



# Deuterium retention in carbon and tungsten–carbon mixed films deposited by magnetron sputtering in $D_2$ atmosphere

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## Abstract

Deuterium (D) retention in carbon (C) and tungsten–carbon (W–C) mixed films deposited by reactive magnetron sputtering in  $D_2$  atmosphere has been investigated by means of secondary ion mass spectrometry and residual gas analysis measurements. In the C and W–C films, D is distributed homogeneously throughout the film thickness. With the deposition temperature increase, the D concentration in the C films is varied from  $\sim 0.4$  D/C (in units of atomic ratio) at 400 K to  $\sim 0.02$  D/C at 973 K. In its turn, the D concentration in the W–C films falls from  $\sim 0.02$  D/(W + C) at 400 K to values below  $10^{-4}$  D/(W + C) at 973 K. In spite of the presence of carbon atoms in the W–C mixed films (up to 30%), the concentration of deuterium in these films is much lower than is expected from the assumption that the W–C mixed film consists of tungsten and graphite inclusions. The deuterium concentration in the W–C mixed films is close in value to that in pure tungsten or tungsten carbides. The co-deposition of carbon and tungsten atoms is speculated to lead to the formation of tungsten carbides even at temperatures as low as 400 K.

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## 1. Introduction

According to requirements and selection criteria in the ITER design, the plasma-facing material of divertor will be chosen from carbon fibre composite and tungsten. Physical and chemical sputtering causes erosion of the plasma-facing materials and impurity release into the plasma. As the sputtered carbon atoms arrive at their new location, they are co-deposited with energetic hydrogen isotope ions and neutrals. The characteristics of the co-deposited carbon layers and other similar coat-

ings are reviewed by Jacob [1]. Summarizing the results on chemical composition of the co-deposited carbon–hydrogen layers [2–5], it can be said that they are primary amorphous, contain a large amount of hydrogen, have hydrogen formed hydride with  $sp^3$ ,  $sp^2$ , and  $sp^1$  hybridized carbon atoms in decreasing probability, and have hydrogen that is chemisorbed on the carbon as well. The retention of hydrogen isotopes in tungsten has been reviewed recently by Causey and Venhaus [6]. Data on the deuterium trapping in tungsten carbides were compiled by Alimov et al. [7].

The purpose of this work consists in studying deuterium profiles in carbon and tungsten–carbon films deposited by magnetron sputtering in deuterium atmosphere. In addition, deuterium profiles in chemically vapour deposited (CVD) tungsten carbide WC coatings exposed to deuterium plasma were measured to compare the results obtained for the W–C mixed films and WC coatings.

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## 2. Experimental

Carbon (C) and tungsten–carbon (W–C) mixed films were deposited in a magnetron system by dc sputtering of graphite and tungsten cathodes, respectively, in D<sub>2</sub> atmosphere at a pressure of 0.3–0.5 Pa. The discharge current was 1.5 A, the discharge voltage was –360 V for graphite cathode or –500 V for tungsten cathode. All films were deposited on silicon substrates which were located over the cathode at a distance of 6 cm. The C films were deposited first, and in doing so a considerable amount of carbon was deposited on the walls of the vacuum chamber. In the subsequent experiments with tungsten cathode sputtering, the carbon atoms deposited on the substrate surface simultaneously with W atoms and O atoms originated from the residual gas. The substrate temperature was fixed in the range 393–973 K.

The chemical composition of the deposited films was determined by electron probe microanalysis (EPMA). The structure of the W–C mixed films was characterized by reflected high-energy electron diffraction (RHEED). The W–C mixed films deposited at temperatures  $\leq 563$  K demonstrate amorphous structure with inclusions of graphite-like and tungsten crystallites about 1 nm in size. As the deposition temperature increases, the graphite-like and tungsten crystallites increase in size (up to 10 nm for graphite inclusions and  $\sim 100$  nm for tungsten crystallites). In the mixed films deposited at temperatures above 733 K, W<sub>2</sub>C carbide phase is also observed in the RHEED pattern. The C films have amorphous structure with graphite-like inclusions.

