Thermal nanostructuring of metal-containing carbon films

and their nanoindentation testing

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Abstract

Annealing up to 1300 K of metal-doped (Ti, V, W, Zr) amorphous carbon layers with metal content up to 20 at% leads to carbide formation and grain growth (several nm). Composition, distribution and diffusion of the metal in the carbon were investigated by Rutherford backscattering spectroscopy (RBS), showing homogeneity laterally and in depth and diffusion in a neighbouring a-C film of less than 20 nm. The layer and surface morphology was examined by scanning electron microscopy (SEM), atomic force microscopy (AFM), and profilometry. X-ray absorption spectroscopic (XAS) analysis have shown how the local atomic environment of the metal and carbon was affected by thermal treatment up to 1300 K from amorphous non-metallic bonding to carbidic ordering. The grain sizes obtained from X-ray diffraction (XRD) varied from 2 nm for W to 9 nm for V after annealing at 1300 K. The experimental boundary conditions of film thickness (200-1800 nm) and substrate (Si, SiC, Cu) were varied to quantify the film hardness. The pure carbon films exhibited a hardness of ~13 GPa, which is only slightly increased up to ~14 GPa by the doping. No significant variation of hardness with dopant type (V, Zr), dopant concentration and annealing temperature (<1300 K) was observed.
1. Introduction

For metal-containing carbon films a wide range of application is envisaged, ranging from wear protection due to their tribological properties to electronics due to their electrical, optical, and magnetic properties. These properties are related to the nanocomposite structure of the films [1,2,3,4,5,6,7]. Our interest is based on having well-characterized materials for investigating the reduction of the chemical erosion of metal-doped carbon materials by hydrogen impact and elucidating underlying mechanisms [8,9,10]. The chemical erosion is the main drawback for using carbon materials in future fusion devices like the next step device called ITER [11], an international project. Nevertheless, carbon is envisaged - beside W and Be - as plasma-facing material (PFM) in this device [12,13]. Erosion of the materials leading to re-deposition of metal-containing carbon layers with unknown re-erosion properties.

By studying the chemical erosion behaviour under hydrogen impact of artificial produced, well characterised films as model material, two aims are followed: i) predicting the re-erosion behaviour of mixed layers and ii) selecting a dopant element with high reduction of erosion for the development of large-scale graphitic material as PFM.

To simulate the re-deposition process, magnetron sputter deposition was chosen. In this deposition process, the metal arrives dominantly as single atoms on the substrate followed by a possible clustering. Therefore, the films must be investigated on atomic and nanometer scale. In general, this type of characterisation is essential for getting an understanding of the behaviour of metal-containing carbon nanocomposites in their different applications. The films were characterized in respect to the composition, morphology, phase, and structural ordering by thermal treatment – all are necessary for understanding the chemical erosion by
hydrogen impact. In addition, the mechanical properties of the films were determined to correlate to other applications [1, 2].

The carbide forming metals, Ti, V, W, and Zr, were selected as dopants. The W-C system is of particular interest for fusion [12, 13], because both elements will be used as PFM. From the other three dopants, it is known that their carbides show a strong catalytic effect on the graphitisation in carbon-based materials [14,15].

The W-C system was quite recently investigated by several groups [2, 16,17,18,19] as well as the Ti-C system [20,21,22,23,24,25], but mainly for higher metal concentrations. The exception is for Ti-C system [24, 25]. The V-C [26] and Zr-C systems are less popular [3,18].

In this study doped carbon films with metal concentrations up to 20 at% have been produced by dual source magnetron sputter deposition, characterized in respect to various properties, and their effects of thermal annealing were investigated.

2. Experimental

2.1. Coating and specimen production

The metal-containing amorphous carbon films were produced by dual-source magnetron sputter deposition (Discovery 18, Denton Vacuum) using metal (Ti, V, W, Zr) and graphite targets. Different materials were used as substrates: polished P-type B-doped (100) and (111) silicon single crystals (CrysTec), polished poly crystals of SiC (ESK Ceramics GmbH & Co. KG), polished pyrolytic graphite (Grade HPG, Union Carbide), polished Cu (unspecified), and glass (microscope slides, Carl-Roth). All substrate plates were cleaned in an ultrasonic
bath of isopropanol, dried, and weighed. Immediately prior to deposition, the substrate and cathode materials were cleaned by Ar$^+$ plasma etching.

