Molecular depth profiling with reactive ions, or why chemistry matters in sputtering.

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Important notice: this document is not in a proceeding format yet. It only shows some figures with short comments. It should be used as an **extended abstract**, only intended for conference attendees, in order to prepare for the discussion day.

Abstract

Depth profiling of organics has long been considered as a dream impossible to reach, owing to fast molecular degradation upon ion irradiation. The advent of polyatomic ion sources has dramatically defeated this assumption and spectacular advances in the field have occurred over the last five years. More recently, we have shown that low energy reactive ions, like Cs^+ or O_2^+, can also be used quite successfully for organic depth profiling.

In this paper, we will review the recent knowledge on cesium and, to a lesser extent, oxygen depth profiling of organics. We will show that most polymers, but also smaller organic molecules, like amino acids, sugars or vitamins, are amenable to molecular depth profiling with reactive ions. We will discuss how the ion energy, the enhanced ionization and the high chemical activity of the ions work together to preserve the molecular integrity of the analyzed species. In contrast with cluster depth profiling, in which the mechanistic aspects of the cluster surface interaction are dominant, leading to very high sputtering yields, we show how chemical effects dominate in reactive ion sputtering. Two "mechanically" identical ions such as cesium and xenon, at identical experimental conditions, lead to extremely different results: stable molecular signals with cesium, but an immediate degradation with xenon. Only the ion chemistry changes, proving that cesium reactivity plays a major role in organic depth profiling, most likely by preventing crosslinking reactions. Quite surprisingly, we also show that low energy (below 1 keV) Xe^+ ions can be used to perform molecular depth profiling on some organic compounds with high yields and very limited damages.

Short introduction

We will discuss in the paper the major role played by the sputtering ion's chemistry on molecular depth profiling. Two types of organic materials will be considered: polymers and (non-polymerized) organic compounds. First we will recall some recent data obtained with low energy Cs^+ ions on polymers. We will then concentrate on sputtering yields measurements on three polymers (PMMA, PC and PS) obtained with Xe^+ and Cs^+ ions. The role of the energy will also be discussed. From those measurements, a model explaining why Cs is so successful on polymers will be given. In the second part of the paper, we will show our newest data on various organic solids (amino acids, vitamins) obtained with low energy Cs^+, Xe^+ and O_2^+ ions. We will finally summarize those observations, comparing the pros and cons of different projectiles.

Experimental

TOF SIMS IV (IONTOF) in a dual beam mode:
-analysis: Ga^+, 15 keV, 1 pA
-sputtering: Cs^+, Xe^+, O_2^+, 150-1000 eV, 10-50 nA
-non-interlaced mode to limit the Ga fluence

Part I: Polymers

Several polymers were successfully depth profiled with low energy Cs^+ ions: PMMA, PC, PS, PET, PEO, PP, PE, PPS… This paper will focus on PMMA, PC and PS. It is know that PMMA is a polymer of the "degrading" type, meaning that it fragments upon irradiation, whereas PC and PS are of the "cross-linking" type, meaning that they cross-link upon irradiation.

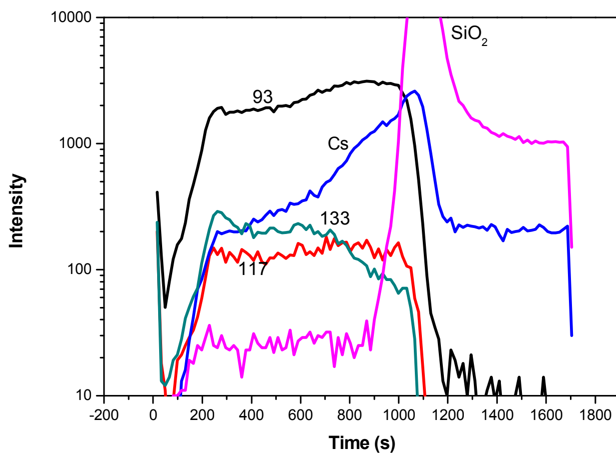


Fig.1. 200 eV Cs^+ on polycarbonate (50 nm/Si), negative depth profile. Specific molecular fragments (*m/z* 93, 117, 133) are measured throughout the depth profile. In the initial transient, the molecular signals decrease first rapidly then recover when the implanted Cs subsurface layer is reached.

