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Kinetic energy distribution of molecular fragments sputtered from poly(ethylene terephthalate) under indium ion bombardment: effects of the primary beam energy and angle

A. Delcorte [a], X. Vanden Eynde [a], P. Bertrand [a,*], D.F. Reich [b]

[a] *Unité de Physico-Chimie et de Physique des Matériaux (PCPM), Université Catholique de Louvain, 1, Place Croix du Sud, B-1348 Louvain-la-Neuve, Belgium*
[b] *Physical Electronics, 575 Chesapeake Drive, Redwood City, CA 94093, USA*

Abstract

Thin poly(ethylene terephthalate) (PET) films were bombarded by In^+ ions with different primary beam conditions, and the positive secondary ions were mass- and energy-analysed by means of a Time-of-Flight Secondary Ion Mass Spectrometer. In the context of a wider study devoted to the emission processes of molecular ions sputtered from polymers, the aim of this work was to check the influence of two of these parameters (primary impact energy and incidence angle) on the kinetic energy distributions (KED) of the observed ions. In general, the shape of the measured kinetic energy distributions is almost independent on the primary ion energy, as shown by the similar spectra observed with 7–22 keV In^+ primaries. Nevertheless, the energy spectra of the fingerprint fragment ions obtained at 2 keV with an impact angle of 65° are broader than those observed for higher energy and lower impact angle (7–22 keV; ~40°). Indeed, the KEDs measured in the (2 keV; 65°) bombardment conditions show an additional contribution centred around 5–6 eV, i.e. in the high energy tail of the distributions. The relative intensity of this contribution increases with the fragment size, up to 15% of the total ion intensity for $C_{17}H_{12}O_5^+$. The results are discussed in terms of collision cascade propagation in the surface region of the target, by comparing the experimental observations to simulations realised with the TRIM code. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Secondary Ion Mass Spectrometry; Sputtering; Ion emission; Kinetic energy; Poly(ethylene terephthalate); TRIM

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1. Introduction

Static Secondary Ion Mass Spectrometry (SIMS) is now widely used for the analysis of organic compounds [1], as indicated by the growing number of reference spectra in the databases [2]. Nevertheless, the mechanisms by which large molecular ions may be desorbed are not fully understood yet. In other papers, we have used the kinetic energy distributions (KED) of these organic ions as a means to improve our knowledge of the fundamental processes in molecular SIMS. Among

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[*] Corresponding author. Tel.: +32-10-473581; fax: +32-10-473452; e-mail: bertrand@pcpm.ucl.ac.be

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them, the following mechanisms have been explained: the emission of low-energy, precursor-like species, of faster and strongly dehydrogenated ions [3,4], of rather energetic cationised oligomers and molecules [5], as well as the unimolecular dissociation of excited ejecta [6,7]. In this paper, we investigate the effects of the primary beam energy and incidence angle on the KED of molecular fragments sputtered from PET. In direct relation with this study, the influence of the primary beam nature, energy and angle on the absolute and relative secondary ion yields will be discussed at length in Ref. [8] for poly(styrene), poly(methyl methacrylate) and poly(ethylene terephthalate) (PET) samples, whereas a more detailed study of the KED of PET secondary ions will be available in Ref. [9].

2. Experimental

2.1. Samples

The PET was dissolved in hexafluoro-4-isopropanol. The samples were prepared as thin films cast on silicon substrates (1 cm^2), by depositing a droplet of the solution on the supports. Prior to deposition, the substrates were rinsed in water of HPLC grade from a milli-Q system (Millipore), isopropanol and hexane. The low concentration of the solutions allowed us to deposit very thin polymer layers, ensuring a good electric contact between the top surface and the sample holder. To verify this, all the energy measurements were realised with samples for which the substrate secondary ion peaks were present in the ToF-SIMS spectra and weak enough to avoid any substrate effect [6,7].

