Journal of Nuclear Materials 145–147 (1987) 651–654
North-Holland, Amsterdam

CHARACTERIZATION OF FILMS DEPOSITED BY IN-SITU WALL CARBONIZATION IN TEXTOR

K. BESOCKE [1], G. FLENTJE [1], U. LITTMARK [1], H.G. ESSER [2], P. WIENHOLD [2] and J. WINTER [2]

[1] *Institut für Grenzflächenforschung und Vakuumphysik, KfA Jülich,* [2] *Institut für Plasmaphysik, KfA Jülich, Postfach 1913, D-5170 Jülich, Fed. Rep. Germany (Association Euratom–KfA)*

Key words: TEXTOR, carbon, depth profiles, wall conditioning

Carbonaceous films as produced for in-situ wall conditioning purposes in the TEXTOR tokamak have been investigated with SIMS (Secondary Ion Mass Spectroscopy) and AES (Auger Electron Spectroscopy). The measurements were supplemented by optical analyses and mechanical thickness measurements. The exposure to the in-situ carbonization process has been performed by placing the samples (Si, graphite, glassy carbon, Ni, Cr, and inconel) in liner positions. Independent of the substrate material the obtained films were homogeneous in thickness and composition. Depth profiles revealed impurity-free films with constant C/H ratio and slightly contaminated interfaces. The contaminants, i.e. metals (Fe, Ni, Cr) and O as detected on appropriate substrates, are supposed to be deposited due to sputtering of wall material during the initial period of the carbonization process. It is shown that the hydrogen in the carbon film is strongly bound. Exchange processes of the incorporated hydrogen during plasma discharges have been investigated. Blistering of the carbon films during noble gas ion bombardment have been observed.

1. Introduction

The influence of the wall material on the plasma characteristics of fusion devices has been discussed for a long time. Various wall materials and wall conditioning processes have been proposed and tested in order to improve plasma characteristics and the search for an ideal compromise between optimum performance, easy handling, and low price is still going on.

The recently introduced carbonization of the inner wall, first applied on TEXTOR by the plasma–surface interaction group in Jülich [1] yielded considerably improved tokamak performances regarding stable discharges and reduced plasma contamination. Since the carbonization process can be applied in-situ, and the deposited layers can also be easily removed, this technique is now applied and studied in other facilities like JET [2], ASDEX [3], and JIPPT-IIU [4]. The characterization of layers deposited by carbonization and the understanding of hydrogen exchange processes induced by plasma exposure is of interest not only for the fusion technology but also for the material research in respect of the outstanding mechanical and chemical properties of such carbonaceous films [5]. The amorphous structure of the films, high hardness and wear resistance, low friction and chemical stability favour the application in many fields of modern technology.

In fusion application the low Z property of the first wall has a significant aspect. Since the hydrogen content in those "carbon layers" approaches up to 50% the expression "carbon layer" sounds quite incorrect. Carbonizing the inner wall of a plasma discharge vessel means that the plasma interacts with a material with an atomic number somewhere between carbon 12 and hydrogen 1. Since the carbonization process covers the inner vessel wall completely and the deposited layer proved to be resistant to plasma discharges, an effective shielding of the plasma from the high Z metal wall is achieved.

The intention of this paper is to make an analysis of these carbon layers regarding chemical composition on the surface and in depth (depth profiles), interlayer formation, thickness, adhesion, response to noble gas ion bombardment, and interaction and exchange processes of contained hydrogen with the plasma.

Further investigations concerning thermal desorption and stability properties, chemical erosion due to interaction with atomic hydrogen, and absolute measurements of the hydrogen content are presented by Winter et al. [6] and Vietzke et al. [7].

2. Experimental

The samples were prepared from the following materials: Inconel representative for the liner material), Ni, and Cr (main components in stainless steel), graphite, glassy carbon, and silicon. The samples were polished and cleaned ultrasonically and placed in liner positions using the Stockholm-TEXTOR-probe [8] and the Swiss manipulator [9]. The samples were always partially covered with a stainless steel foil for reference purposes and film thickness measurements. The carbon deposition technique which is described in more detail elsewhere [1] applies RF assisted glow discharge in a mixture of hydrogen (deuterium) and methane at wall temperatures between 100 and 300°C. After the carbonization the samples were either removed immediately or subsequently exposed to tokamak discharges in order to study contamination deposits and hydrogen exchange processes. After removal from the

TEXTOR vessel the samples were transported in air to the analysis station "SEMIRAMIS" – a combined scanning SIMS, scanning AES apparatus – operating under UHV conditions. SIMS depth profiles were taken using a focused and mass separated beam of 5–12 keV positive Xe ions. AES surface analysis was made and depth profiles were measured by sputtering with 5 keV positive Ar ions. A quantitative evaluation of the element concentration was made using the method described in the Handbook of Auger Electron Spectroscopy [10].

