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Journal of Nuclear Materials 241-243 (1997) 1127-1131

journal of nuclear materials

Interaction of energetic oxygen ions with lithium-containing amorphous hydrogenated carbon films: A mass spectrometry study

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Abstract

Lithium-containing amorphous hydrogenated carbon coatings (a-C:H/Li) have been prepared by a modified plasma assisted chemical vapor deposition (rf-PACVD) technique. In order to investigate the interaction of energetic oxygen with these films they were irradiated with oxygen ions of 3 keV energy. Erosion and retention behavior was measured by direct detection of emitted particles using a differentially pumped line-of-sight quadrupole mass spectrometer. Results are compared to those of previous studies on pure and boron-containing carbon materials. Like in these materials, emission of reaction products from a-C:H/Li is dominated by CO and CO_2, to a smaller extent also emission of lithium oxide, Li_2O, is observed. As compared to pure carbon the emission of reaction products is delayed, and the erosion yield after oxygen saturation of the surface layer is lower for lithium-containing films. Taking into account results of X-ray photoelectron spectroscopy, it can be concluded that the interaction of a-C:H/Li with energetic oxygen follows the same general trends as observed for boron-containing carbon materials. However, chemical reactions and their dependence on conditions of irradiation are more complex in a-C:H/Li than in boron-containing carbon.

Keywords: Low Z wall material; Wall impurity trapping; Chemical erosion; Wall coating

1. Introduction

Wall conditioning of the plasma facing walls of controlled fusion test devices decisively influences many plasma parameters, and can in particular drastically decrease the oxygen contamination level of the plasma. A well established and actually widely used technique in tokamaks is the 'boronization' of the walls, i.e. the deposition of pure boron or boron–carbon layers. Detailed investigations on the oxidation behavior and the stability of such coatings have been performed both in tokamaks and in simulation experiments [1–5]. A further improvement of these favorable properties can be expected by the use of carbon films containing the even lighter and more reactive element lithium instead of boron. First promising results have been obtained by lithium evaporation in the tokamak device JIPP T-IIU [6], by lithium pellet injection in the tokamak device TFTR [7], and in model experiments [8,9]. However, the underlying mechanisms of lithium based wall conditioning have not yet been fully understood.

In Refs. [8,9] we reported on in-situ photoelectron spectroscopy studies on the interaction of energetic oxygen ions with lithium-containing amorphous hydrogenated carbon (a-C:H/Li) films. Photoelectron spectroscopy provides a detailed picture of the chemical processes at and the resulting composition of the sample's surface. Mass spectrometry in turn provides complementary information, in a sense that it detects the species (re-)emitted from the sample's surface. In the present work investigations on the interaction of energetic oxygen ions with lithium-containing amorphous hydrogenated carbon (a-C:H/Li) films using mass spectrometry are presented. Results are compared to those of the photoelectron spectroscopy studies [8,9] as

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PII S0022-3115(96)00685-X

well as to those of previous investigations on pure and boron-containing carbon materials [4,5,10].

2. Experimental

Films were deposited at room temperature onto silicon substrates mounted on the negatively biased electrode (cathode) of a custom-built capacitively coupled RF (13.56 MHz) plasma chamber. The achieved base pressure in the plasma chamber was in the low 10^{-8} mbar range. Pure methane was used as process gas. The process gas pressure was set at 5×10^{-2} mbar, the self-bias voltage at the cathode at -200 V, both kept constant throughout the deposition. Lithium has been incorporated in the films by injecting Li^+-ions into the plasma from zeolite dispensers (SAES Getters). Films ranging from pure a-C:H to a-C:H containing up to 20 at% lithium have been synthesized for the present study. Oxygen contaminations in the as-prepared films could be kept below 0.2 at% for pure and in the range of 1 to 3 at% for lithium-containing films. Typical deposition times were 30 min, film thicknesses of about 150 nm were estimated by colorimetric comparison [11]. For the transport through atmosphere samples were covered with a thin overlayer (about 20 nm) of soft amorphous hydrogenated carbon (a-C:H), deposited at a bias voltage of -50 V.

