

Thermal induced structural changes of a-C and a-C:Ti films analyzed by NEXAFS and XPS

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Abstract. Carbon *K*-edge NEXAFS and XPS measurements were performed on a-C and 7.5 at% a-C:Ti films annealed in-situ up to 1300 K. During annealing of a-C, the sp^2 content increased from ~80 to ~95 %, associated with the development of a peak at 285.4 eV in the NEXAFS spectrum, which is assigned to sp^2 carbon atoms in a “graphite-like” local order. After annealing of the a-C:Ti film to 470 K, an additional peak shows up, indicating the creation of carbonyl functionalities. This is explained by the increased reactivity of the carbon phase by Ti-doping. Oxygen contents of ~30 at% are determined by XPS up to 900 K. For a-C at temperatures >420 K, the C 1s peak width (FWHM) decreased continuously with annealing temperature, which is not the case for a-C:Ti. This is explained by oxidised carbon and by Ti diffusion during carbide crystallite formation, partly disturbing the ordering of the carbon phase.

1. Introduction

In the next-step fusion experiment ITER, it is planned to use metals (Be, W) and carbon - in form of CFC - as plasma-facing materials (PFM). Parallel erosion of carbon and metallic PFM during operation will lead to the deposition of metal-containing hydrocarbon layers (mixed materials) in the reactor [1]. The erosion behaviour of such layers is simulated in well-defined deuterium ion beam experiments, using metal-doped amorphous carbon films (a-C:Me) as a model material [2]. Beneath W, also Ti, V and Zr are used as dopants due to the potential use of the respective carbides in doped graphites as PFM [3]. Even small amounts of metals reduce the deuterium erosion yield strongly.

For a better evaluation of the underlying processes, it is important to characterize the a-C:Me film structure in detail. Recent investigations included EXAFS and XRD measurements to follow the formation of nanoscopic carbide crystallites after annealing [4, 5].

X-ray photoemission spectroscopy (XPS) and near edge x-ray absorption fine structure spectroscopy (NEXAFS) are common tools to investigate the structure of carbonaceous materials. Since XPS is available in many laboratories, it is often used to determine the elemental composition, and analysis of the C 1s signal by peak-fitting procedures is generally performed to gain information about the carbon structure (ordering, hybridization). Nevertheless, various methods to fit the C 1s peak are applied, and assignment to different carbon-bonding states is challenging. NEXAFS probes the density of unoccupied states and is widely used to study the bonding structure of carbon materials, e.g. sp^2/sp^3 , since it is possible to quantify sp^2 hybridized carbon atoms. Quantification of the sp^2 content is often done with the analog technique EELS in a TEM. In this paper we report about carbon *K*-edge NEXAFS and XPS measurements on in-situ annealed a-C and a-C:Ti films.

2. Experimental

Pure a-C and 7.5 at% a-C:Ti films ($\sim 1 \mu\text{m}$) were deposited on polished silicon wafers (100) by dual source magnetron sputter deposition using a titanium and a graphite target and Ar as sputtering gas. No external substrate bias voltage was applied and the sample temperature did not exceed 350 K during deposition. Details of the deposition procedure can be found in [6]. Ti is mainly present atomically dispersed in amorphous environment, forming carbide crystallites after annealing to $\geq 900 \text{ K}$ [4].

Film composition was determined depth-resolved by Rutherford backscattering spectroscopy (RBS) at a scattering angle of 165° using 4 MeV He^+ .

The NEXAFS and XPS experiments were done at the synchrotron radiation facility Daresbury, beamline 1.1. In-situ annealing at 470 (a-C: 420), 700, 900, 1100 and 1300 K was performed in UHV by resistive heating for 15 minutes at the desired temperature. An IR-pyrometer was used for temperature control; NEXAFS and XPS spectra were recorded after cooling down near room temperature.

