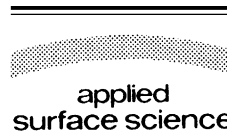




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# The formation of singly and doubly cationized oligomers in SIMS

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## Abstract

The cationization of sputtered organic species via metal particle adduction is investigated using poly-4-methylstyrene molecules in combination with Cu, Pd, Ag and Au substrates. Metal-cationization occurs for these four substrates. The cationized molecule yields vary with the considered substrate and they are not correlated with the metal ion yields. In addition, double cationization with two metal particles is observed with a very significant intensity for Cu, Ag and Au supports. We interpret the results with an emission scheme in which excited molecules and metal atoms recombine above the surface and decay via electron emission, thereby locking the complex in the ionic state.

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## 1. Introduction

The detection of large organic species in SIMS requires an extrinsic mechanism by which neutral molecules (M) capture a metal particle (Me) in order to become ions  $(M + Me)^+$ . This *metal-cationization* process is not completely understood yet. To improve our knowledge of the underlying physics, we started a systematic study of molecule cationization using a wide series of molecules and metallic substrates [1]. This paper focuses on the case of poly-4-methylstyrene and the chosen substrates are Cu, Pd, Ag and Au.

## 2. Materials and methods

Samples of poly-4-methylstyrene (P4MS; Mn = 3933 Da) are dissolved in toluene with a concentration of 1 mg/ml. The samples are prepared as thin films cast on 0.25–1 cm<sup>2</sup> substrates by depositing a droplet of the solution on the supports. The substrates are either thin metal foils (Cu, Ag, Pd) or metallized supports (Ag, Au). The metallized substrates are prepared by evaporating a 100 nm layer of the chosen metal (Ag, Au) on clean silicon wafers.

The secondary ion mass analyses are performed in a PHI-EVANS Time-of-Flight SIMS (TRIFT 1) using a 15 keV Ga<sup>+</sup> beam (FEI 83-2 liquid metal ion source) [2]. To improve the measured intensities, the secondary ions are post-accelerated by a high voltage (7 kV) in front of the detector. Measurements performed with two different detectors, Det 1 and Det 2, are compared throughout the article. In comparison with Det 2, Det 1

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exhibits a much more pronounced efficiency decrease as a function of ion velocity (see Section 3).

### 3. Results

P4MS has been chosen to illustrate the process of single and double cationization of organic molecules by metal particles. The high-mass parts of the mass spectra of P4MS, adsorbed on Au, Ag and Pd, are shown in Fig. 1. The mass spectrum of P4MS adsorbed on copper (not shown) is qualitatively similar to that observed with the gold substrate. In Fig. 1, we compare results obtained with Det 1 and Det 2 (*inset of second frame*). The mass spectra obtained with Det 1

exhibit two distributions of peaks, except for Pd substrates. Between 2500 and 5000 Da, one notices the regular distribution of metal-cationized oligomers  $(M + Me)^+$ , with a series of peaks separated by the mass of the P4MS repeat unit, i.e. 118 Da. The intensity is weak because the efficiency of Det 1 in this mass range is low. For comparison, the inset of the second frame shows the much higher intensity distribution obtained with Det 2 in the case of silver substrates.

The data provided by Det 1 are primarily valuable because they reveal a second series of peaks in the range 1500–2500 Da in the spectra corresponding to Ag and Au (Cu) substrates. The maximum of this distribution is close to half the molecular weight of the

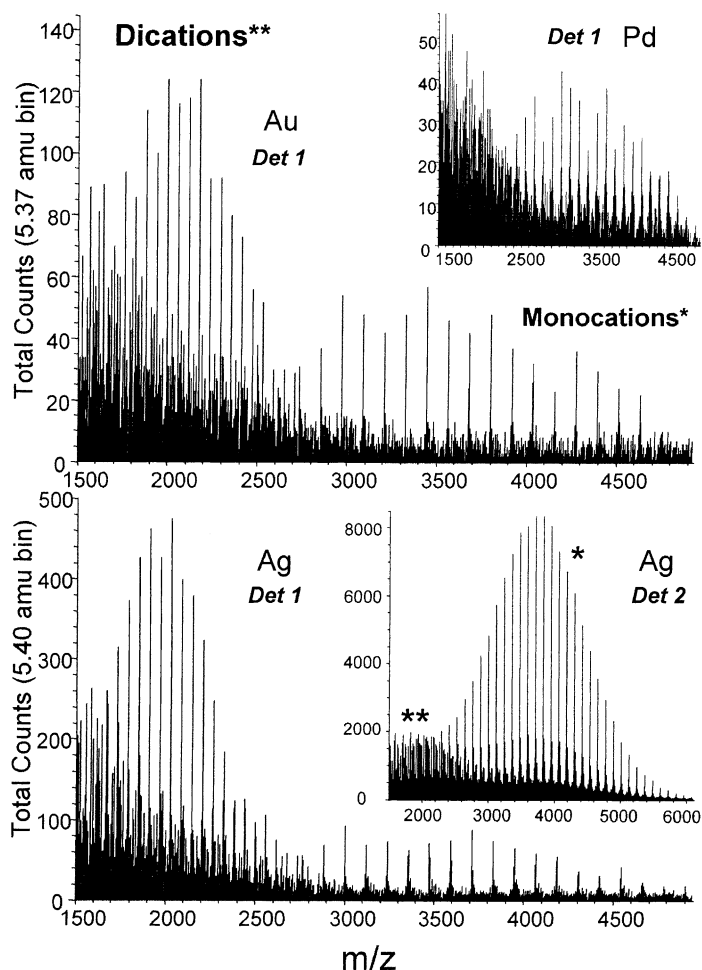


Fig. 1. High-mass range of the mass spectrum of P4MS cast on various substrates (Au, Pd, Ag).