CVD coatings of tungsten carbide WC were chemically deposited on nickel substrates from a vapor mixture of tungsten fluoride, carbon-containing gases and hydrogen at temperature of 750–900 K [7]. The coatings were exposed to a deuterium plasma at temperatures in the range 450–650 K. A plasma source with heated cathode was used to produce low energy deuterium particles. During D plasma exposure the samples were under ground potential and the energy of impinging D ions (mainly D<sub>2</sub><sup>+</sup>) was estimated to be about 60 eV (30 eV/D<sup>+</sup>). The flux density of low-energy D particles (ions and neutrals, in the flux ratio  $\sim 1:1$ ) was estimated to be  $\sim 2 \times 10^{20}$  D/(m<sup>2</sup>s).

The deposited and plasma-exposed samples were transferred into an analytical UHV chamber for SIMS measurements of D<sup>–</sup> secondary ion species and RGA measurements of the partial pressure of D<sub>2</sub> molecules in the course of sputtering of the surface with 4 keV Ar<sup>+</sup>.

The sputtering rates of the deposited C and W–C mixed films were assumed to be equal to those for highly ordered pyrolytic graphite (HOPG) and CVD WC coating, respectively. Both for HOPG and CVD WC coating, the sputtering rate was determined as the ratio of the depth of the crater produced on the surfaces by sputtering (using optical interferometer) to the sputter-

ing time with an accuracy of about 20% for HOPG and 40% for CVD WC (note that the surface roughness of the CVD coating is  $\sim 1$   $\mu$ m).

We attribute the appearance of the SIMS D<sup>–</sup> signal to the existence of separate D atoms within the matrix [8,9]. The cause of the RGA D<sub>2</sub> signal appearance seems to be the recombination of D atoms as well as the direct release of D<sub>2</sub> molecules from the sputtered layers. A procedure for the separation of the recombination and molecular fractions has been described in [8,9]. The scale factor of D<sub>2</sub> concentration to RGA mass 4 intensity was estimated taking into account the sensitivity of the RGA QMS and the known sputtering yields [10] and pumping speed. The total error of the RGA QMS calibration was about 30%.

The calibration of the D<sup>–</sup> SIMS signal was carried out with the use of HOPG implanted with 3 keV D ions at 300 K and W single crystal implanted with 10 keV D ions at 100 K to fluences below  $3 \times 10^{20}$  D/m<sup>2</sup> by comparing the integral SIMS signal (over the implantation depth) with the total amount of deuterium in this sample. Taking into account the calculated concentrations of deuterium in the implantation zone and the sputtering yields of graphite and tungsten [10], it was revealed that the D<sup>–</sup> ionization coefficients for these materials are very close in value. Therefore, we can conclude that the D<sup>–</sup> ionization coefficients for the W–C mixed film and CVD WC coating are also equal to those for graphite and tungsten. With this provision the error of the calibration was estimated to be about 30%.

The detection limit in the SIMS/RGA measurements of D atom and D<sub>2</sub> molecule concentration was  $\sim 10^{-5}$  D/(W + C) and  $\sim 10^{-4}$  D<sub>2</sub>/(W + C), respectively.

## 3. Results and discussion

The deposition rate of C films was found to be practically zero in the temperature range 500–650 K (Fig. 1). Note that the temperature dependence of the erosion of C films by thermal D atoms peaks at  $\sim 600$  K with the erosion yield of  $\sim 0.1$  C/D [11]. Therefore, the zero value of the C film deposition rate can be explained by the dominating erosion caused by D atoms and ions formed in magnetron plasma.

