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Electronic sputtering of fullerenes and the influence of primary ion charge state

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Even-numbered positive ion carbon clusters, fullerenes (C_{2n}, $n = 20, 21, \cdots$), are formed and ejected as a result of the interaction of swift atomic ions with a solid film of organic polymer – poly(vinylidene difluoride), PVDF. Studies of that phenomenon including the dependence of fullerene yield on the incident MeV ion's stopping power and initial radial velocity distributions of ejected ions, have been reported earlier [G. Brinkmalm et al., Chem. Phys. Lett. 191 (1992) 345; Phys. Rev. B 47 (1993) 7560]. In this paper, the dependence of the yield of the ejected cluster ions from PVDF as a function of the charge state of the incident MeV ion is reported. Swift 72.3 MeV ^{127}I ions in charge states ranging from +13 to +25 from the Uppsala EN-tandem accelerator are used in the experiments, and the secondary ion yield is measured in a time-of-flight mass spectrometer, equipped with an electrostatic ion mirror. The results are compared to data for secondary ions, ejected by the same primary ions, from samples of synthetic fullerenes (C_{60} and C_{70}). No dependence of the yield on the charge state of the incoming ion is observed for the high mass even-numbered carbon clusters from PVDF, while yields of C_{60} and C_{70} ions from synthetic fullerene targets show a weak charge state dependence. This finding indicates that excited polymer material from layers deeper than the MeV ion charge equilibration length in the solid contributes to the formation of ejected carbon cluster ions ejected from PVDF.

1. Introduction

The fullerenes [3–5] – a new allotropic form of carbon – have been the subject of an explosively increasing number of studies in the last two years. The fullerenes are all carbon molecules with closed three-dimensional shell structure, consisting of 12 pentagons and varying number of hexagons [3–5]. A most notable representative of the fullerene family is the C_{60} fullerene, containing 20 hexagons, and thus forming the perfectly symmetric structure of a truncated icosahedron. Different techniques for the formation of gas-phase carbon clusters with enhanced yield of C_{60} [3–10], have been reported. These include laser vaporisation of graphite and different carbon-containing materials with [3] or without [6] subsequent supersonic expansion in a gas jet, sooting hydrocarbon/oxygen burning [7], as well as low energy He ion sputtering and 10 keV electron beam evaporation of graphite [8]. In 1990 Krätschmer et al. [9] developed the first method for synthesis of macroscopic amounts of C_{60} and C_{70} by condensing atomic carbon vapour (formed in a carbon arc) in a 100 torr He atmosphere and this breakthrough led to an explosive growth of the field.

In ^{252}Cf plasma desorption mass spectrometry (PDMS – a secondary ion mass spectrometry method employing MeV fission fragments from ^{252}Cf as incident ions) studies of a specific polymer – poly(vinylidene difluoride) (PVDF) – Feld et al. [10] have observed carbon cluster ions (C_{2n}^+, $n = 20, 21, \cdots$). These studies have been expanded [1,2] by using swift atomic ions from the Uppsala EN-tandem accelerator for energy deposition in the PVDF films. The observation of only even-numbered (beginning from C_{40} and up to at least C_{376}) and positive carbon cluster ions as well as the cluster size distribution suggests that indeed stable closed carbon cage structures, fullerenes, are formed as a result of a single MeV ion impact [1,2]. The ejection of pure carbon clusters as a result of the interaction of a single fast MeV ion with a polymer, containing only 30% of carbon atoms, is a new specific effect of the electronic sputtering phenomenon [11–15]. We have investigated the dependence of the fullerene ion yield from PVDF on the electronic stopping power of the incident-projectile and the initial radial velocity distributions of ejected ions [1,2]. These experimental data suggest that fullerenes are formed as a result of a single primary ion impact and that they are ejected

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from an axially expanding infratrack plasma region [1,2].

Electronic sputtering of organic solids, i.e. material ejection as a result of energy deposition in the electronic subsystem of a molecular target by swift heavy ions, has been the subject of a number of experimental and theoretical investigations for the past few years [11–15]. An important parameter providing insight into the mechanism of electronic sputtering is the charge state of the incident ion at constant velocity [16–24]. It has been established that the charge state behavior of swift heavy atomic ions is complex, e.g. reaching of the charge state equilibrium is preceded by the "fast pre-equilibrium charge state" [23]. Experiments demonstrate that emission of H^+ ions in electronic sputtering does not depend on the nature of the incident projectile if they have the same velocity, but rather on its charge state before impact [16]. Studies on the charge state dependence of the yield of H^+ ions, electronically sputtered from thin foils, have resulted in a method for determination of the equilibrium charge states of MeV ions in a solid and in the gas phase [20]. The charge state dependence of the yield for heavier secondary ions has been more complicated. It has prompted introduction of the concepts of interaction and desorption depths in electronic sputtering, based on both experimental results and theoretical considerations [16,21,22,23].