2.2. Kinetic energy measurement

The KED measurements were performed in a PHI-EVANS Time-of-Flight SIMS (TRIFT 1) using a (5 kHz) pulsed In$^+$ beam ($\sim$500 pA DC) [10]. The angle between the primary ion source and the spectrometer axes (perpendicular to the surface) was 35°. Four different primary beam energies (at impact) were used in this study: 2, 7, 12 and 22 keV. Due to the primary beam deflection by the high electric field in the acceleration section of the spectrometer (the sample surface was at +3000 V and the extractor was at ground potential), these different energies corresponded to different beam impact angles (with respect to the surface normal): 65.1°, 43.3°, 39.9° and 37.7°, respectively. To obtain the energy spectra, a $+(3000-\Delta)$ V potential was applied to the sample. At the crossover following the first electrostatic analyser, where the energy dispersion is maximum, the secondary ions were energy selected by a slit of fixed width (100 μm corresponding to a passband of 1.5 eV). The acquisition of mass spectra for different sample voltages (different Δ) allowed us to collect the signal corresponding to different energy windows of the KED, a one V increase of the sample potential corresponding to a one eV decrease in the KED. To improve the measured intensities in these KEDs, the secondary ions were post-accelerated by a high voltage (10 kV) in front of the detector. In order to avoid polymer degradation and surface charging during the experiment, the stability of the characteristic $C_6H_4CO^+$ ion intensity was checked up to a larger primary ion fluence than that needed for one set of measurements on the same area. At least two sets of measurements were realised on different sample areas for each KED. Between successive measurements, the energy slit was slightly shifted by a distance corresponding to $\sim$0.5 eV. By this means, the second data set covered the intermediate energy windows that were not available from the first data set. The zero of energy scale was estimated from the intersection between the tangent to the increasing part of the KED of atomic ions and the energy axis. The corrected value of the sample voltage, giving the initial kinetic energy of the secondary ions, will be called ‘apparent kinetic energy’ in the following.

3. Results

The positive ion mass spectra of PET obtained using the same mass spectrometer but with 12 keV, Ga$^+$ [11] and 8 keV, Cs$^+$ primary ions have been shown elsewhere [12]. The most characteristic secondary ions are: $C_6H_4^+$ ($m/z = 76$), $C_6H_4CO^+$ ($m/z = 104$), $C_4H_6(COOH)CO^+$ ($m/z = 149$), and the deprotonated and protonated monomer ($m/z = 191$, 193) [2]. Fragments larger than the monomer, including dimers and trimers are also detected. The mass spectra obtained with In^+ primary ions are qualitatively closer to that realised with Cs^+ primary ions (not shown). Indeed, in contrast with gallium measurements, the large characteristic ion $C_6H_4CO^+$ ($m/z = 104$) is much more intense than the smaller $C_2H_3^+$ ($m/z = 27$) for both cesium and indium bombardment. This may be explained by the significantly larger mass of these two ions in comparison with gallium [13]. As mentioned in the introduction, the spectra obtained under indium bombardment will be shown in a more detailed paper, as well as the effect of the primary ion energy on the secondary ion yields [8].

In order to improve our knowledge of the desorption mechanisms, KED measurements were performed with (2 keV; 65°), (7 keV; 43°), (12 keV; 40°) and (22 keV; 38°) indium primary ions. In Fig. 1, we report the energy spectra of several molecular ions observed in the mass spectrum of PET ($C_3H_3^+$: $m/z = 39$; $COOH(C_6H_4)CO^+$: $m/z = 149$; $(M–H)^+$: $m/z = 191$). As expected from previous measurements realised with polymer targets [4,6,7], the high energy tail of these distributions is very steep (steeper than E^{-2} as predicted by the Sigmund–Thompson model) and the measured intensities become negligible beyond 10 eV, especially for large characteristic ions. With decreasing ion size, the KED broadens regularly [3]. This is obvious when comparing the KED of $C_3H_3^+$ to that of larger molecular ions ($COOH(C_6H_4)CO^+$: $m/z = 149$; $(M–H)^+$: $m/z = 191$). In addition, Fig. 1 demonstrates that the dependence of the KED shape on the primary beam energy is insignificant. Indeed, the distributions are similar for 7, 12 and 22 keV, i.e. where the angular variation is weak. The small differences between these measurements are within the experimental error. However, the shape of the KEDs obtained with the (2 keV; 65°) conditions looks different, especially for large characteristic ions. As main difference, one may remark the relative augmentation of the 'high energy' fraction beyond 5 eV. In addition, this fraction increases with the mass of the considered ions in the range $27 \leqslant m/z \leqslant 296$.