Carbon *K*-edge NEXAFS spectra were recorded in total electron yield (TEY) mode by collecting the sample drain current (*I*) and normalized by simultaneously recording the beam current using a gold grid with 85 % transmission (I_0). To exclude contributions from adsorbed hydrocarbons on the gold grid and beamline optics, all spectra (I/I_0) were normalized by the obtained NEXAFS-spectrum of a carbon free silicon wafer, which was previously annealed to 1450 K for 30 minutes. The NEXAFS measurements were performed in “magic angle” configuration with $\sim 54.7^\circ$ between sample normal and beam to exclude any effects related to the polarization of the synchrotron light [7]. All spectra shown in figure 1 and 2 are normalized to unity at 320 eV. The sp^2 content of the a-C film was quantified by integration of the π^* peak (282 - 286.5 eV), normalization to the area between 290.5 - 305 eV and comparison with the integration result of graphite (100 % sp^2).

XPS C 1s spectra were recorded at 400 eV photon energy using 0.05 eV step width, 20 eV pass energy and a dwell time of 0.4 s. Survey spectra, O 1s and Ti 2p spectra were measured with 600 eV photons, a stepwidth of 0.1 eV (survey: 0.5 eV) and a pass energy of 20 eV.

The NEXAFS information depth is roughly 5-8 nm, XPS is more surface sensitive ($\sim 2 \text{ nm}$).

3. Results and Discussion

Figure 1a shows NEXAFS spectra of an annealing series for the **pure a-C** sample. The first feature of the carbon near edge structure is the π^* resonance at 285 eV, due to the transition of a C 1s electron into the antibonding π^* orbital of sp^2 hybridized carbon atoms (C=C). The increase in absorption starting at 292 eV covers $1s \rightarrow \sigma^*$ transitions, occurring for σ bonds in both sp^2 and sp^3 hybridized carbon (C=C and C-C bonds). Annealing leads to the formation of a significant fine structure in the σ^* region, which is an indication of increased local order due to clustering of the sp^2 phase in “graphite-like” regions. The broad peak occurring with increasing intensity at 330 eV is due to a multi electron transition and is related to developing microscopic short range-order beyond the next neighboring carbon atoms [8]. The thermal induced changes of the π^* resonance are depicted magnified in figure 1b.

Annealing to 420 K reduces adsorbed or chemisorbed surface contaminations due to film storage in air for several months. Carboxylic carbon species (COOH) have their resonance energies at $\sim 288.7 \text{ eV}$ [9] and decompose at relatively low temperatures ($>400 \text{ K}$) [10]. The $\sigma^*_{\text{C-H}}$ transition resulting from adsorbed hydrocarbons could also contribute to intensity at around 289 eV [11]. With increasing annealing temperature, the π^* peak becomes more asymmetric, a result of increasing intensity at 285.5 eV. We attribute this to the existence of different π^* states occurring from sp^2 bonded carbon atoms in different local order. The increase of intensity at 285.5 eV with annealing suggests an increasing fraction of sp^2 carbon atoms which are well ordered in respect to their next neighbours. Since the peak maximum of graphite is located at 285.4 eV, we label this *ordered* state π^*_o . A sp^2 carbon bonding state with a more *disordered* local environment should be responsible for the resonance around 284.7 eV, π^*_d . During annealing, the sp^2 content increases from $\sim 80\%$ (as-deposited) to $\sim 95\%$ (1300 K).

Earlier investigations on the temperature-induced evolution of the C=C π^* feature in a-C films distinguish at least 2 different underlying bonding states and also found increasing intensity with annealing temperature between 285 and 285.5 eV [12, 13]. They attribute π^* intensity $<285 \text{ eV}$ to carbon

