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DEPTH PROFILING A NEAR SURFACE CARBON CONTAMINANT IN IMPLANTED FIRST WALL MATERIALS *

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Current attempts to generate stable plasmas in CTR devices are encountering severe material problems. Plasma species, interacting with the surface of the containment vessel, can desorb surface species which can contaminate the plasma or, interacting with surface impurities, can change the properties of the near surface region. Although methods to minimize these synergistic effects have been suggested, there exists only minimal information related to the fundamental surface and near surface (< 100 Å) processes involved. One process of interest, the interaction of energetic plasma species with adsorbed hydrocarbon contaminants has been examined using Imaging, Field-Desorption Mass Spectrometry. Angstrom resolved depth profiles of a carbon contaminant produced by ion-beam decomposition of an adsorbed surface hydrocarbon layer have been measured for tungsten, molybdenum and stainless steel specimens. The observed, 30 Angstrom penetration of carbon into the near surface region suggests that conventional first-wall cleaning techniques may be ineffective in completely removing this impurity.

Les essais habituels pour engendrer des plasmas stables dans les dispositifs CTR se heurtent à de nombreux problèmes de matériaux. Les espèces du plasma, réagissant avec la surface de l'enceinte le contenant, peuvent désorber des espèces de surface qui peuvent contaminer le plasma, ou réagissant avec les impuretés de la surface, peuvent modifier les propriétés de la région proche de la surface. Bien que des méthodes permettant de minimiser ces effets synergétiques aient été proposées, il n'existe qu'une information minimale relative aux processus fondamentaux concernant la surface et les régions proches de la surface (< 100 Å). Un processus intéressant, celui de l'interaction des espèces énergétiques du plasma avec les contaminants d'hydrocarbure adsorbés, a été étudié en utilisant les méthodes d'image, de spectrométrie de masse à désorption de champ. Des profils en profondeur de pouvoir, de résolution atteignant l'Angstrom, relatifs au contaminant carbone produit par décomposition sous l'effet du faisceau ionique d'une couche d'hydrocarbure adsorbée à la surface, ont été mesurés sur des échantillons de tungstène, de molybdène et d'acier inoxydable. Une pénétration de 30 Angstroms de carbone observée dans la région proche de la surface suggère que les techniques conventionnelles de nettoyage de la première paroi peuvent être inefficaces pour éliminer complètement cette impureté.

Die derzeitigen Versuche zur Erzeugung stabiler Plasmen in CTR-Anlagen stossen auf schwierige Materialprobleme. Plasmaspezies, die mit der Oberfläche des Kessels in Wechselwirkung treten, können Oberflächenspezies desorbieren, die das Plasma kontaminieren oder bei Reaktion mit Oberflächenverunreinigungen die Eigenschaften des oberflächennahen Bereichs verändern können. Obwohl Methoden zur Minimalisierung dieser synergistischen Einflüsse vorgeschlagen wurden, gibt es nur geringe Informationen über die grundlegenden Prozesse an und nahe (< 100 Å) der Oberfläche. Ein bedeutender Prozess, die Wechselwirkung von energiereichen Plasmaspezies mit adsorbierten Kohlenwasserstoffverunreinigungen, wurde mit abbildender Felddesorptionsmassenspektrometrie untersucht. Tiefenprofile mit einer Auflösung im Å-Bereich wurden an einer Kohlenstoffkontamination gemessen, die durch Zersetzung einer an einer Wolfram-, Molybdän- und rostfreien Stahl-Oberfläche adsorbierten Kohlenwasserstoffschicht durch einen Ionenstrahl entstanden war. Die beobachtete Tiefenwirkung des Kohlenstoffs im oberflächennahen 30 Å-Bereich weist darauf hin, dass die konventionellen Reinigungsmethoden der innersten Wand für eine vollständige Entfernung dieser Verunreinigung unwirksam sind.

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1. Introduction

The contamination of a CTR plasma by species resulting from first-wall interactions may prevent the successful attainment of a sustained fusion reaction. It is, therefore, important to understand the interaction of plasma species such as hydrogen and helium with candidate first-wall materials, and the role of surface impurities in such interactions. Of particular interest is the interaction of energetic plasma species with adsorbed hydrocarbon contaminants since the products of such interactions may alter the surface composition of first wall materials. Because reaction products are expected to remain within the first ten or twenty atomic layers, conventional surface sensitive techniques cannot be used to reliably profile their depth distribution.