The investigations were completed by measurements of surface roughness, layer thickness, and sputter crater depth using a Sloan Dektak II surface profile measuring system. In addition, an analysis with interference phase contrast microscopy was made in order to look for exfoliations and ion bombardment-induced damages.

3. Results

The visual appearance of the carbonized sample surface right after the removal from TEXTOR was in general homogeneous, uniform and independent of the used substrate material. A uniform interference color indicated transparent or at least partially transparent layers of constant thickness over the sample. The surface roughness was measured with the profiling stylus and turned out to be smooth within the detection limit of ± 100 Å. The film thickness was measured and the correlation between interference colors and layer thickness determined [11]. Dependent on substrate temperature and deposition parameters, the carbon films varied in thickness between 50 and 4000 Å. The surface contamination arising from the transfer of the samples in air was almost negligible. As seen from AES measurements (fig. 1) only small concentrations of oxygen (below 5%) can be attributed to adsorption from the atmosphere, demonstrating the inertness of these layers to gas adsorption. This behaviour is in agreement with former measurements on graphite samples [12]. However a strong influence of the air exposure on the film adherence properties was detected on some carbonized metal samples. Depending on the carbonization parameters the film adherence on metals varied from excellent to poor. On Si, graphite and glassy carbon, the adhesion proved to be always excellent. In some cases the carbon layers started to wrinkle and peel off after exposure to air. The peeling off started always on deposition edges and surface defects supporting the assumption of oxygen and water diffusion into the metal carbon interface.

The adhesion aspect is still under investigation and not understood. SIMS and AES investigations of the interlayer indicate that the formation of a metal carbide interlayer is probably essential for a good adhesion [5]. It seems that the surface roughness of the substrate material promotes good adhesion properties. Compared to the polished samples a defective adhesion was never observed on the rough walls of the metallic TEXTOR liner. The element distribution of the deposited layers were analyzed with AES. In fig. 1 the depth profile of an in-situ carbonized Si sample is shown. The normalized concentration of the detected elements are plotted versus the depth. Hydrogen is not detectable with AES and is therefore not considered in this graph. The film thickness was about 2400 Å. The depth profile reveals clean 100% graphitic carbon throughout the entire depth of the layer (notice the interrupted depth scale). Small traces of oxygen (below 5%) are accumulated on the first atomic layers of the surface due to air exposure of the samples. Within the interlayer small concentrations of oxygen and metallic deposits are found. The metallic depositions are attributed to sputter deposition of wall material during the initial period of the carbonization process. The amount of deposited metals (Ni, Cr, Fe) is in fair agreement with the expected sputtered particle flux during the build-up of the interface [1]. The

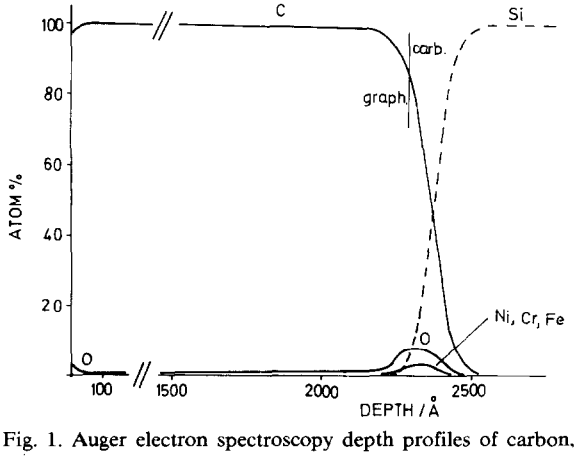

Fig. 1. Auger electron spectroscopy depth profiles of carbon, oxygen, Ni and Si of a carbonized Si sample, sputter-etched with 5 keV positive Ar ions.