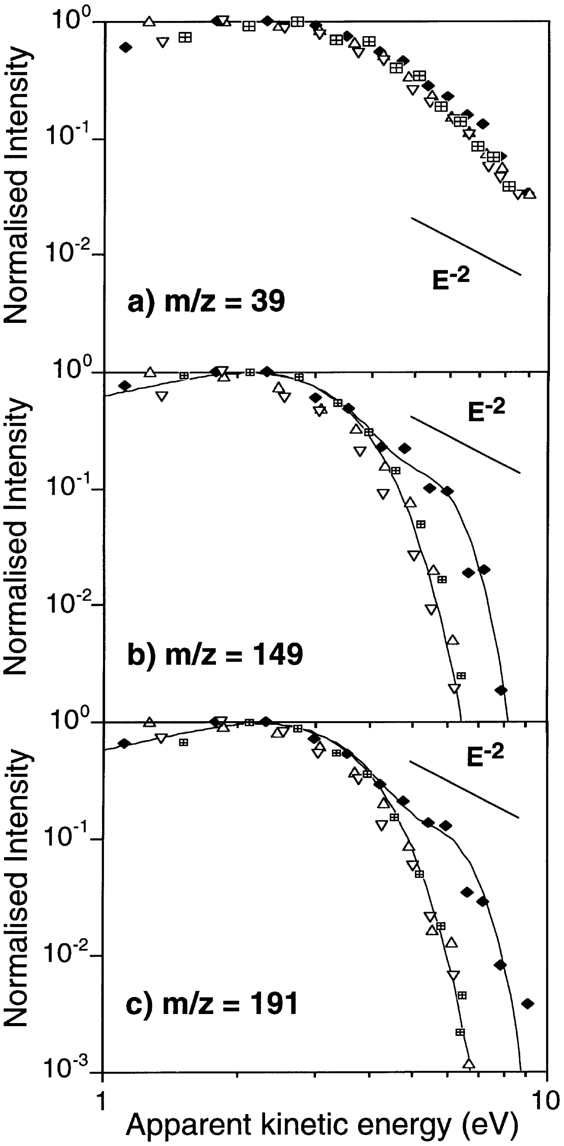

Fig. 1. Kinetic energy distributions of characteristic molecular ions sputtered from PET samples bombarded by (2 keV; 65°) (◆), (7 keV; 43°) (×), (12 keV; 40°) (▽) and (22 keV; 38°) (⊞) In^+ primary ions. (a) $C_3H_3^+$: $m/z = 39$; (b) $COOH(C_6H_4)CO^+$: $m/z = 149$; (c) $(M–H)^+$: $m/z = 191$.

To quantify this high energy contribution, the KEDs obtained with 7, 12 and 22 keV have been fitted, and the additional function needed to account for the high energy part of the 2 keV distributions has been calculated. After integration of the two curves, the intensity corresponding to the low-energy (I_{LE}) and to the high-energy (I_{HE}) contributions have been obtained. The histogram of Fig. 2 shows the relative fraction corresponding to the high-energy contribution, $I_{HE}/(I_{LE}+I_{HE})$, as a function of the secondary ion mass. It increases gradually up to 15% for ion at $m/z = M + 104$. Although the KED of higher mass ions like dimers and trimers is poorly resolved due to the low signal to noise ratio, they indicate that the high-energy contribution is important for the 2 keV measurement, too [9].

Between the (2 keV; 65°) bombardment conditions and the other measurements, both the impact energy and angle have been drastically modified. Nevertheless, the insensitivity of the KEDs on the primary beam energy between 7 and 22 keV (Fig. 1) might suggest that the difference observed at 2 keV is rather related to the important variation of the primary beam angle. To check this hypothesis, simulations of the different bombardment conditions have been realized using the TRIM code (SRIM-2000/v.06, using the detailed calculations with full damage cascades) [14]. [1] Despite the limitation of this code for sputtering evaluation in these materials, the development of the collision cascades in the solid has been computed for the different bombardment conditions used in practice. The (2 keV; 65°), (7 keV; 43°), (12 keV; 40°) and (22 keV; 38°) configurations have been simulated. As a first indication, the primary ion ranges give an insight into the size of the excited volume. In this respect, the TRIM calculations indicate that the vertical and lateral ranges increase proportionally to the primary beam energy between 2 and 22 keV (*vertical range: from 26 to 189 Å*; *lateral range: from 57 to 147 Å*). Although the value of the vertical range is larger or equivalent to that of the lateral range at 7, 12 and 22 keV, the lateral range becomes two times greater than the vertical range for the 2 keV measurement. The low value of the vertical range at 2 keV (26 Å) shows that the collision cascades are confined in the top surface layer of the polymer coating. This difference between the (2 keV; 65°) bombardment and the other experimental conditions is also indicated by the average number of 'vacancies' (atom displacements) and 'phonons' (internuclear energy transfers that do not generates vacancies, i.e., vibrational excitations) calculated by TRIM. The simulations show that the number of 'vacancies' and 'phonons' created in the first 15 Å of the solid is almost independent on the primary beam conditions, except at (2 keV; 65°), where it is two times greater. Comparing the (7 keV; 43°) and the (2 keV; 65°) bombardment conditions, the TRIM results show clearly that the particular shape of the excited volume, indicated by the ranges, as well as the increased number of atom displacements and vibrational excitations in the topmost polymer layer are mostly due to the increase of the impact angle, rather than to the reduction of the impact energy. This increase of the impact angle leads to a significant number of primary ion trajectories remaining in the sub-surface region after penetration into the solid, with the development of many collision cascades next to (or at) the surface. As a direct