It is the purpose of this paper to describe how a relatively new surface analytic technique, Imaging Field-Desorption Mass Spectroscopy (IFDEMS) [1], can be used to detect and depth profile all species in the near surface region of first wall materials. Since depth profiles can be obtained with angstrom resolution, depth profiles within the first few atomic layers of the surface can be accurately determined. In order to demonstrate the unique profiling capability of the IFDEMS technique, depth distributions of a carbon impurity formed on the surface of candidate first-wall materials, and its penetration into the near surface region, will be presented.

Imaging Field-Desorption Mass Spectrometry combines the atomic resolution of the field-ion microscope with the single particle detection sensitivity of a sensitive time-of-flight mass spectrometer. Using the high-field effects of field-ionization and field-evaporation [2], the surface of a specimen can be non-destructively imaged in atomic resolution, and then "peeled away", layer-by-atomic layer, to determine the depth profile of species with angstrom resolution in the near surface region. For IFDEMS analysis, a positive high voltage pulse is applied to the specimen, and adjusted in amplitude to initiate field evaporation of surface atoms. Simultaneously, this pulse starts suitable timers which are stopped by the arrival of the resulting ions at an imaging detector [3], placed a known distance from the specimen. From the measured travel times, known kinetic energy, and drift distance, the mass-to-charge ratio of the surface species can be determined. But an additional analytic capability exists as well. Since the ions arrive at the detector preserving their relative crystallographic positions on the specimen surface, a photograph of the fluorescent screen of the detector, taken during each pulse, will give the relative locations of the arriving species. By time-gating the detector to be active coincidently with the arrival of only one selected species, its distribution on the surface can be

	AUGER SPECTROSCOPY	IMAGING FIELD-DESORPTION
ELEMENTS THAT CAN BE DETECTED	$Z \geq 3$	$Z \geq 1$
ELEMENTAL IDENTIFICATION	VERY GOOD	EXCELLENT
TYPICAL SURFACE RESOLUTION (Å)	10^6 (0.1 mm)	4
SENSITIVITY (TYPICAL NUMBER OF ATOMS ATOMS NEEDED FOR ANALYSIS)	10^8 (.01 monolayer)	2
DEPTH PROBED DURING ANALYSIS (Å)	20	2
DEPTH DISTRIBUTION	YES / DESTRUCTIVE	YES / DESTRUCTIVE
MAXIMUM PROFILE DEPTH (Å)	10^4	800
DEPTH PROFILES ARE	RELATIVE	ABSOLUTE

Fig. 1. A comparison of Auger Electron Spectroscopy and Imaging Field-Desorption Mass Spectroscopy (IFDEMS). Since the former can only detect species for $Z \geqslant 3$, it is not suited for direct surface analysis of implanted plasma species. Also, its limited depth resolution (≈ depth probed during analysis) makes accurate profiling in the near surface region difficult.

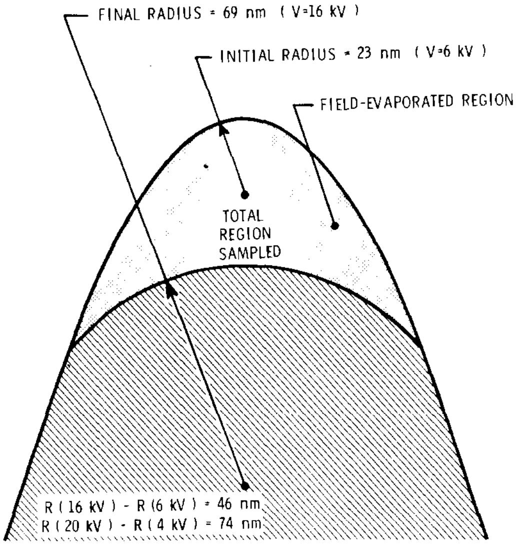

Fig. 2. A summary of the effects of depth profiling on an Imaging Field-Desorption Mass Spectroscopy specimen. The area from which species are detected, at a given specimen radius, is determined by the fraction of the total species intercepted by the spectrometer detector.

selected from those of the other species arriving at the detector at other times. The resulting two-dimensional picture, when compared to a field-ion-image showing surface structure, gives the crystallographic location of the selected species. Since each pulse applied to the specimen corresponds to a deeper, known penetration into the specimen, a three-dimensional profile of the species within the near surface region can be obtained.