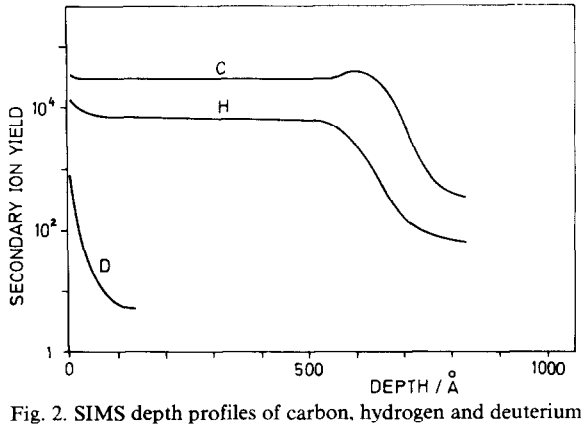

Fig. 2. SIMS depth profiles of carbon, hydrogen and deuterium of a carbonized inconel sample sputter-etched with 12 keV positive Xe ions. The carbonized sample was exposed to 35 tokamak discharges in deuterium.

AES carbon peak changes from the graphitic to the carbidic shape just at the beginning of the interface indicating carbide formation which is considered to be essential for a strong binding of the carbon layer.

The hydrogen distribution in the carbon layer was determined by SIMS depth profiling (fig. 2). In agreement with the AES measurements the profiles reveal a constant carbon concentration throughout the whole layer. Hydrogen is distributed homogeneously. The carbon to hydrogen ratio is constant within the entire layer. With Rutherford backscattering and related methods an absolute C/H ratio of 0.4 has been determined [1]. The stability of the hydrogen inside the carbon layer is of great interest for fusion application. Exchange processes with the plasma may influence the discharge properties and the layer composition. In order to study the effect of tokamak discharges on the hydrogen content of the carbon layers we exposed in-situ carbonized samples to 35 tokamak discharges in deuterium. Thereafter the samples were removed and analyzed with SIMS tracing C, H, and D. Apart from

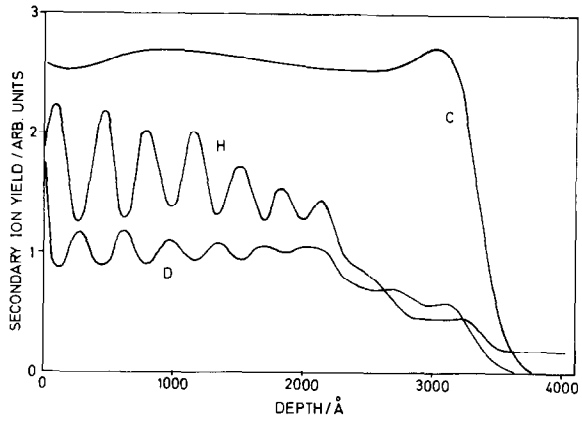

Fig. 3. SIMS depth profiles of carbon, hydrogen and deuterium of a carbonized Ni sample. The deposition was frequently altered by glow-discharge periods in deuterium.

the usual impurity enhancement of all SIMS signals in the first 10–50 Å the measurements reveal that deuterium is implanted in a narrow layer, 50–100 Å,