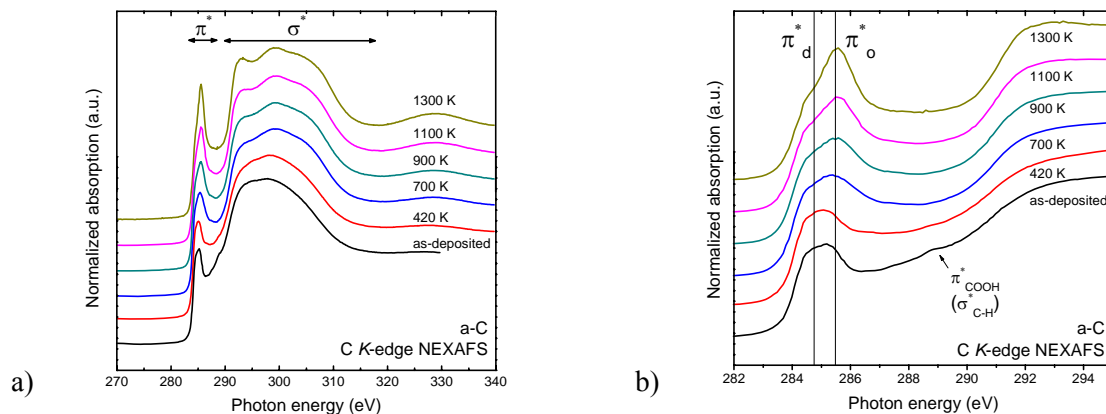


Figure 1. a) Normalized C *K*-edge NEXAFS spectra of the pure a-C film, as-deposited and annealed up to 1300 K. b) Enlarged region between 281 and 295 eV.

atoms in sp^2 sites with defects [12] or to carbon in chain-like structures or single C=C pairs [13]. Intensity in the π^* resonance between 285 and 285.5 eV is attributed to the promotion of sp^2 carbon atoms in disordered "graphite-like" environments like aromatic rings.

Figure 2 shows the evolving NEXAFS spectra of the **7.5 at% doped a-C:Ti** film annealed up to 1300 K. Pure TiC has two sharp peaks at ~ 285.5 eV and 289 eV, due to transition of a C 1s electron into Ti-C hybrid orbitals, and a shoulder at ~ 282.5 eV [14]. Overlapping of a-C and TiC resonances at ~ 285 eV precludes detailed π^* analysis and sp^2 quantification in a-C:Ti.

The region between 284 and 286 eV shows a main signal at 284.6 with a shoulder at 285.4 eV for the as-deposited sample. Annealing makes the signal more featureless. At 1100 K the shoulder at ~ 282.5 eV indicates carbide formation. The total intensity and shape of the NEXAFS spectra for 1100 and 1300 K has to be taken with care, due to the influence of the normalization procedure (at 320 eV), which is problematic because the carbide signature alters the region > 295 eV strongly.

The as-deposited a-C:Ti sample shows a more pronounced peak at ~ 288.7 eV (COOH) compared to a-C. Annealing to 470 eV reduces this peak slightly, but a new peak occurs at 286.5 eV indicating the formation of C=O bonds, present in carbonyl functionalities [9]. This suggests that physisorbed oxygen containing species (e.g. H_2O , O_2) react with carbon and form stable C=O bonds, probably due to the increased polarity (and therefore reactivity) through Ti-doping. Nevertheless, it can not be excluded that this feature is due to a Ti-C bonding state different as in TiC. After annealing to 700 K, COOH groups are completely removed, and the $\pi^*_{C=O}$ resonance is slightly shifted towards lower energy. The high oxygen concentration compared to a-C up to 1100 K is confirmed by XPS data (figure 3), which can not be explained by simple TiO_2 formation. Nevertheless, the Ti 2p signal suggests mainly Ti-O bonding up to 700 K, at 900 K Ti-O and Ti-C bonds are present, whereas at higher temperatures Ti is in carbide environment. After annealing to 1100 K, the C=O functionalities seems also to be reduced which is in line with the reported decomposition temperature > 1000 K [10]. RBS did not show an increased oxygen content in the bulk of the a-C:Ti film after annealing. Therefore, the high O concentrations are restricted to the surface-near region, which is probed by NEXAFS and XPS.

In figure 3 the FWHM of the C 1s peak (excluding the carbide signal) is shown as a function of annealing temperature. After an increase for the first annealing step (which should be due to desorption of hydrocarbons), a continuous decrease in FWHM with temperature is observed for a-C. This is in line with decreasing oxygen content and increasing order of the carbon phase (figure 1). For a-C:Ti, the FWHM is always higher, especially at 470 K (formation of C=O bonds) and 1100 K, where significant Ti diffusion leads to formation of carbide crystallites. This result suggests that temperature-induced ordering of the carbon phase is hindered by oxidation (470 K) and onset of carbide formation (1100 K), leading to a more distorted carbon phase than in the case of a-C. The decrease at 1300 K

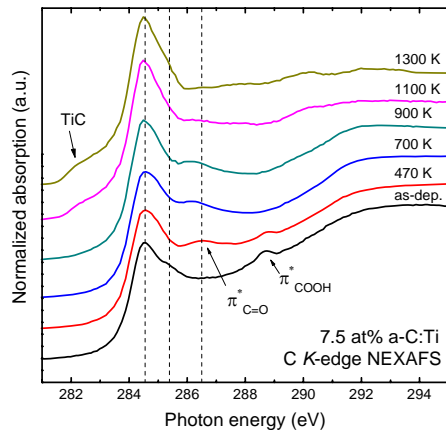


Figure 2. As deposited and annealed C K-edge NEXAFS spectra of the 7.5 at% a-C:Ti film.

