



Characterization of nano-structured W-, Ti-, V-, and Zr-doped carbon films

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ABSTRACT

Bonding structure of carbon and metal as well as nanostructural changes of metal-doped amorphous carbon films (a-C:Me) were investigated depending on metal type (W, Ti, V, and Zr), concentration (<25 at.%) and annealing temperature (<1300 K, except W: <2800 K). Pure C films exhibit ~2 nm distorted aromatic and graphene-like regions. Both increase in size with annealing. After deposition the metals have carbide-like bonding and are mainly distributed atomically disperse in an amorphous environment. Annealing leads to the formation of carbide crystallites (TiC, VC, ZrC, WC, W₂C, and WC_{1-x}) of several nanometers. The VC particles reach the largest size up to 1300 K. All metal dopings reduce the erosion rate against oxidation (except V) and hydrogen impact.

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1. Introduction

Metal-containing carbon films (a-C:Me and a-C:H:Me) are intensively studied regarding their various possible applications [1–21]. Their outstanding tribological and mechanical properties, especially wear resistance and hardness, pushed their research forward [2–11]. In recent years also their optical and electrical properties as well as their biocompatibility got more and more attention [11–21]. Detailed knowledge of the formation of their nanostructure is necessary for designing their properties for the different applications.

In the field of nuclear fusion, such metal-containing films appear as by-product due to the used mixture of plasma-facing materials (PFM) in existing and future fusion plasma devices [22–27]. The PFMs are eroded by intensive energetic particle and high power loads. The nowadays used and proposed PFMs for future devices are tungsten, carbon and beryllium.

The use of carbon as PFM has resulted to some breakthroughs in fusion plasma physics [28]. But its strong chemical reactivity with hydrogen leads to high erosion yields under hydrogen impact and to high hydrogen amounts in deposited films [29,30]. This leads to the safety issue of tritium inventory in future fusion plasma devices using the mixture of deuterium and tritium—the fuel for a fusion power plant. Therefore, it is required that the possibly eroded amount of carbon is minimized, e.g., by limiting the use of carbon or by reducing the erosion yield by doping graphite with metal carbides, as it is shown for TiC, ZrC or VC [31,32]. For trustable assessments of the tritium inventory, basic knowledge about the hydrogen retention behaviour in the used materials as well as in the deposited films is needed. To manage the tritium inventory, removal techniques of

tritium or even of the complete films, e.g., by oxidation, are considered [29,33,34].

In order to obtain basic knowledge about the mechanism of the reduced chemical erosion of doped graphite as well as the re-erosion of deposited mixed films in fusion plasma devices, magnetron sputtered a-C:Me films (Me: W, Ti, V, and Zr) with metal concentration between 0 and 25 at.% are investigated in detail as a model system over the last years leading to several publications [35–51].

This paper reviews and summarises the results of the detailed characterisation regarding the distribution of the metal atoms in the a-C:Me films, their clustering and phase formation due to annealing as well as the bonding situation in the carbon matrix. Furthermore, fusion relevant properties are studied, e.g., erosion and hydrogen retention in the films by hydrogen impact as well as their oxidation behaviour.

2. Film production and annealing

2.1. Film production

The studied a-C and a-C:Me films were produced by non-reactive multisource magnetron sputter deposition. Argon was used as sputtering gas with a working pressure of ~0.5 Pa resulting from controlled Ar influx of 20 sccm (base pressure $2-5 \times 10^{-5}$ Pa). A RF power of 500 W was applied to the graphite cathode, while the metal cathode was operated in DC mode with different powers to achieve a metal concentration ranging from 0 to 25 at.% metal in the films. Deposition rates of about 0.05 nm/s were reached. The specimens were not intentionally heated. Their temperature did not exceed 350 K during deposition. The specimen holder rotated with 10 rounds/min. All 10–30 specimens of each deposition run were placed on a circle to ensure equality of the deposited films. The specimens were cleaned by Ar plasma for a few minutes (100 W, 550–600 V). No bias was applied

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during film deposition. More details about the film deposition can be found in Ref. [38]. More than 100 different deposition runs were performed over the years.

Polished graphite plates and Si wafer pieces were usually used as substrate. For some special experiments glass, sapphire and SiC were required as substrate. All substrates were cleaned in ultrasonic bath of isopropanol. The films were deposited as single layer or as triple layers, sandwiching the metal-containing layer between two pure a-C layers in order to reduce surface and substrate effects.

2.2. Annealing of films

The annealing in vacuum up to 1300 K was performed in different furnaces with a base pressure better than 5×10^{-4} Pa. Annealing durations between 0.25 and 2 h were applied.

The annealing above 1300 K up to 2800 K was performed in a furnace with graphite interior under He or Ar atmosphere. The annealing temperature was held for 1 h. Only W-doped specimens were annealed above 1300 K until now.

For the oxidation experiments, the specimens were heated in air to 550, 600 and 650 K. Various oxidation durations between 0.25 h and 48 h were applied to the different specimens. For mass loss time series, the samples were removed from the furnace and cooled down to room temperature before further oxidized.