It is instructive to compare several features of the IFDEMS technique to those of Auger Electron Spectroscopy, a widely known and recognized surface analytic technique. This is done in fig. 1. Specifically, IFDEMS can detect all elements with excellent identification capability (isotopes can be resolved in many cases), can determine two-dimensional surface distributions with angstrom resolution, and can probe the depth of the specimen with angstrom resolution as well. However, such capability does have its price. Only very small regions of specially prepared specimens * can be examined, with the usual profiling depth limited to about 500 Å. The reason for this limit is a constraint on the initial and final specimen radius. Successive field-evaporation of the specimen increases the specimen radius, requiring a higher potential to produce the field necessary to field-evaporate the surface. As the specimen potential is increased, the kinetic energy of the resulting ions is increased, and the arrival time between adjacent species at the detector, decreased. Finally, for a large specimen radius, the arrival time separation becomes too small for adequate mass resolution and time-gating of the detector. The initial specimen radius is limited by sample preparation techniques to about 200 Å (corresponding to a 6 kV ion-imaging potential), although for the refractory metals, 150 Å (4 kV) specimens can often be obtained. Fig. 2 summarizes IFDEMS depth profiling capability and also shows that the actual region sampled is smaller than that from which species are produced. The extent of the sampled region is fixed by the fraction of the total species intercepted by the

MASS (TIME) RESOLUTION
.118m DRIFT DISTANCE

T (2,1) = T (M/n = 2) - T (M/n = 1)

V	R	T(2,1)	T(3,2)	T(4,3)	T(6,4)	T(8,6)	T(12,8)	T(16,12)
4	15	56	43	36	60	51	85	72
6	23	45	35	29	49	41	70	59
12	50	32	25	21	35	29	49	41
16	69	28	21	18	30	25	43	36
18	79	26	20	17	28	24	40	34
20	89	25	19	16	27	23	38	32

V = TOTAL SPECIMEN POTENTIAL (kV)

R = AVERAGE SPECIMEN RADIUS (nm)

T(2,1) = (ns)

Fig. 3. Time resolution (and therefore mass-to-charge resolution) with Imaging Field-Desorption Mass Spectroscopy. As the specimen radius increases (due to successive field-evaporation), the specimen potential required to establish the evaporation field increases and the time separation of adjacent species decreases. For large specimen radii mass-to-charge resolution suffers (the species enclosed by the dotted region can just be resolved).

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* The same specimen preparation procedures used for field-ion microscopy are used for IFDEMS. That is, wire specimens are electropolished to a sharp point (typically 400 Å in diameter). However, since field-desorption imaging (not field-ion imaging) is used as the primary analytic technique, restrictions on the type of material which can be examined are considerably relaxed. Low melting point materials, or those having small yield stress, can be analyzed since considerably lower electric fields are required for field desorption of these materials.

spectrometer detector. However, the important point si that if one assumes a conservative initial and final radius of 230 Å and 690 Å, respectively; a total depth greater than 400 Å can be examined. Fortunately, this includes the near surface region of the bulk expected to be most greatly influenced by low energy impacting plasma species in CTR devices.

Fig. 3 shows the time separation expected for low Z species arriving at the spectrometer detector as a function of specimen potential (or specimen radius). In practice, two species can be resolved if they are separated by at least 15 ns in time, so that the species enclosed by the dotted area can be just marginally resolved. With the possible exception of separating $m/n = 4$ and $m/n = 3$ (18 ns separation at 16 kV), all low Z species expected in CTR devices can be isotopically resolved.

For the IFDEMS technique to be viable, the specimen must survive irradiation by plasma species and neutrons in a hostile CTR environment, and be capable of being transported between the CTR device and the analyzing spectrometer without damage. Neutron irradiation damage of initially perfect field-ion specimens has been studied by several workers [4,5] using conventional field-ion imaging techniques. For high doses ($10^{20}/\mathrm{cm}^2$) of fast neutrons, lattice damage has been reported but at least for refractory metals, specimens have survived repeated field evaporation. In order to investigate the survival of specimens as a result of irradiation with typical plasma species at a remote location, specimens were irradiated in an ion implantation facility separated from the IFDEM Spectrometer. Medium energy (20 kV) He_3^+ and D_2^+ ions were implanted into stainless steel, molybdenum and tungsten specimens at several fluences. Although 20 kV ions penetrate deeper than IFDEMS profiling capability, an examination of the specimens following irradiation was expected to provide valuable information regarding surface interactions, particularly since the ambient vacuum conditions (which influence surface contamination) approximated those expected in operating CTR devices. Deuterium and He_3^+ were used as implantation species so that their effects on the specimen could be separated from those of normal helium and hydrogen background species found in the analyzing spectrometer.

Table 1 indicates the conditions under which eight representative specimens were examined. Two specimens did not survive. One was damaged upon insertion into the spectrometer, the other experienced a large change in radius probably due to ion-beam heating as a result of poor thermal contact with its mounting. Two controls specimens were employed. One was subjected to ambient accelerator environment, but was not irradiated. The other was exposed to laboratory ambient.