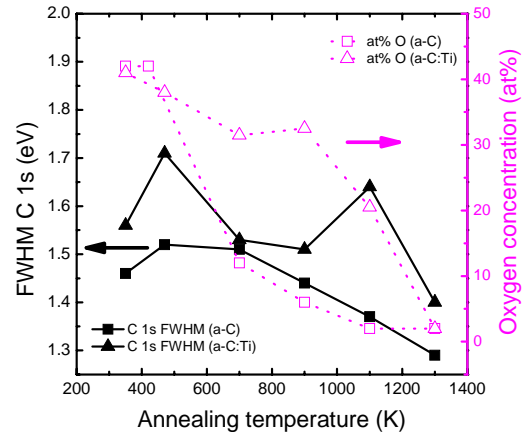


Figure 3. XPS data for the annealing series of a-C and a-C:Ti (7.5 at%).

should be related to C=O decomposition and the fact that Ti diffusion is strongly reduced since carbide crystallites have already formed and crystallite growth only slightly affects the carbon phase.

4. Conclusion

The temperature-induced change in the NEXAFS spectra of a-C is explained by an increase of local order and sp^2 content. At least two states of sp^2 bonded carbon are identified, a more disordered at ~ 284.7 eV and an ordered at ~ 285.5 eV, the latter increasing during annealing. No information about the sp^2 phase can be gained from the NEXAFS spectra of a-C:Ti. Annealing of a-C:Ti to 470 K leads to reaction of oxygen species with carbon and the formation of surface-near C=O bonds, identified by NEXAFS. High O concentrations at the surface were determined by XPS up to 1100 K.

5. Acknowledgments

J. Purton is acknowledged for assistance during the measurements at SRS. Part of this work has been performed within the framework of the Integrated European Project "Extremat" (contract NMP-CT-2004-500253) with financial support by the European Community. It only reflects the view of the authors and the European Community is not liable for any use of the information contained therein.

6. References

- [1] Doerner R P, *J. Nucl. Mater.* 2007 **363-365** 32
- [2] Balden M and Adelhelm C, *Phys. Scr.* 2007 **T128** 121
- [3] Garcia-Rosales C, Ordas N, Oyarzabal E, Echeberria J, Balden M, Lindig S and Behrisch R, *J. Nucl. Mater.* 2002 **307** 1282
- [4] Adelhelm C, Balden M and Sikora M, *Materials Science and Engineering: C* 2007 In Press
- [5] Balden M, Adelhelm C and Sikora M, *J. Nucl. Mater.* 2007 In Press
- [6] Balden M, Adelhelm C, de Juan Pardo E and Roth J, *J. Nucl. Mater.* 2007 **363-365** 1173
- [7] Stöhr J *NEXAFS Spectroscopy* Springer: Berlin 1992 p 403
- [8] Comelli G, Stöhr J, Robinson C J and Jark W, *Phys. Rev. B* 1988 **38** 7511
- [9] Diaz J, Anders S, Cossy-Favre A, Samant M and Stöhr J, *J. Vac. Sci. Technol. A* 1999 **17** 2737
- [10] Muckenhuber H and Grothe H, *Carbon* 2006 **44** 546
- [11] Stöhr J, Outka D A, Baberschke K, Arvanitis D and Horsley J A, *Phys. Rev. B* 1987 **36** 2976
- [12] Diaz J, Anders S, Zhou X, Moler E J, Kellar S A and Hussain Z, *Phys. Rev. B* 2001 **64** 125204
- [13] Gago R, Vinnichenko M, Jager H U, Belov A Y, Jimenez I, Huang N, Sun H and Maitz M F, *Phys. Rev. B* 2005 **72** 014120
- [14] Kapoor R, Oyama S T, Frühberger B, Devries B D and Chen J G, *Catal. Lett.* 1995 **34** 179