P4MS oligomer sample, and the separation between consecutive peaks is about 59 Da, i.e. half the mass of the P4MS repeat unit. The mass assessment procedure indicates that these peaks correspond to the formula  $(M + 2Me)^{2+}$ . In contrast with Ag and Au (Cu) supports, Pd substrates give rise to  $(M + Me)$  monocations but do not seem to produce  $(M + 2Me)$  dications. Complementary measurements with a lower mass polystyrene sample show that Pd substrates induce the emission of  $(M + 2Me)$  dications but with a lower efficiency than the three other substrates [1]. The dication distribution would probably have remained unnoticed using only Det 2 because the obtained spectrum is strongly dominated by the more intense singly charged parent and fragment ion distributions (*inset of second frame*). In contrast, large dications are highlighted by Det 1, probably because they hit the detector with a two times larger momentum which allows them to preferentially overcome the detection threshold of Det 1. A qualitatively similar effect can be observed with Det 2 when decreasing the post-acceleration voltage from 7 to 2 kV.

The measured yields of singly cationized molecules are between  $10^{-7}$  (Det 1) and  $10^{-5}$  (Det 2) and the yields of dications are in the  $10^{-6}$  range irrespective of the detector. Obviously, these are just indicative values because the measured yields are strongly influenced by the detection efficiency, which varies with the detector properties, the secondary ion mass and the post-acceleration voltage.

#### 4. Discussion

The commonly accepted description of the metal-cationization process involves the association of a *neutral molecule* and a *metal cation*. Several experimental results show that this simple depiction is questionable.

First, the absolute yields of metal cations are generally low. In our case, the measured metal ion yields, listed in Table 1, vary between  $10^{-4}$  ( $Au^+$ ) and  $10^{-2}$  ( $Ag^+$ ). Therefore, the recombination of a sputtered molecule with a metal cation should be a very low probability event, more so the recombination of a molecule with two of them (dications). In a previous article, a yield of cationized molecules that is 50 times that of the metal ion is reported for tetraphenylnaph-

Table 1

Measured<sup>a</sup> yields of metal ions and calculated<sup>b</sup> yields of metal atoms (number of secondary particles/primary particle)

	Cu	Pd	Ag	Au
Ions <sup>a</sup>	$5.3 \times 10^{-3}$	$1.7 \times 10^{-3}$	$9.3 \times 10^{-3}$	$1.8 \times 10^{-4}$
Metal atoms <sup>b</sup>	15.3	15.2	17.1	18.5
Metal oxide	7.5	7.2	11.9	13.5

<sup>a</sup> SIMS measurements.

<sup>b</sup> TRIM calculations.

talene molecules adsorbed on gold [3]. Such a high yield indicates a recombination probability almost equal to one in the hypothesis of the molecule-cation clustering hypothesis, which is not realistic.

The quoted study also shows that yields of metal-cationized molecules and metal cations are generally not correlated. In particular, the strong dependence of the metal cation yield on the work function of the surface contrasts with the independence of the cationized molecule yield towards this physical parameter [3]. In the present study, the yields of singly cationized molecules are similar (for a given detector), whereas the yields of metal cations vary by almost two orders of magnitude (Table 1).

Because of these inconsistencies, we propose that neutral molecules recombine with metal atoms rather than ions and become ionized as a result of the clustering process [4]. In this framework, the issue of the low metal particle yield is alleviated. Indeed, Table 1 shows that the neutral yield, calculated by TRIM [5], is 3–5 orders of magnitude larger than the ion yield for pure metal as well as oxidized surfaces. Considering that each event induces the sputtering of about 10 metal particles, not only single, but also double cationization should be possible. In contrast with metal ion yields, the atom yield variation as a function of oxidation is very limited (Table 1), which can explain why cationization does not strongly depend on that parameter, as observed in Ref. [3]. Finally, the observed yields of cationized P4MS molecules are not very sensitive to the chosen substrate in Fig. 1, which is also true for neutral atoms, but not for metal ions (Table 1).

Mechanistically, the metal particle and the organic molecule may approach closely enough to pass a crossing between the neutral and ion potential energy curves during the sputtering event. At this point, the complex becomes auto-ionizing and the ejection of an

electron is favored (Hornbeck–Molnar process [6]). Considering the cationization of styrene-based polymers, e.g. P4MS, the vibrationally excited functional groups (e.g. phenyl) of the molecule and the metal atom will be the reactants. The emission of an electron constitutes a way to dissipate the energy released by the reaction. Once the electron is ejected, the isolated complex is locked in the ionic state. A detailed treatment involving *ab initio* calculations is proposed elsewhere to describe this associative ionization process in a quantitative way, with benzene molecules and Cu, Ag, Au atoms as reactants [4].

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