Samples were irradiated with oxygen ions at normal direction. The irradiated area was $2*2$ mm^2, ion energy was chosen to 6 keV. Assuming the ion beam to contain only O_2^+-ions yields 3 keV per O^+ ion, typical ion fluxes were of the order of 10^{18} O_2^+ ions/s · m^2. Here the oxygen isotope ^{18}O was used in order to distinguish between chemical reaction products due to irradiation and ^{16}O contaminations due to the transport of the samples. Emitted particles were detected directly in line-of-sight by a two-stage differentially pumped quadrupole mass spectrometer (QMS) at 45° with respect to the ion beam direction (for a detailed description see Ref. [12]). The range of masses was set from 5 to 80 mass units, i.e. a search for lithium-containing compounds up to $Li_2C^{18}O_3$ was done. The calibration of the QMS and its transmission dependence on the mass of the incoming particles were determined by effusing a certain amount of He, CH_4, CO, CO_2 and Kr from a Knudsen cell at 285 K in the target position. The ionization cross sections for the above gases were taken from the literature [13] and the ones for the lithium-containing compounds assumed to be 25% larger than those of carbon (the ratio to ionize C and Li) to be ($\sigma_{LiO} = \sigma_{LiC} = 2 * 10^{16}$ cm^2 and $\sigma_{Li_2O} = \sigma_{Li_2O_2} = 3 * 10^{16}$ cm^2. For the particles emission from the surface a cosine distribution is assumed. The accuracy of the determined reaction yields for CO and CO_2 is estimated to be in the order of 15% and for the lithium-containing compounds within a factor of two. As a reference, also the emission from pure carbon (graphite EK98) was measured.

3. Results

3.1. O^+ irradiation on samples at room temperature

From mass spectra taken at different stages of the erosion process significant species for the interaction of energetic oxygen ions with a-C:H/Li were selected. In order to come to a more detailed understanding the time dependence of the erosion/sputter yield of these selected species was measured. As can be seen in Fig. 1 the emission of chemical reaction products is dominated by CO and CO_2. Only to a smaller extent lithium-containing species are detected. In addition, of course also reflected/reemitted oxygen together with sputtered carbon and lithium are found in the order of 1% of the CO yield. Unfortunately, due to surface ionization effects in the quadrupole, the lithium signal can not be quantified. However, regarding the time dependence of the lithium signal in Fig. 1a two pronounced peaks can be seen. The first peak has to be attributed to lithium enrichment in the soft a-C:H layer on top of the a-C:H/Li (intended to serve as a protecting layer for the transport through atmosphere). The second peak detects the increased lithium concentration at the interface of the a-C:H/Li to the silicon substrate.

Time dependence of the $C^{16}O$ (not shown in Fig. 1) and $C^{18}O$ signals reveals a contamination of a rather thin surface layer due to transport through atmosphere, but after removal of this contaminated layer emission of $C^{18}O$ dominates. Similar observations can be made for $C^{16}O_2$ and $C^{18}O_2$. As can be seen in Fig. 2, emission of CO starts almost immediately after starting the irradiation and rises steadily until saturation is reached at an implanted ion fluence of about 2×10^{21} O^+/m^2. However, as compared to pure carbon, this transient regime in which the incident oxygen is retained in the sample increases in the a-C:H/Li

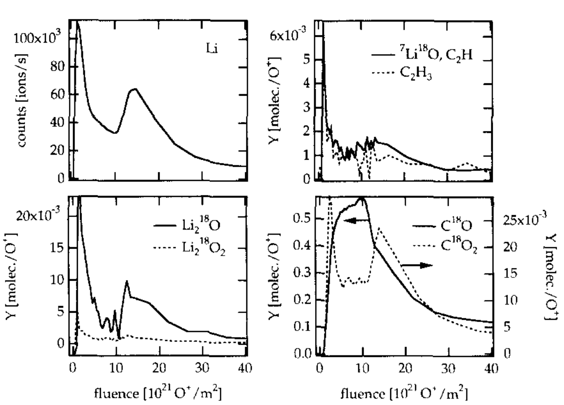

Fig. 1. Fluence dependence of count rate/reaction yield for a number of selected species during irradiation of an a-C:H/Li (20 at%) sample with 3 keV $^{18}O^+$-ions.