The metal concentration in the films was controlled by the DC power to the metal target, while the RC power of the graphite target was always 500 W. Films with metal concentrations between 0 and 20 at% were produced. A detailed determination of the rates and description of the experimental setup can be found in [27]. A film growth rate of about 0.05 nm/s was achieved. With a rotation speed of 10 turns per minute of the specimen holder, this growth rate corresponds to about 1 monolayer per turn. Argon was used as sputtering gas. The base pressure in the chamber was 2x10^{-5} Pa before deposition and 0.4 Pa during the deposition process controlled by the Ar flow rate (20 cm$^3$/min). The maximum temperature during deposition at the bottom plate of the specimen holder was 330 K. The specimen holder was not biased for all depositions.

To avoid substrate and surface effects during annealing (e.g. oxidation), triple layer films with a metal-containing layer sandwiched between two pure amorphous carbon (a-C) layers were deposited. Note, it is claimed that the layers in this study are a-C films without proofing if they are better described as tetrahedral amorphous carbon (ta-C) or diamond like carbon (DLC) films. The metal sputter source was switched on and off while carbon is continuously sputtered to deposit on the substrates ~300 nm thick a-C, then ~300 nm thick a-C:Me, and finally ~200 nm thick a-C films. The triple layers are ideal to study diffusion processes of the metal in the carbon without any influence of the surface or film-substrate interface. The protecting pure a-C layer on top does not cumber analyses by XRD, RBS, and XAS of the metal-containing layers.

For other investigations, like chemical erosion or hardness, films with a single metal-containing layer were produced with a variation in thickness between 0.1 – 2 µm and metal
concentrations of 0 – 20 at%. Also, multi layers consisting of alternating pure C (three) and pure metal (two) layers were produced with a total thickness of about 1.3 µm.

In each deposition run, about 30 specimens on different substrates were produced. The homogeneity of thickness in each run and, therefore, of concentration is better than 5%.

To investigate the thermal stability, specimens were heated in vacuum (10⁻⁵ Pa) at various temperatures up to 1300 K for up to 2 h, except the multi layers, which were annealed in He atmosphere at 1700 K for 2 h.

2.2 Characterization

A large variety of techniques were used to characterise the films.

Simple optical inspection was applied to check the film homogeneity and adhesion. The heights of edges generated by partially covering the substrate were quantified by profilometry (Alpha-Step 200, Tencor). Scanning electron microscopy, SEM (XL 30 ESEM, Philips), was performed on cross-sections of films to double-check the film thickness and homogeneity and to study its morphology. With atomic force microscopy, AFM (Rasterscope 4000, DME), the surface morphology was studied on the nanometre scale, which is important to estimate the reliability of low indentation depth (<100 nm). From AFM data as well as from profilometer scans, parameter Rₐ and R₉ were obtained to describe the surface roughness (according to [28]). The mass of the coatings was determined by weighing the specimens before and after the deposition with a micro-balance (Sartorius MC21S). The density of the films was obtained from specimen size, film thickness, and mass gain.
An even more powerful method to investigate the film thickness and its homogeneity is Rutherford backscattering spectrometry (RBS) [29]. Backscattered ions from a MeV ion beam were detected at a scattering angle of 165°, providing information about the depth distribution of the film components, including the impurities (very sensitive to heavy impurities in the light carbon). Mainly 0.8, 2, and 4 MeV $^4$He beams restricted to less than 1 mm$^2$ and several ten nA were used to investigated the films. The spectra were evaluated with the simulation program SIMNRA [30]. Under these experimental conditions, the depth resolution for diffusion was ~20 nm for both interfaces between metal-containing and the metal-free C layers of triple layer specimens.

The crystalline structure and the phases existing in the films were studied with X-ray diffraction, XRD (XRD-3003 PTS, Seifert). The phase determination was done by comparison with the JCPDS ICDD database. The crystallite size was calculated by using Scherrer’s formula [31] under the assumption that the width of the XRD peaks is dominated by the crystallite size.