Table 1
A summary of the irradiation conditions and samples used for the IFDEMS examination reported in this paper.

Sample material	Approx. initial radius (nm)	Irradiation species	Dose ($\mathrm{C/cm}^2$)
Molybdenum	40	helium	2.4×10^{-6}
Tungsten	40	deuterium	2.4×10^{-6}
Molybdenum	40	helium	2.4×10^{-5}
302 S.S.	40	deuterium	2.4×10^{-5}
Molybdenum	40	helium	2.4×10^{-4}
302 S.S.	40	deuterium	2.4×10^{-4}
Molybdenum	40	helium	2.4×10^{-3}
302 S.S.	40	deuterium	2.4×10^{-3}
302 S.S.	40	none (in situ control)	
302 S.S.	40	none (air exposure only)	

All specimens examined, with the exception of the two controls, exhibited a dense layer of carbon contamination at the surface. This layer was always removed at fields below those required for ion-imaging of the substrate and therefore represented a carbon deposit on the surface. Since the deposit was removed below ion-imaging fields, its thickness could not be accurately determined. However, the total amplitude of the observed carbon peaks (C^+, C^{2+}) was approximately an order of magnitude greater than that observed for the non-irradiated, in-situ control. The control exposed to ambient laboratory atmosphere showed no appreciable carbon contamination. Since the samples were analyzed by IFDEMS prior to irradiation, and exhibited no carbon contamination, these observations suggest that the surface carbon build-up resulted from ion-beam decomposition of continually adsorbing hydrocarbon vapor known to be present. The in-situ control exhibited less carbon build-up. Only a monolayer of hydrocarbon species would be expected to adsorb, with no appreciable decomposition of the adsorbed layer occurring until the high field, used for IFDEMS examination, was applied. The control exposed to laboratory ambient showed no appreciable carbon build-up as would be expected for a specimen exposed to a clean, hydrocarbon-free environment.

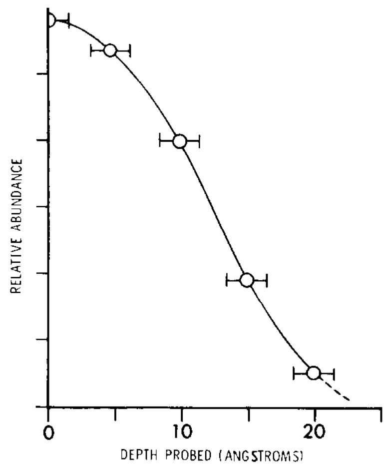

Fig. 4. Depth profile of a carbon impurity in the near surface region of a 302 SS specimen irradiated with 2.42×10^{-3} C/cm^2 of 20 kV D_2^+ ions. Background pressure = 8×10^{-8} torr. The carbon impurity, found after irradiation of an initially "clean" specimen, was caused by decomposition of an adsorbed hydrocarbon contaminant with subsequent penetration into the near surface region.

Surprisingly, field evaporation of the irradiated specimens showed that the carbon impurity usually extended 30 Å into the bulk. Fig. 4 shows a representative depth profile of the observed carbon contaminant in the near surface region of 302 stainless steel. The other irradiated specimens exhibited similar behavior with carbon contamination extending to a maximum depth of 30 Å from the surface *.

The depth profiles indicate that a carbon contaminant (produced at the surface by hydrocarbon decomposition) will penetrate the near surface region of the bulk as a result of ion-bombardment of the surface. This observation may have important, practical consequences for clean-up procedures in operating CTR devices. Since carbon contamination may be expected to penetrate the near surface region, cleaning techniques which only remove surface contamination may prove inadequate. This suggests that every effort should be made to eliminate surface contamination *initially,* since it will usually be much more difficult to remove the species produced by interaction with plasma species. Although one can argue that carbon contamination is not presently limiting CTR device operation, it is not clear that it will not prevent a sustained fusion reaction from being achieved. What is clear is that a primary source of carbon, hydrocarbon contamination, can be effectively minimized by attention to proper vacuum technique. Unlike many potential CTR surface problems, the elimination of this surface contaminant depends not on the availability of exotic materials, but on a commitment by those responsible for reactor design to eliminate all sources of hydrocarbon contamination.

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* Obviously, the penetration of carbon (or any surface contaminant) into the near surface region will be influenced by many factors including crystallography and lattice imperfections, specimen temperature, and probably the concentration gradient of impurities at the surface. As a result, the 30 Å maximum depth reported here may change, if different initial conditions are imposed.