An assumption was advanced earlier [8] that the D<sup>–</sup> SIMS signal is related to deuterium atoms bonded to sp<sup>2</sup> trigonal hybrid orbitals of C atoms in configurations of the form D–(sp<sup>2</sup>)C, whereas deuterium involved in configurations D<sub>2</sub>–(sp<sup>3</sup>)C is detected solely by RGA as D<sub>2</sub> molecules. SIMS/RGA depth profiling has shown that the D-containing configurations are distributed homogeneously throughout the whole film thickness. The concentration of deuterium measured by SIMS and RGA (or in other words, the concentration of the

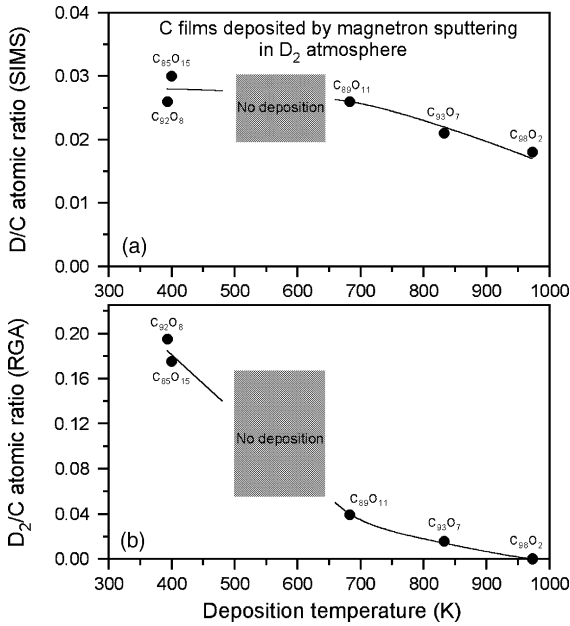


Fig. 1. Concentration of deuterium measured by SIMS (a) and RGA (b) (as speculated, involved in D-(sp<sup>2</sup>)C and D<sub>2</sub>-(sp<sup>3</sup>)C configurations, respectively) in the bulk of C films deposited by magnetron sputtering in D<sub>2</sub> atmosphere as a function of deposition temperature. The chemical composition of the films is shown for each deposition temperature. Note that the C film deposition rate is practically zero at temperatures 500–650 K.

D-(sp<sup>2</sup>)C and D<sub>2</sub>-(sp<sup>3</sup>)C configurations) in the grown C films are shown in Fig. 1 as a function of deposition temperature. With the temperature increase, the value of the D-(sp<sup>2</sup>)C concentration varies from ~0.03 [D-C]/C (in units of atomic ratio) at 400 K to ~0.02 [D-C]/C at 973 K (Fig. 1(a)). As this takes place, the D<sub>2</sub>-(sp<sup>3</sup>)C concentration value reduces from ~0.20 [D<sub>2</sub>-C]/C at 400 K to values below 10<sup>-4</sup> [D<sub>2</sub>-C]/C at 973 K (Fig. 1(b)).

In the course of SIMS/RGA profiling of deuterium in the W-C films, D<sub>2</sub> molecules were released from the sputtered layers. The appearance of D<sub>2</sub> molecules can be related both to formation of the D<sub>2</sub>-(sp<sup>3</sup>)C configurations in carbon inclusions and creation of D<sub>2</sub> gas filled cavities in the growing W-C film. The variation of the concentration of D atoms and D<sub>2</sub> molecules in the bulk of the W-C mixed films as a function of the substrate temperature is demonstrated in Fig. 2. As in the C films, the D atoms and D<sub>2</sub> molecules in the W-C mixed films distributed homogeneously throughout the film thickness. At 400 K, the concentration of the D atoms and D<sub>2</sub> molecules in the deuterated W-C mixed film is ~0.007 D/(W + C) and ~0.008 D<sub>2</sub>/(W + C), respectively. As the deposition temperature increases up to 800 K, the concentration of D atoms and D<sub>2</sub> molecules falls to values below the threshold of detectability (Fig. 2).