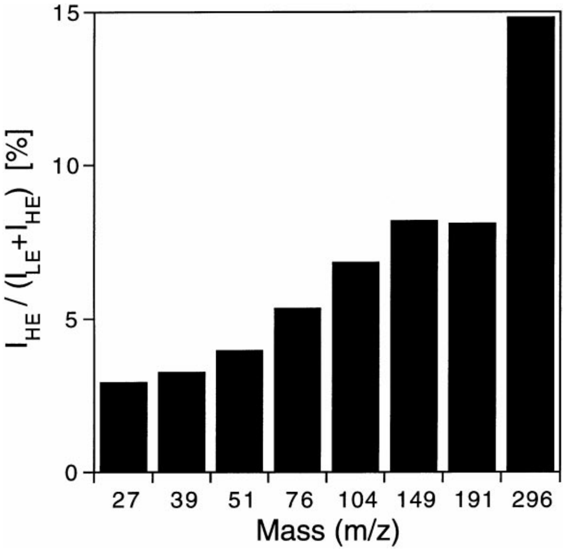

Fig. 2. Percentage of secondary ions constituting the high-energy contribution in the 2 keV measurement, $I_{HE}/(I_{LE}+I_{HE})\times 100$. See text for details.

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[1] Information concerning this program can be found at the following internet address: http://www.research.ibm.com/ionbeams/SRIM/.

consequence, an important number of primary ions are backscattered in the (2 keV; 65°) configuration (1%), as observed experimentally [9].

4. Discussion and conclusion

If one excepts the 2 keV data, the observed independence of the KEDs on the primary ion energy indicates that the kinetic energy of molecular ions is related to the energy required for the particular fragmentation channel leading to their production [3,4], rather than to the primary beam features. To understand this insensitivity, one may assume that the molecular ion emission processes occuring in the late stages of the ion–solid interaction, are almost completely independent on the early energy transfer from the primary ion to the matrix, which follows the primary ion scattering events. In this respect, it is interesting to note that the increase of the ejection time with increasing particle size has been predicted by MD simulations [15–17].

The 'vacancy' and 'phonon' numbers, as well as the stopping powers (not shown), calculated by TRIM for (7 keV; 43°), (12 keV; 40°) and (22 keV; 38°) indicate that several of the relevant parameters in the sputtering process vary weakly in this range of experimental conditions. Instead, the (2 keV; 65°) KED measurement and the corresponding simulation show both special features. In this case, the increased number of displaced atoms and vibrational excitations together with the concentration of the collision cascades in the extreme surface region might explain different emission processes for molecular ions. In these conditions, the probability of sputtering induced by a cooperative motion of the target atoms, or by the collective vibration of several nuclei might be increased. In addition, a correlated momentum transfer might explain the high kinetic energy contribution observed in the energy spectra of molecular ions sputtered under 2 keV ion bombardment [6,7]. These hypotheses should be verified using more sophisticated MD simulation algorithms [14,18].

In summary, our new data show that the KED of molecular ions sputtered from PET is almost independent on the primary ion energy, except for the 2 keV measurement. In this case, the fraction of molecular ions with a 'high' kinetic energy (5–6 eV) is significantly greater and it increases with the ion size. The variation of the collision cascade volume as well as the increase of the atomic displacements and vibrational excitations indicated by TRIM calculations at (2 keV; 65°) suggest that the observed experimental effect might be related to the increase of the incidence angle accompanying the reduction of the beam energy in our system. In a near future, more detailed results and interpretations will be given in an comprehensive study of the secondary ion yield [8] and kinetic energy [9] variations for of polymer targets sputtered under different primary beam nature, energy and angles.

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