Additional information on the local bonding of the dopant atoms was obtained from X-ray adsorption spectrometry, XAS, including both energy ranges of extended X-ray adsorption fine-structure spectrometry, EXAFS, and X-ray adsorption near-edge structure spectrometry, XANES. The XAS measurements around the metal $K$- or $L$-edge were performed using synchrotron radiation from the A1 and E4 beamline at HASYLAB, DESY, Hamburg. About 1 mm$^2$ was illuminated with the X-rays. The spectra were recorded using fluorescence yield of the respective $K$- and $L$-line. For comparison pure metal and carbides were used. The software ATHENA [32] was used for spectra normalization and background correction.

The hardness and the elastic modulus of the films were obtained from Nanoindentation (NanoTest 600, Nano Materials) measurements with a Berkovich diamond tip using loads
from 0.5 to 200 mN. The indentations were performed under load control with a rate between 0.05 and 4 mN/s depending on the chosen final indentation depth (30 to 1000 nm), e.g., for 50, 200, and 600 nm with 0.1, 0.5, and 2 mN/s, respectively. The maximal load was hold for 30 s. For each indentation depth, 10 to 40 indents were performed with a lateral spacing of 25 µm. Each depth-displacement curve was individually analysed and the values given in the paper are the average values. For calibrating the nanoindenter, quartz was used for the indenter area function and machine compliance calibration. The data evaluation followed, in general, to Oliver/Pharr [33], except that no cyclic loading-unloading was performed. Taken the critical review of Fischer-Cripps [34] into account, another function was used for calibrating the indenter area (Polynom of 5th order). The geometric constant \( \varepsilon \) of 0.72 was used. Pile-up was observed, but does not impact in the analysis [34]. Low creep was observed, but neglected in the analysis [33]. To obtain the elastic modulus of the films, the elastic modulus and poisson’s ratio of diamond and the poisson’s ratio of the films were needed [33, 34]. The values 1141 GPa, 0.07, and 0.02 were used, respectively.

3. Results and Discussion

3.1 Composition and morphology

Fig. 1 shows a RBS spectrum typical to obtain the composition through the layer together with the impurity content. The backscattered energy is non-linearly connected with depth scale, which starts from the surface for each element at a specific backscattered energy. The surface and the interface lead to the edges in the spectrum. Signals generated by O, Ar, and W atoms are clearly visible in the film on graphite substrate. The contamination with metals (here W) is untypical. The thickness is given in at/m², the natural unit of RBS. A very small
decrease in dopant concentration with the distance from the surface was observed by simulating the spectrum of the film [30]. The concentration in more than 90% of the layer thickness was 18 at% V with 1.5 at% O. Comparing the spectra from the specimens with Si and graphite substrate, it could be noted that (i) the layers are equal in thickness and composition, i.e., indication for homogeneous film, (ii) the signals from the Si substrate overlap with the oxygen signal, i.e., destroy the possibility to obtain the oxygen content, and (iii) more Ar is implanted in the graphite than in the Si substrate. This Ar content was released at least by annealing to 1100 K.

In Fig. 2 the triple layer structure is clearly visible. In case of V-doping, the columnar growth of the carbon seem not to be affected by implementing it in the continuous growth; in the case of Zr (not shown), strong hints exist that Zr changes the growth. But further studies have to be performed before drawing final conclusions. Also visible in Fig. 2 is the surface topography. To be able to quantify the height of the structures on the surface, AFM was applied. In Fig. 3 the surface of the pure Si and graphite substrate and with V-containing coatings are shown. Clearly, the roughness of the graphite induces the roughness in the film surface. In the Si case, the roughness of the substrate can be neglected and only then the observed roughness in Fig. 3, lower left, can be attributed to the layer. Fig. 4 summarizes the roughness of different films on different substrates, showing again that for all substrates except Si, the surface roughness is dominated by the roughness of the substrate polishing. In addition, it can be concluded for the films on Si that the roughness induced by the coating itself, does not saturate. It still increases about linearly with layer thickness.