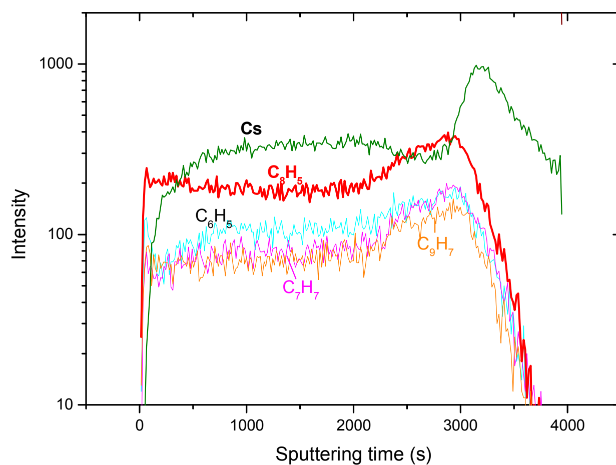


Fig. 2. 200 eV Cs^+ on polystyrene (50 nm/Si), negative depth profile. Many hydrocarbon fragments were measured in the negative mode, such as $C_8H_5^-$ (likely C_6H_5-C≡C^-) indicating that the polymer keeps its molecular integrity upon Cs irradiation. Other evidences come from XPS measurements in the steady state, showing that the aromatic shake-up peak remains.

Similar depth profiles will be shown at the conference on PET and PMMA. When 200 eV Xe^+ ions are used on PC and PS, no molecular depth profiling is possible since molecular signals disappear after a few seconds of sputtering. However, some molecular information persists on PMMA. This is not really surprising as PMMA fragments easily upon irradiation. In order to understand the role of the projectile's chemistry on sputtering, sputtering yields were measured on PS, PC and PMMA with 250 eV Xe^+ and Cs^+ ions. The data are summarized in table 1:

Sputter Ion	Sputtering yield (atoms/ion)		
	PS	PC	PMMA
250 eV Xe^+	0.61	0.63	17
250 eV Cs^+	4.9	3.4	23

Table 1: Sputtering yields obtained with Xe^+ and Cs^+ ions on PS, PC and PMMA

The sputtering yield on PS and PC (cross-linking type) are much higher with Cs than with Xe. The sputtering yield on PMMA (degrading type) is much higher than on PS and PC with both projectiles. On PS and PC, Xe ions rapidly produce cross-linking reactions, degrading the polymer into a graphitized structure, with a very low sputtering yield. When a reactive ion like Cs is used, the implanted Cs atoms react with the free radicals created in the polymer, which prevents the cross-linking (Please note: this will be discussed in detail at the conference).
The sputtering yields were also measured at six different energies: the data are summarized in figure 3:

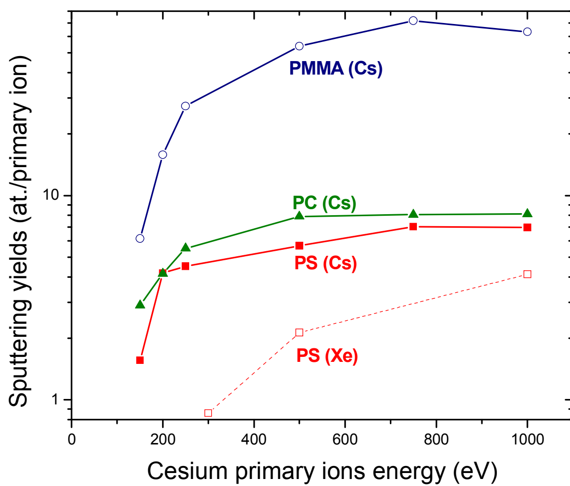


Fig. 3. sputtering yields on PC, PS and PMMA with 150-1000 eV Cs^+ ions. The Xe^+ sputtering yields on PS are also shown. Sputtering yields increase rapidly up to 500 eV then start to saturate. Cross-linking polymers (PS, PC) behave in a similar way, whereas sputtering yields on PMMA are always much higher, due to the easy fragmentation of such polymer.