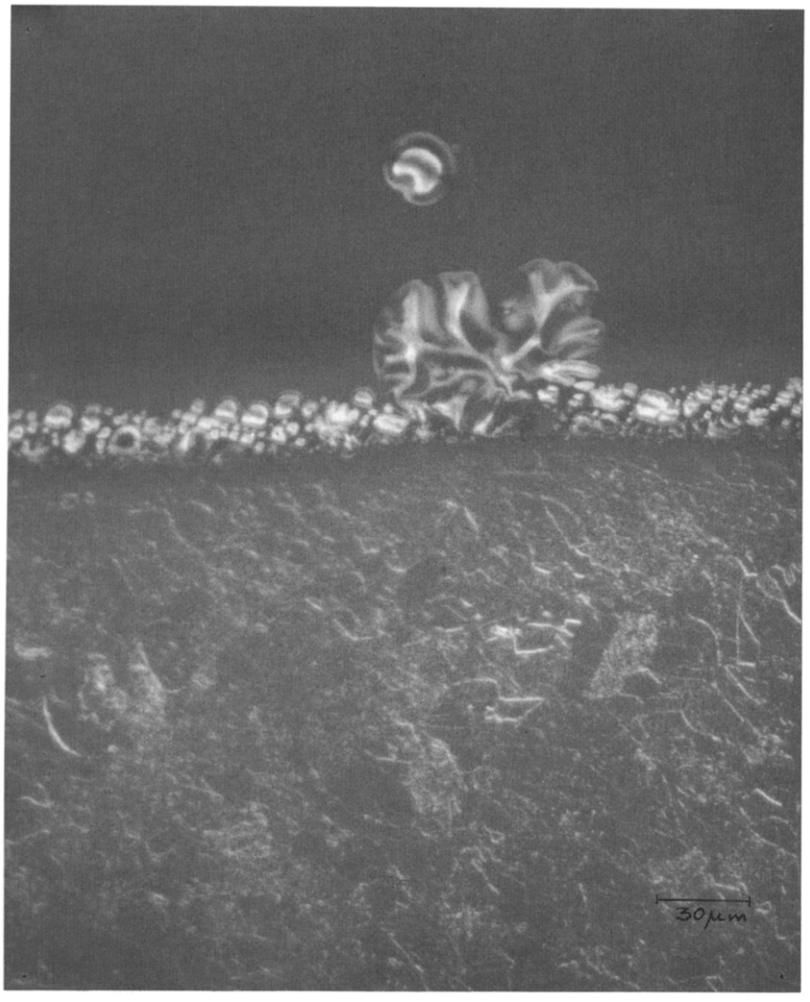

Fig. 4. Blister formation in the metal–carbon film interface due to Ar ion bombardment

below the surface, whereas the content of hydrogen remains unchanged throughout the C layer. The H plateau does not represent a saturation value but depends on the deposition parameters.

In a different experiment for H–D exchange studies we investigated a layer with a periodically changing H–D structure. The sample was prepared as follows: first carbon was deposited in a mixture of D and CH_4 at a temperature of 170°C. After 30 min, the deposition process was stopped by closing the CH_4 supply. Then followed a glow discharge in deuterium for another 30 min. Thereafter the deposition process started again. The change between deposition and glow discharge in deuterium was repeated 11 times. After cooling down the sample was removed and analyzed by SIMS and AES. Fig. 3 shows the SIMS depth profiles of the C, H, and D composition. The modulation of the H and D signal is well preserved and phase shifted by 180° indicating that even at temperatures of 170°C the H–D exchange is rather small.

The analysis of the hydrogen-exchange and diffusion processes resulting from the H and D concentration profiles in figs. 2 and 3 yields in first approximation a diffusion coefficient for H in these amorphous carbon layers of less than 10^{-17} cm^2/s. This rather small value (compared to the diffusion data of H in most metals) indicates a strong binding state and immobility of the hydrogen in the C layer. The decrease of the modulation of the H and D signal towards the film–substrate interface has to be attributed rather to interatomic mixing during sputter ion bombardment than to diffusion processes.

The strong decrease of the H and D signal close to the interface reveals new properties of amorphous carbon films concerning the influence of noble gas ion bombardment. Fig. 4 shows a microscopic picture of the carbon layer on a Ni substrate adjacent to a sputter crater. Inside the crater the covering carbon layer is etched away revealing the rough sputter etched structure of the polycrystalline Ni substrate. Outside the crater the predominantly smooth surface of the carbon coating is visible. Along the crater rim, however, a chain of circular blisters with a diameter below 10 μm is visible. Blisters start to form in the interlayer due to ion bombardment. The breakdown of the H and D signal in fig. 3 near the interface might be attributed to the exfoliation of these structures. This effect was observed only on carbonized metal samples during noble gas ion bombardment, but not on materials with good adhesion strength like Si, graphite, and glassy carbon.

The mechanism behind the blister formation is not clear. It could be caused by the collection of noble or hydrogen gas in bubbles with sufficiently high pressure to be self-bursting when the above-lying C layer gets thin, or the flaking-off could be triggered by the relief of the large compressive stresses known to be built into such H-containing hard carbon films. In both cases one would expect, as observed, that the exfoliation starts at weakly bonded regions like interfaces and grain boundaries. Blisters are only observed when the C layer becomes thin.

4. Conclusions

In-situ prepared carbonized wall materials were investigated with SIMS, AES, and microscopic methods. The carbon layers are homogeneous, smooth and free of contamination. The hydrogen concentration is high and constant throughout the layer. The exchange of hydrogen with the plasma during tokamak discharges is restricted to only a few atomic monolayers indicating a strong bond, and small effective mobility. Blistering and weakening of the adhesion strength due to noble gas ion bombardment was observed near the interface to the metal substrate.

We would like to thank U. Linke for sample preparation and G. Comsa for helpful discussion.

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