Annealing to 1300 K did not affect the appearance of the surface, neither the distribution of metals and carbon nor the surface roughness, e.g., the triple layer structure was unchanged, implying that the movement of all four metals in the carbon was less than 20 nm (resolution...
limit). The only significant change was the release of the Ar. The diffusion could be strongly increased as indicated by measurements on metal-carbon multi layer annealed at 1700 K (see also XRD results).

3.2 Crystallinity and local bonding

In contrast to the film composition and morphology, the crystallinity and the local bonding was strongly affected by thermal annealing. Fig. 5 shows the change with annealing temperature in the XRD pattern of V-containing and Ti-containing carbon films, starting from the absence of any peak from the as-deposited film indicating that V and Ti are in the films in amorphous state. With annealing temperature, the characteristic XRD peaks for nearly stoichiometric VC and TiC grow in intensity and narrow down. Fig. 6 summarizes the XRD patterns for V, Zr, and W of as-deposited and 1100 K annealed single layer films on graphite. For comparison, the XRD patterns of the metal-carbon multilayer annealed to 1700 K and of the pure graphite substrate are inserted. The observed phases for these three dopants are in agreement with the published phase diagrams [35]. Clearly, Ti, V, and Zr behave analogous—amorphously deposition and formation of carbide crystallites due to annealing. The size of nanocrystallites is most easy to increase for V and less easy for Ti.

In contrast, the as-deposited W-containing films show already crystallites. The diffraction peaks do not change significantly after annealing to 1300 K. The peak width stays constant, corresponding to less than 2 nm, and only the intensity increases. The phase of the tungsten is not clearly distinguished. The W2C phase looks slightly preferred. Higher annealing temperature drives the W in WC. Also Schiffmann et al. [16] observed 2 nm tungsten carbide particles in their films.
No hint of a crystalline C phase was found on silicon substrates, meaning also that the C matrix was amorphous up to 1300 K. Small graphitic regions may exist as observed in transmission electron microscopy (TEM) studies for several other metals including Ti [22].

Fig. 7 summarizes normalized XAS spectra for the four dopants of as-deposited specimens and after annealing at 1100 K. For comparison, spectra from the metals and carbides are given, too. Again, Ti, V, and Zr behave similar in the films. The EXAFS modulations above the absorption edges are only weak for the as-deposited specimen and clearly pronounced after annealing, comparable to those of the carbides and totally different to those of the metals. By taking notice only of the pre-edge peak and the exact edge position (XANES), the metal atoms in the as-deposited layer are already in bonding configuration like in the carbides. The nearly missing of modulations in the as-deposited layer hints to an amorphous, disordered surrounding for the metal.

Again, W behaves differently. Modulations farer above the absorption edge are already present in as-deposited films. The changes in the spectra due to annealing are not strongly pronounced like for the three other dopants. The modulations are still not as strong as for carbide W, but already positions in energy are the same, i.e., the signature of the carbide is present. Only a qualitative comparison of the spectra is not sufficient to distinguish between $W_2C$ and WC phases. The high peak at the edge is the so called “white line”, a dominant feature of transition-metal $L_3$ absorption edges.

The following picture for the formation of the nanostructure can be drawn. From the thermodynamics of the systems, it is expected that metals react with carbon directly to form carbide phase, which is indicated by the edge position in XANES data. The order is still low to produce modulations, except for W. With increasing temperature the order increases, but still crystallites are very small ($< 1$ nm); they enlarge using higher annealing temperatures.
(~1000 K). Some diffusion is present, which decreases from V over Zr to Ti. It is sufficient to produce particle of around 5 nm at 1100 K.

For W the picture is different. During the deposition a process exists which enlarge the mobility to create already small agglomeration. Perhaps W atoms attract each other and, therefore, more W\textsubscript{2}C-like structure is formed. Then with increasing temperature up to 1300 K, the order increases only slightly and these temperatures are not sufficient to switch on the diffusion. It is still negligible. Higher temperatures will be necessary to induce the growth of crystallites.