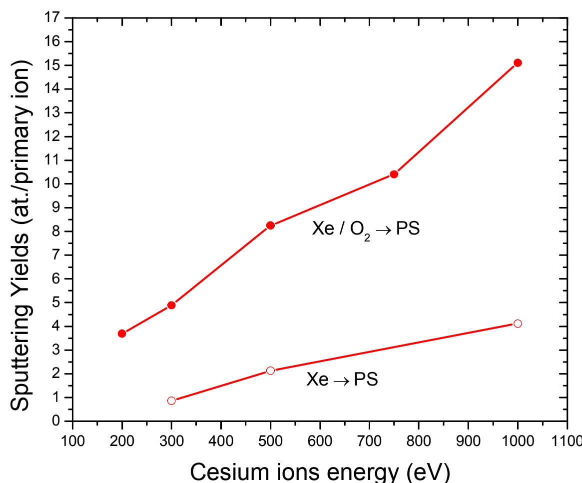


Fig. 4. Sputtering yields on PS obtained with Xe^+ and Xe^+ with O_2 flooding. The sputtering yields are remarkably increased just by the presence of O_2 molecules at the surface. The oxygen plays a role similar to Cs, reacting with the free radicals and inhibiting cross-linking. In this case however, the aromaticity of the polymer seems to be destroyed.

As a first conclusion, Cs^+ ions allow true molecular depth profiling on polymers owing to three factors:

1. The low energy

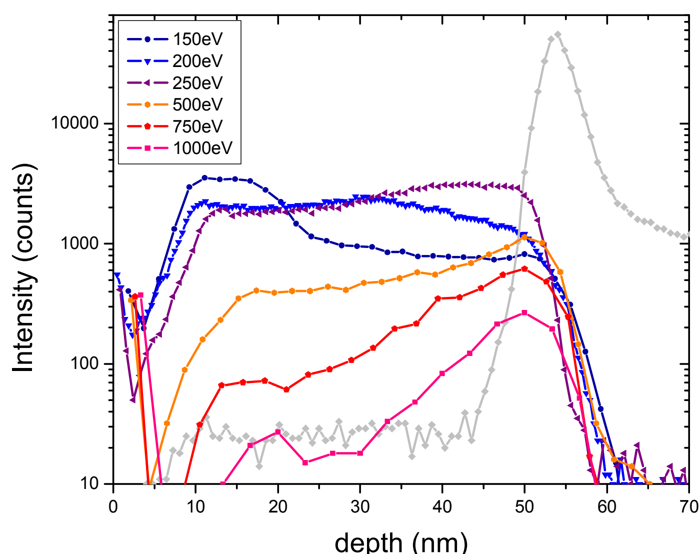
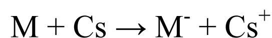


Fig. 5. Depth profiles on PC layers obtained with 150-1000 eV Cs^+ ions. The best profiles are obtained at low energy and severe polymer damages are measured at 1 keV. The steady state signals decrease with the energy and the transient becomes longer with the energy. The latter effect is due to the implantation depth of Cs, which increases with the energy.

2. The ionization enhancement

Cs is the most electropositive element (0.79 Pauling electronegativity) and a very strong reducer (redox potential -3.026 V). Polymer fragments are easily ionized in the presence of implanted Cs through electron transfer from the Cs (reduction):


$$M + Cs \rightarrow M^- + Cs^+$$

3. Chemical effects

Cross-linking reactions in polymers constitute a major limitation for depth profiling with ions. The extreme reactivity of Cs hinders the cross-linking reactions and help fragmenting the polymer. Xe^+ ions have similar masses but are inert: in this case, the polymer turns immediately into a heavily cross-linked, irreversibly damaged, material.