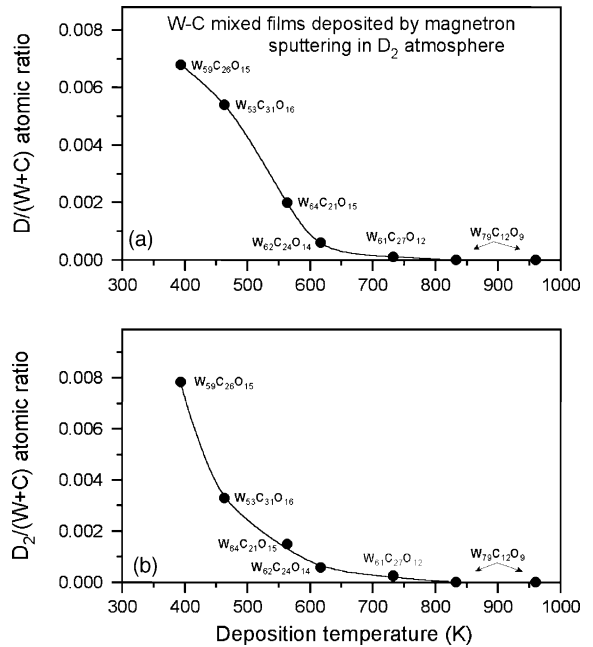


Fig. 2. Concentration of D atoms (a) and D<sub>2</sub> molecules (b) in the bulk of W-C mixed films deposited by magnetron sputtering in D<sub>2</sub> atmosphere as a function of deposition temperature. The chemical composition of the films is shown for each deposition temperature.

Depth profiles of D atoms in CVD WC coatings exposed to D plasma to a particle fluence of ~ 7 × 10<sup>23</sup> D/m<sup>2</sup> at T<sub>exp</sub> = 450, 550 and 650 K are shown in Fig. 3. D<sub>2</sub> molecules were not detected in our experiments and we conclude that deuterium is accumulated solely as D atoms. At T<sub>exp</sub> = 450 K, the D atom concentration within the near-surface layer of about 40 nm in thickness

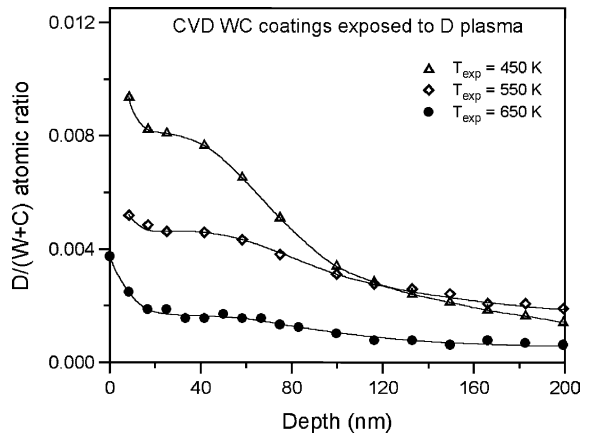


Fig. 3. Depth profiles of D atoms in CVD WC coatings exposed to D plasma to a particle fluence of ~ 7 × 10<sup>23</sup> D/m<sup>2</sup> at T<sub>exp</sub> = 450, 550 and 650 K.

reaches a value of about  $8 \times 10^{-3} D/(W + C)$  which is thought to be saturated and reflect the efficiency of D trapping by intrinsic defects. The surface concentration peak (Fig. 3) can be related to deuterium associated with the surface contamination. Note that a maximum value of D atom concentration in the implantation zone of CVD tungsten carbides WC and  $W_2C$  irradiated with 10 keV D ions at 300 K is about  $1.5 \times 10^{-2} D/(W + C)$  [7], in doing so the radiation-induced defects are also responsible for the D trapping. Turning back to the CVD WC exposed to D plasma, we see that the D concentration within the near surface layer decreases as the exposure temperature increases (Fig. 3).