This picture could only hold, if at least the main part of the metals is represented by the observed XRD peaks. Parts of dopant, which are still not ordered to crystallites larger than 1 nm are not detected by XRD. From the XAS, it is determined that the metals are in carbidic bonding, because this method “sees” all metal atoms in the investigated volume, but not their size. Extended TEM investigations should allow quantifying the part of metal present in the crystallite and with grazing incident small angle X-ray scattering (GISAXS) the grain size distribution could be measured.

### 3.3. Indentation testing

**Fig. 8** shows a typical load-displacement curve of a 19 at% V-doped C single layer film on SiC and Cu. The maximal indentation depth of 200 nm corresponds to 14% of the film thickness (1440 nm) and is definitely too high to be free of substrate influence, indicated by the differences in the curves. Following the argumentation of Fischer-Cripps [34], indentations over a larger range of maximal indentation depth and on a variation of film thickness were performed. The hardness and elastic modulus for a thick pure C film on SiC...
and 19 at% V-doped C single layer films on SiC and Cu with two film thicknesses of 520 and 1440 nm, are displayed in Fig. 9. The hardness of the thick films on SiC is constant over the full displayed range of indentation depth and could be assign to be the hardness of the pure C and the doped film, ~13 GPa and ~14 GPa, respectively. On Cu, nearly the same value is only obtained to an indentation depth of about 200 nm. Also for the thinner coating on SiC, the substrate influences significantly the hardness above an indentation depth of 200 nm. The variation in the load-displacement curves in Fig. 8 is mainly due to the substrate influence on the elastic behaviour, which is visible in the elastic modulus data of these specimens given in Fig. 9. Even for the thick film on SiC no constant modulus is found, showing the complications of determining mechanical data from thin films [34, 36,37,38,39,40].

The most reliable data could only be obtained from films of more than 1μm in thickness. For pure C films a value of 13 GPa was determined, which was only slightly lower than all doped ones. No significant changes in hardness by varying the dopant type and concentration and by annealing the films were observed as well as a strong increase by annealing can be excluded. The same is true for the elastic modulus.

4. Conclusion

Transition metal doped amorphous carbon films produced by magnetron sputter deposition exhibit a nanostructuring by annealing. The systems, carbon plus around 10 at% of Ti, V, W, or Zr, were investigated by IBA, XRD, XAS, and nanoindentation. Carbides are formed, and the crystallite size could be changed by varying annealing temperature and time. In the as-deposited doped layers, Ti, V, and Zr have an amorphous, disordered surrounding which already starts to order at annealing temperatures below 1000 K while W create already small
crystallites (~2 nm) during deposition. Correlated to that growing of the nanoscopic carbide crystallites, the metal atoms have an certain mobility in the carbon matrix, increasing from W over Ti and Zr to V. Nevertheless, no diffusion of the metals into the pure a-C layers over distances larger than 20 nm is observed. The phases for Ti, V, and Zr are the predicted ones of carbon-poor TiC, VC, and ZrC, respectively. Tungsten-doping behave unexpected, even if a similar unexpected behaviour was observed previously in photoelectron spectroscopy (XPS) studies on annealed C layers on metallic tungsten [41]: W_2C was observed between 1000 and 1300 K. No clear conclusion can be drawn from this.

The findings about the mobility are relevant for the understanding of the catalytic effect of these transition metals on the graphitization of carbon. This catalytic effect is explained by the mobility of carbide through carbon matrix [14]. Graphitisation is usually performed at higher temperatures than those used in this study, but it could already start at those temperatures [22]. Tungsten shows the lowest catalytic effect on graphitization of carbon doped with micrometer-sized carbide grains, which could be correlated with possible formation of W_2C or the lowest diffusion [15].

The effect of the doping and of annealing on the hardness and the elastic modulus is small. It could be speculated that the amount of nanoparticles is too low, to have a strong effect on the hardness.

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**Figure captions:**

Fig 1: RBS spectra of a V-containing carbon single layer on graphite and on Si (a-C:V). Impurities are visible, like the typical increased Ar in the substrate surface and oxygen. Unusual is the presence of W and its peak on the interface. The signals of the impurities are magnified by a factor of 40 in the bottom part. The layer thickness and composition used for the simulated spectrum (lines) [30] are 8.6x10^{22} at/m^2 containing 18 at% V, 1.5 at% O, <1% Argon, and <0.01% W followed by 0.2x10^{22} at/m^2 close to the Si substrate with 10 at% V, 2.5% Ar, and 0.1% W.

