^{3}He energy of 0.69 MeV by analyzing the emitted α particles with a small solid-angle surface barrier detector at the laboratory scattering angle of 102°. For determining the D concentration at larger depths, the energy of the analyzing beam of ^{3}He ions was varied from 0.69 to 2.4 MeV. The protons from the D(^{3}He,p)^{4}He nuclear reaction were counted using a proton detector placed at a scattering angle of 135°. In order to analyze the D concentration profile in the whole layer both SIMNRA [15] and NRADC [16,17] were used for the deconvolution of the proton yields measured at different ^{3}He ion energies. The total amount of D retention was finally determined by integrating the D profile over the measured depth.

3. Results and discussion

3.1. Structural changes due to annealing

All tungsten–carbon multilayer samples used in this work were produced in one batch. To achieve different structures as-deposited samples were annealed at different temperatures and annealing durations. Fig. 1 shows RBS spectra of the tungsten–carbon multilayer film after different heat treatments, in which the backscattering counts are plotted as a function of channel. The corresponding backscattering energy is shown on the top axis of the figure. All RBS spectra were measured after D implantation. The as-deposited tungsten–carbon multilayer (W–C) sample (Fig. 1a) shows a broad structure ranging from about 1700 to 3600 keV backscattering energy. This broad structure is due to backscattering from W atoms. The increasing trend towards lower backscattering energy is due to the increase of the scattering cross section with decreasing energy. The W backscattering signal is interrupted by two dips which correspond to the two carbon interlayers. Because the W concentration in the C layers is zero, the signal decreases to almost zero. The remaining signal in these regions is due to multiple scattering and/or broadening. The three tungsten layers are marked as W-1, W-2, and W-3 in Fig. 1a. The first (W-1) and second (W-2) tungsten