The concentration of all deuterium (involved in  $D-(sp^2)C$  and  $D_2-(sp^3)C$  configurations) in deuterated C films varies from  $\sim 0.4 D/C$  at 400 K to  $\sim 0.02 D/C$  at 973 K (Fig. 4). In the W–C mixed films, the concentration of all deuterium varies from  $\sim 0.02 D/(W + C)$  at 400 K to values below  $10^{-4} D/(W + C)$  at 973 K. The saturation concentration of deuterium in the near surface layers of polycrystalline tungsten exposed to D plasma [7] and irradiated with 500 eV D ions (that below the threshold for displacement) [12] and CVD WC coatings exposed to D plasma is plotted also in Fig. 4 as a function of implantation temperature. The results presented show that the D concentration in the W–C

mixed films is comparable with that in tungsten and tungsten carbide implanted with low-energy D ions. It is pertinent to note that deuterium implanted in polycrystalline tungsten at energies below the energy required for defect creation diffuses far beyond the implantation range into the bulk even at room temperature and is captured by the intrinsic defects, mainly dislocations and grain boundaries [7,13].

The D concentration in the C films is more than one order of magnitude higher than that in the W–C mixed films (Fig. 4). Thus, in spite of the presence of carbon atoms in the W–C mixed films (up to 30%), the concentration of deuterium in these films is much lower than it is expected from the assumption that the W–C mixed film consists solely of the separate tungsten and graphite inclusions. Thus, the co-deposition of carbon and tungsten atoms is speculated to lead to the formation of tungsten carbides even at temperatures as low as 400 K. It should be mentioned that tungsten carbide formation has been observed when separate layers of W and C are sputter- or ion beam-deposited successively on each other at, or slightly above room temperature [14–16]. When the W–C mixed film is deposited, the substrate surface is bombarded with tungsten, carbon, deuterium atoms and ions and  $C_xD_y$  particles as well. In doing so, precipitators of tungsten carbide phases (along with carbon and tungsten precipitators) are concluded to be formed in the bulk of growing film. EMPA analysis has shown that oxygen atoms are present in the films, and it is believed that the tungsten oxide precipitators are also formed in the growing film. Deuterium implanted as low energy ions and neutrals is captured by dissimilar defects formed during the film growth—carbon inclusions, tungsten oxides [17], grain and precipitate boundaries, microvoids, microcracks, etc.

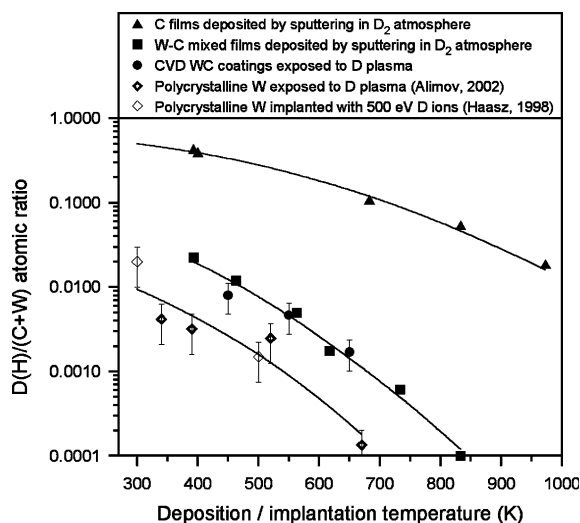


Fig. 4. Deuterium concentration in: (i) the bulk of C and W–C mixed films deposited by magnetron sputtering in  $D_2$  atmosphere, (ii) the near-surface layers of CVD WC coatings exposed to D ions plasma, (iii) the near-surface layers of polycrystalline tungsten exposed to D plasma [7] and irradiated with 500 eV D ions [12] as a function of implantation/deposition temperature. For materials irradiated with low-energy D ions, the error bars indicate the error in determination of D concentration in the near-surface layers caused by the D concentration non-uniformity with depth.