Fig 2: SEM cross-section micrograph of an a-C:V triple layer (a-C/a-C:V/a-C) on graphite. The a-C:V layer contains 13 at% of V.

Fig 3: AFM images of the pure Si (upper left) and graphite substrate (upper right) and, respectively, with a 1870 nm 7.5 at% V containing a-C film (lower left) and a 1440 nm 19 at% V containing a-C film (lower right). The grey/colour scale for the two left images and for the two right images are about the same with a maximum of 30 and 125 nm, respectively. The area of the images is 1 × 1.1 µm^2 for the pure Si and 4.1 × 4.4 µm^2 for the three other ones. In addition, an indentation in the pure Si is shown.

Fig 4: The R_a value obtained from AFM images for pure a-C, a-C:V, and a-C:Zr single films on Si substrate (large diamonds, left y-axis) from an analysed area of ~18 µm^2. With ten times smaller y-axis, R_a value obtained from AFM images (Si, C) and profilometry (SiC, Cu) for films on various substrates (small symbols, right y-axis) are implemented, too.
Fig. 5: XRD patterns of 13 at% V-doped and 8.5 at% Ti-doped triple layer films on graphite: as-deposited and after annealing to 1100 and 1300 K for 2 h. The patterns are vertical shifted for better visibility. Card numbers from ICDD and diffraction peak positions are labelled. The crystallite size for the VC and TiC calculated by Scherrer’s formula from the peak width are tabulated behind the preparation conditions, respectively.

Fig. 6: XRD patterns of doped single layer as-deposited and after annealing at 1100 K for 15 minute containing 18 at% V (top), 15 at% Zr (middle), and 15 at% W (bottom). For comparison, patterns of metal-carbon multi layers heated to 1700 K and for the pure graphite substrate were added. The peak positions for the expected carbides are given (ICDD number labelled). The patterns are vertical shifted for better visibility.

Fig. 7: Four XAS spectra for each dopant, Ti, V, W, and Zr: (1) triple layer film as-deposited, (2) after annealing at 1100 K for 2h, (3) carbide, and (4) metal. The spectra are vertical shifted for better visibility.

Fig. 8: Typical load-displacement curves of a 1440 nm thick 19 at% V-doped C film on SiC and Cu.

Fig 9: Indentation hardness and elastic modulus versus indentation depth of 19 at% V-doped C films.
References:


Figure: 18 at% V-doped C layer

- as-deposited
- simulated on C
- as-deposited
- simulated on Si

C$_{\text{surface}}$, Si$_{\text{interface}}$, V$_{\text{interface}}$, V$_{\text{surface}}$, O$_{\text{surface}}$, Ar$_{\text{interface}}$, W$_{\text{interface}}$

4 MeV $^4$He, 165°, x 40

Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6

Intensity (a.u.)

Scattering angle

0 graphite substrate
3 multi layer, 1700 K, 2 h

single layer
2 1100 K, 0.25 h
1 as-deposit

V$_8$C$_7$
35-786

V

ZrC
32-1381

Zr

WC
25-1047

W$_2$C
35-776

W

Cu K$_\alpha$, fixed incident angle: 2°
Fig. 7 (two column figure)
Fig. 8

19 at% V doped C film, 1440 nm

Load (mN)

Indentation depth (nm)

30 s hold time

loading: +0.5 nm/s

unloading: -0.5 nm/s

on SiC

on Cu
Substrate
SiC: 34 GPa, Cu: 8 GPa

Substrate
SiC: 410 GPa, Cu: 110 GPa


c- C film

a-C:V, 19 at% a-C:V film

Indentation hardness (GPa)

Indentation depth (nm)

Fig. 9
Correction of errors:

Fig. 5: The ICCD no. for TiC is wrong. It must be "32-1383" instead of "32-183"

Fig. 6: The ICCD no. for ZrC is wrong. It must be "35-784" instead of "32-1381"