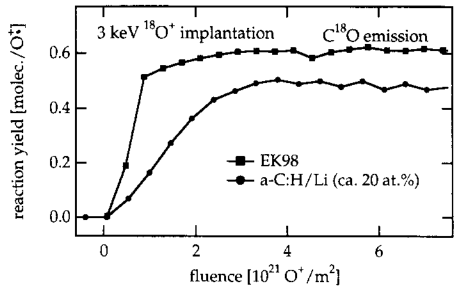

Fig. 2. Fluence dependence of the emission of CO during irradiation of pure carbon (graphite EK 98) and a a-C:H/Li sample (20 at%) with 3 keV $^{18}O^+$-ions at room temperature.

case and the quasi-saturation value of the reemitted CO flux is reduced. This behavior already reflects the higher oxygen-gettering effect of lithium-containing carbon films. Presuming the same velocity distribution as for the pure carbon case [5], a steady-state reaction yield of 0.48 molecules/O^+ for CO can be estimated from Fig. 2 for the a-C:H/Li (20 at%) sample. For a-C:H/Li (10 at%) samples a chemical reaction yield for CO of about between those of pure carbon and a-C:H/Li (20 at%) was found (not shown in Fig. 2), suggesting a dependence on the lithium content. As compared to pure carbon also the emission of CO_2 is significantly reduced in a-C:H/Li; while $Y = 0.1$ molecules/O^+ is found for EK98 [10] a steady-state value of only $Y = 0.015$ molecules/O^+ in a-C:H/Li (20 at%) can be estimated from Fig. 1. From the detected species only ^7LiC, $^7Li_2{}^{18}O$, and $^7Li_2{}^{18}O_2$ can unambiguously be attributed to lithium compounds, the others can not be distinguished from coinciding hydrocarbons. There might be also a contribution to $^7Li_2{}^{18}O$ (mass 32) from $^{16}O_2$ due to a contamination during the transport through atmosphere. However, the contributions of all these species to the total chemical reaction yield are rather small; using the same velocity distribution as for the boron oxides [5] for ^7LiC and $^7Li_2{}^{18}O$ values of about $Y = 5 \times 10^{-3}$ molecules/O^+ can be estimated, for $^7Li_2{}^{18}O_2$ only about $Y = 5 \times 10^{-4}$ molecules/O^+ is found. If these lithium-containing species also undergo surface ionization the estimated yields are only upper limits. The reaction yield of neither of the other detectable species up to mass 80 ($^7Li_2C^{18}O_3$!) exceeds 1×10^{-4} molecules/O^+.

This amounts to a total chemical erosion yield of about 0.5 molecules/O^+, as compared to 0.7 molecules/O^+ in pure graphite [5]. The oxygen retained in the sample was not determined.

3.2. O^+ irradiation on samples at higher temperatures

The results obtained for irradiation at higher sample temperatures resemble those obtained for pure [10] and boron-containing [4,5] carbon materials: as compared to irradiation at room temperature the reaction yield of CO drops to below 0.4 molecules/O^+ at 470 K and slightly increases at 580 K. The reaction yield for CO_2 shows an opposite behavior: from 0.015 at room temperature it increases to 0.03 at 470 K and slightly decreases above. The reaction yield for both ^7LiC and $^7Li_2O$ also slightly increases from $Y = 5 \times 10^{-3}$ molecules/O^+ at room temperature to $Y = 8 \times 10^{-3}$ molecules/O^+ but decreases significantly to only $Y = 2 \times 10^{-3}$ molecules/O^+ at 580 K, respectively. The other possible lithium compounds arc below the limit of detection at 580 K. This amounts to a reduced total chemical reaction yield of about $Y = 0.4$ molecules/O^+ at 470 K and $Y = 0.42$ molecules/O^+ at 580 K. The net erosion rate can be determined from the time necessary for a complete removal of the a-C:H/Li layer, determined from the time of appearance of the second peak in the lithium emission. As shown in Fig. 3b this time decreases with increasing sample temperature. While the sputter yield for carbon is almost constant over the temperature range investigated here, we have to conclude that the total erosion yield for lithium increases steadily by a factor of 1.4 upon raising sample temperature at irradiation from room temperature to 580 K.

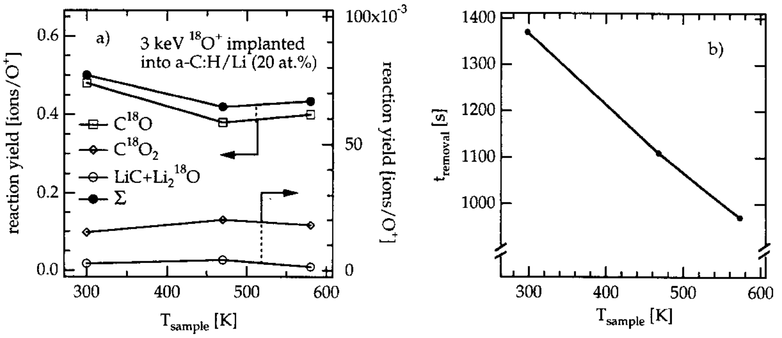

Fig. 3. Influence of sample temperature on (a) reaction yields and (b) time necessary for complete removal of the film due to irradiation of the a-C:H/Li (20 at%) sample from Fig. 1 with 3 keV $^{18}O^+$-ions.