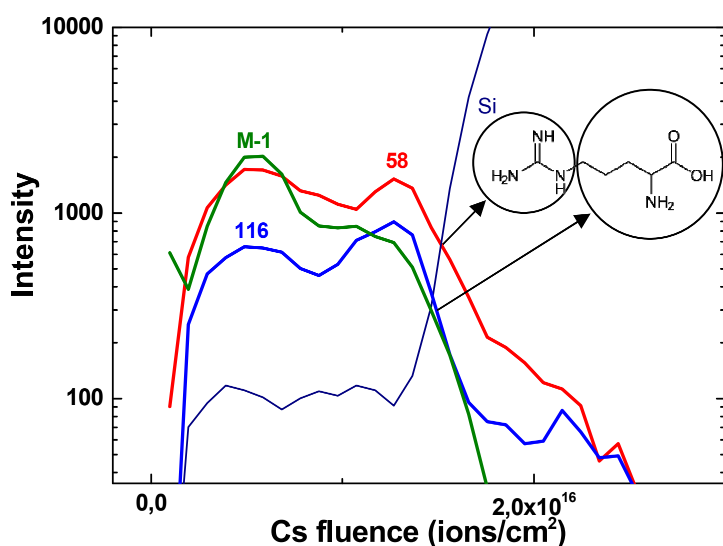
Part II: Organic compounds

Cs, Xe and O_2 depth profiles were obtained on various amino acids, sugars and vitamines. Only data on arginine and ascorbic acid are briefly reviewed in this extended abstract.

a) arginine (~100 nm layers):

Depth profiles were obtained with Cs^+ and Xe^+ at different energies. The molecular ion (M-1) can be followed with 250 eV Cs^+ throughout the depth profile (Fig. 6.), but no steady state is reached and the signal drops beyond a critical Cs dose. Large molecular fragments (m/z 58 and 116) remain, with relatively constant intensities. With 200 eV Xe^+ (Fig. 7.), a steady state

was surprisingly obtained, proving that molecular depth profiling is indeed possible with low energy Xe, with limited molecular damage.



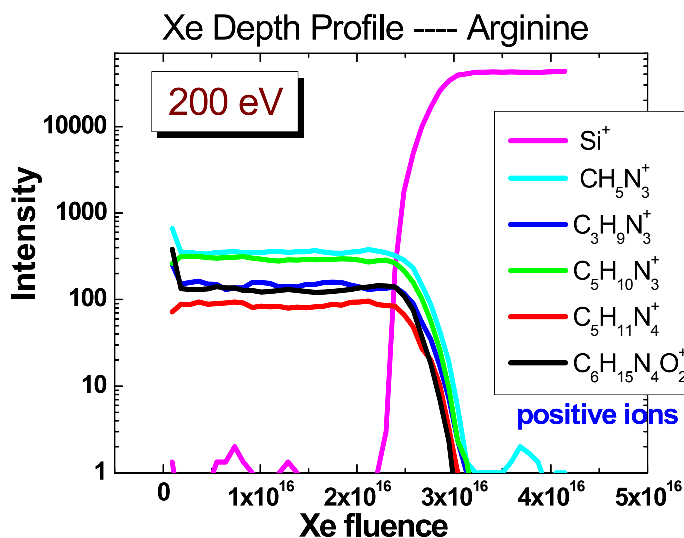


Fig. 6. 250 eV Cs^+ on arginine

Fig. 7. 200 eV Xe^+ on arginine

b) ascorbic acid $C_6H_8O_6$ (~70 nm layers)

On this compound, the molecular depth profiling with 200 eV Cs was unsuccessful, with all molecular signals dropping rapidly (Fig. 8.). On the other hand, an excellent depth profile was obtained with 200 eV Xe (not shown) and was even improved with O_2 flooding (Fig. 9.). This result again confirms that low energy Xe^+ can be used to depth profile organic compounds. Similar results were obtained on other amino acids and sugars.