#### 4. Conclusions

In C and W–C films deposited by dc magnetron sputtering in  $D_2$  atmosphere, deuterium is distributed homogeneously throughout the whole thickness. With an increase in deposition temperature, the deuterium concentration in the C film is varied from  $\sim 0.4 D/C$  at 400 K to  $\sim 0.02 D/C$  at 973 K.

W–C mixed films deposited by dc magnetron sputtering in  $D_2$  atmosphere contain graphite-like, tungsten and inclusions of tungsten carbide  $W_2C$ . At 400 K, the deuterium concentration in the W–C mixed film is  $\sim 0.023 D/(W + C)$ . Thus, in spite of the presence of carbon atoms in the W–C mixed films (up to 30%), the deuterium concentration in these films is much lower than it is expected from the assumption that the W–C mixed film consists solely of tungsten and graphite precipitators.

The co-deposition of carbon and tungsten atoms is speculated to lead to the formation of chemical compounds, namely tungsten carbides, even at temperatures as low as 400 K. Deuterium incorporated into this process is accumulated in the growing film up to concentrations which are typical for pure tungsten or tungsten carbides but not for graphite inclusions.

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### References

- [1] W. Jacob, *Thin Solid Films* 326 (1998) 1.
- [2] W. Jacob, W. Möller, *Appl. Phys. Lett.* 63 (1993) 1771.
- [3] B. Dischler, A. Bubenzer, P. Koidl, *Appl. Phys. Lett.* 42 (1983) 636.
- [4] A.R. Nyaiesh, W.B. Nowak, *J. Vac. Sci. Technol. A* 1 (1983) 308.
- [5] M.P. Nadler, T.M. Donovan, A.K. Green, *Appl. Surf. Sci.* 18 (1984) 10.
- [6] R.A. Causey, T.J. Venhaus, *Phys. Scr. T* 94 (2001) 9.
- [7] V.Kh. Alimov, A.P. Zakharov, R.Kh. Zalavutdinov, in: A. Hassanein (Ed.), *Hydrogen and Helium Recycling at Plasma Facing Materials*, Kluwer, Dordrecht, 2002, p. 131.
- [8] V.Kh. Alimov, A.E. Gorodetsky, A.P. Zakharov, *J. Nucl. Mater.* 186 (1991) 27.
- [9] V.Kh. Alimov, V.N. Chernikov, A.P. Zakharov, *J. Nucl. Mater.* 241–243 (1997) 1047.
- [10] H.H. Andersen, H.L. Bay, in: R. Behrisch (Ed.), *Sputtering by Particle Bombardment I*, Topics in Applied Physics, vol. 47, Springer, Berlin, 1981.
- [11] E. Vietzke, V. Philipps, *Fusion Technol.* 15 (1989) 108.
- [12] A.A. Haasz, J.W. Davis, M. Poon, R.G. Macaulay-Newcombe, *J. Nucl. Mater.* 258–263 (1998) 889.
- [13] V.Kh. Alimov, K. Ertl, J. Roth, K. Schmid, *Phys. Scr. T* 94 (2001) 34.
- [14] A.F. Jankowski, L.R. Schrawyer, M.A. Wall, et al., *J. Vac. Sci. Technol. A* 7 (1989) 2914.
- [15] A.H. Carim, A.F. DeJong, P. Houdy, *Thin Solid Films* 176 (1989) L177.
- [16] A.K. Petford-Long, M.B. Stearns, C.-H. Chang, et al., *J. Appl. Phys.* 61 (1987) 1422.
- [17] V.Kh. Alimov, V.M. Sharapov, A.E. Gorodetsky, in: *Proceedings of the International Workshop on Hydrogen Isotopes in Fusion Reactor Materials*, Tokyo, Japan, 22–24 May, 2002 (to be published in *Phys. Scr.*).