4. Discussion

In a previous study combining photoelectron spectroscopy and quartz crystal film thickness monitoring the time dependence of oxygen retention and erosion of a-C:H/Li films upon irradiation with energetic oxygen ions was investigated. A general resemblance was found with the results obtained for boron-containing carbon materials. For films of lithium contents < 40 at% the behavior can well be described by a so-called local-mixing-model [14]. In a transient regime the irradiated material traps oxygen at the depth of implantation up to a saturation concentration. Once this saturation concentration is exceeded locally, oxygen and chemical reaction products start being (re-)emitted. Together with surface sputtering this (re-)emission results in a steady erosion of the films. However, graphite retains implanted oxygen only up to an saturation concentration of 0.25 O/C or $c_o = 20$ at% in a surface layer [4]. In contrast, like for the boron-containing carbon in a-C:H/Li oxygen retention as measured by photoelectron spectroscopy is increased to 0.55 O/(Li + C) or $c_O = 35$ at% [8,9]. This behavior is reflected by the mass spectrometry measurements presented here in form of a reduced chemical erosion yield of $Y = 0.5$ molecules/O^+ for irradiation at room temperature and a stronger delayed CO emission. Differences in the chemical reactions at the surface of boron- and lithium-containing carbon materials are found by photoelectron spectroscopy [9]: Upon irradiation with energetic oxygen in the boron-containing carbon materials mainly a non-volatile boron-oxide is formed in the implantation zone, carbon is not involved in the retention of oxygen. In contrast, in the implantation zone of a-C:H/Li already at room temperature besides CO, CO_2 and Li_2O a ternary compound, Li_2CO_3 or $LiHCO_3$, can be detected. In spite of these differences, in both cases the emission of particles during oxygen irradiation as observed by mass spectrometry is clearly dominated by CO and CO_2. Boron- and lithium-oxides emission is only found to a rather small extent. Moreover, while from the increased oxygen uptake at higher temperatures observed in photoelectron spectroscopy a decrease of the erosion rate with increasing temperature could be expected, this could not be confirmed here. This discrepancy might be explained by an increased sputtering yield and beginning of lithium evaporation at higher temperatures.

In summary, like in pure and boron-containing carbon materials emission from a-C:H/Li upon irradiation with energetic oxygen ions is dominated by CO and CO_2. Only to a smaller extent lithium oxide, Li_2O can be detected. The chemical erosion rate decreases in dependence on the lithium content from 0.7 molecules/O^+ in pure graphite to 0.5 molecules/O^+ in a-C:H/Li (20 at%). At higher sample temperatures the ratio of the chemical reaction yields changes slightly towards lower CO, and higher CO_2 and Li_2O yields; in total it slightly decreases. However, the net erosion rate, including also sputtering yields and evaporation of lithium, increases steadily by a factor of 1.4 upon raising sample temperature at irradiation from room temperature to 580 K.

In the literature, very often the argument is used that all implanted oxygen reacts with carbon or lithium, which means that the reaction yield for volatile products or surface oxide formation is unity. Since we have not performed thermal desorption experiments we cannot balance the oxygen as it was done for graphite and boron–carbon films [4]. It is very likely that the two compounds formed during the irradiation of the a-C:H/Li film, probably Li_2O and Li_2CO_3 [9], are still present at the surface after all lithium is eroded away since the lithium oxide signals in Fig. 1 stays constant also for large fluences.

In fusion applications, clearly results of lower oxygen bombarding energies are needed. We do not expect any large dependence down to 100 eV for two reasons. First, various energies of oxygen ions (100 eV...3 keV) were used in experiments for our previously published photoelectron spectroscopy study [9], but no differences in terms of samples surface composition or chemical structure could be detected. Second, the chemical erosion of carbon by oxygen impact does not show large dependence on the oxygen ion energy down to 50 eV [10,15].

Acknowledgements

Financial support of the Basel group by the Swiss Bundesamt für Bildung und Wissenschaft as well as the Bundesamt für Energiewirtschaft is gratefully acknowledged.

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