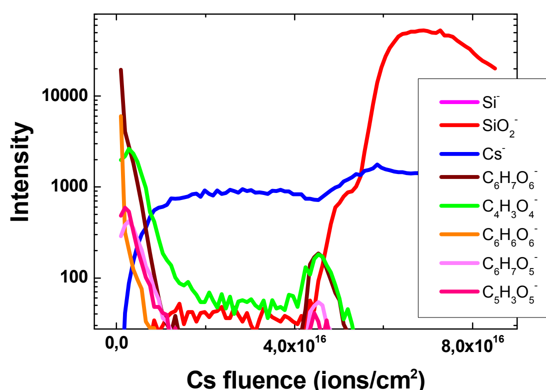


Fig. 8. 200 eV Cs^+ depth profile on ascorbic acid: molecular signals are rapidly lost and no steady state can be reached. The molecule is destroyed by the impinging Cs^+ ions.

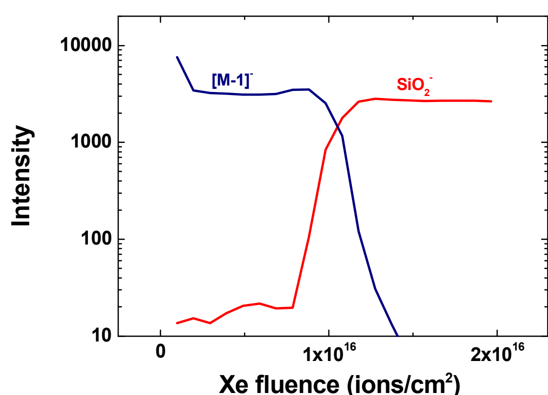


Fig. 9. 200 eV Xe^+ (plus O_2 flooding) depth profile on ascorbic acid: a high steady state value is measured on the molecular ion (M-1), proving that the molecule is only weakly damaged by low energy Xe^+ ions.

The results measured with Xe^+ will be discussed at the conference with damage accumulation and erosion models. Our measurements on different organic compounds generally indicate that a steady state is obtained with low energy Xe^+ ions but not always with Cs^+ ions. It appears that the compounds are more fragmented with Cs, which could again be explained by the high Cs reactivity. In addition to ion bombardment damages, implanted Cs atoms react directly with the molecules, what triggers fragmentation and sometimes destruction of the molecules.

Conclusions

As a short general conclusion, it turns out that the reactivity of implanted Cs atoms plays a dominant role in organic depth profiling. In the case of polymers, this reactivity is strongly beneficial as it promotes negative ionization and inhibits cross-linking reactions. In the case of organic compounds, while molecular depth profiling is still possible in most cases, the Cs reactivity induces fragmentation of the molecules. The molecular ion is often lost throughout the depth profile, but large fragments are still present in the profile. Surprisingly, Xe^+ ions can be used at low energy (<1 keV) to obtain molecular depth profiles on organic compounds.
The following table attempts to summarize the use of different projectiles on different classes of organic materials. This is of course extremely simplified and could be a starting point for further discussions at the conference.

	Cs^+	Xe^+	O_2^+	Cluster beams
PS, PC, PET (‘cross-linking’ type)	++	-	-	-
PMMA (‘degrading’ type)	++	+	+	+(+)
Organic compounds	+ / -	+(+)	+	++

Table 2: a comparison between different projectiles.
- - : no molecular depth profiling
- + : molecular depth profiling possible
- ++ : recommended for molecular depth profiling

Bibliography

A complete bibliography will be given in the proceedings paper. Part of this work is –or will be- published in the following references:

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