3. Applied characterisation techniques

3.1. Ion beam analysis: RBS and NRA

Rutherford backscattering spectrometry (RBS) measurements were performed at the tandem accelerator (High Voltage) facility, IPP, Garching. For depth resolved composition determination, usually 4 MeV ^4He backscattered by 165° were used [38,39]. Lateral homogeneity was controlled by analysing several spots of 1 mm² size on several specimens of the same deposition run. For better depth resolution just beneath the surface, lower energies down to 500 keV were used. For determination of total carbon loss, also 1.5 MeV protons were used. The deuterium retention was measured with an 800 keV ^3He beam performing nuclear reaction analysis (NRA) [49].

3.2. X-ray diffraction: XRD

Crystallographic phases and crystallite sizes were determined by XRD with Cu K α radiation. A parabolic multilayer mirror (W/Si) was used on the primary side to achieve a parallel beam. Most diffractograms were recorded at a grating angle of 1° to 5° [44,45]. Applying the Scherer formula after adequate peak deconvolution and fitting leads to the mean crystallite sizes [52].

3.3. Microscopy

The surface morphology of the film was examined with scanning electron microscopy (SEM) and atomic force microscopy (AFM) in contact and non-contact mode [39,43,45,46]. In order to investigate the build-up of the films, cross-sections and thin lamellas were prepared by simple breaking of the specimen or by focused ion beam (FIB) cross-sectioning. They were analysed with SEM as well as with conventional and scanning transmission electron microscopy (TEM and STEM) [45,51]. In addition, nanodiffraction was performed on selected specimens in STEM [52].

3.4. X-ray absorption fine structure measurements: XAFS

In order to get information about the local surrounding and order of the metal atoms and their bonding in the films, XAFS measurements at the K absorption edges of Ti, V, and Zr and the L1 and L3 edge of W were

performed at Hasylab (Hamburg) on beamline C and at the ESRF (Grenoble) on beamline ID26 [39,40,44,45]. To obtain the sp² carbon bonding content, the near edge structure of the carbon edge was investigated at the SRS Daresbury Laboratory on beamline 1.1 [45,47].

3.5. Raman spectroscopy

The sp² carbon bonds were investigated by Raman spectroscopy. The spectra were recorded between 900 and 1900 cm⁻¹ with a Renishaw 1000 microscope using an argon ion laser at 514.5 nm. The resulting peak structures known as D and G peak [53] were fitted by an asymmetrical line shape of Breit–Wigner–Fano type [45,48]. The interpretation of the D to G intensity ratio as well as the peak width and shift is accordingly to Ref. [53].

3.6. Deuterium exposure

The films were exposed to energetic hydrogen by a mass-separated, mono-energetic ion beam and by RF low temperature plasma [35,36,43]. The hydrogen isotope deuterium (D) was always used. The total erosion yield was determined by weight loss and by RBS measurements [37,41,42]. The time dependence of the yield was obtained from mass spectrometer data (ion source) and optical emission spectroscopy (RF plasma). In addition, the mass spectrometer data gave an indication for the chemical erosion of the carbon by deuterium, i.e., the formation of methane (CD₄) [42].

Furthermore, the retained deuterium in the films was determined with NRA in dependence on doping, pre-annealing and implantation temperature, and D fluence [49].

4. Characterisation results

4.1. Composition, thickness, morphology, adhesion and hardness

Metal concentrations of films in the range of 0–25 at.% are deposited. A slight increase of concentration with distance from substrate interface is observed [38]. The deposition is laterally homogenous, less than 5% variation. As impurities O and Ar are always present. The O concentration is normally below 1 at.%, while the Ar concentration of around 2 at.% is slightly varied by the dopant. The dopant cross-contamination from previous deposition is below 0.01 at.% at the interface substrate to coating.

The thickness of all films is between 0.1 and 4 μm , but the most films are about 1 μm thick. The thickness is obtained by profilometry on an artificial film edge of one specimen per deposition run, by microscopy on cross-sections, by weighing the specimens before and after film deposition and by RBS. The combination reveals reasonable density of around 10²³ at/m³ [38].

The appearance of the surface topography of all films after deposition is very similar. Fig. 1(a) shows the surface of a pure carbon film. Small, about 10 nm large structures are dominating the surface, while larger nearly circular structures (several 100 nm) are present. On Si wafer substrate, the latter ones cover less than 1% of the surface, but their density strongly increases on other substrate, i.e., graphite. In cross-sections they exhibit their columnar structure, Fig. 1(b). The roughness obtained from AFM for all initial films on Si is similar, too [39].

A simple scratch test with a needle exhibits good adhesion and high hardness of the films. No aging is observed for the most films, even after >5 years storage at air. For some films, the hardness is determined by nanoindentation to be ~14 GPa, while their elastic modulus is ~200 GPa [39]. Note that hydrogen exposure (see section 4.4) could soften the films drastically so that the contact mode in AFM fails to image the surface [43].

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