In this paper experiments are reported with the aim to elucidate further the mechanism of carbon cluster formation in electronic sputtering from polymers. The yield of ejected secondary ions from a PVDF target has been studied as a function of the primary ion charge state. For comparison purposes, sputtering induced by MeV atomic ions in different charge states from targets of C_{60} and C_{70} fullerenes synthesized according to the method of Krätschmer et al. [9] (and henceforth referred to as synthetic fullerene targets) has been also investigated.

2. Experimental

2.1. *Instrumental setup and performance*

A beam of 72.3 MeV ^{127}I ions in charge states ranging from +13 to +25 was generated in the Uppsala EN-tandem accelerator. The method for production of ions in different charge states was similar to that described earlier (Fig. 1a) [24]. A thin (5 μg/cm^2) carbon foil was installed in the accelerator beam tube between the analysing and switching magnets. MeV ions passing through that foil resulted in projectiles with the same velocity and in a distribution of charge states around the equilibrium charge state (about +21 for 72.3 MeV ^{127}I). The switching magnet was then used to select projectiles in a particular charge state. The secondary ion yield was measured in a time-of-flight mass spectrometer, equipped with an electrostatic ion mirror (Fig. 1b) [25,26], installed on one of the accelerator beam lines. The vacuum in the spectrometer chamber was better than 10^{-8} Torr. The MeV ions were incident on a thin target (diameter 6 mm) at an angle of 45°. Since the range of the incident MeV ion was longer than the target thickness, the primary ions could be detected in a microchannel plate detector, placed behind the target (Fig. 1b). The signal from that detector provided the start pulse for the timing electronics. The target was floated at an acceleration potential V_a of +14.30 kV, and desorbed positive secondary ions were accelerated towards a grid at ground potential through a distance of 4.5 mm. The secondary ions were detected by a microchannel plate detector in the reflected mode (with the ion mirror at

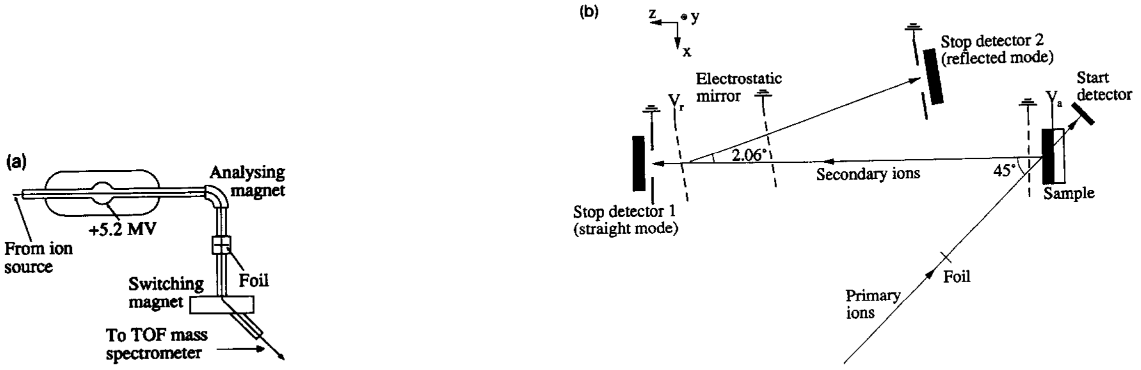

Fig. 1. (a) A schematic of the experimental arrangement for generation of MeV incident ions in different charge states. (b) A schematic of the time-of-flight mass spectrometer, viewed from above. Note: Both foils (on (a) and (b) respectively) are retractable.

V_r of +15.66 kV). The ion flight time registration was performed in a pulse counting mode by employing a multistop (up to 255 stops per start) time-to-digital converter (CTN-M2, IPN, Orsay, France) with 0.5 ns time resolution per channel. Data were acquired in an event-by-event mode (at a rate of approximately 10^3 incident MeV ion events per second) with an ATARI Mega personal computer. Spectra were accumulation of $1-3 \times 10^6$ start events, which excluded radiation damage effects.

A thin (5 $\mu g/cm^2$) carbon foil at a distance of ~ 100 mm before the target could be purposely inserted into or removed from the primary ion beam path. Thus MeV primary ions in different charge states were equilibrated to the same equilibrium charge state after passing through the C foil and before impacting the target. For each data point a spectrum was taken under the same experimental conditions with the carbon foil placed in the two different positions. This experimental arrangement provided a check for the reproducibility of the charge state measurements by comparing the respective ion yields.

2.2. Target preparation

Thin aluminium foils (250 $\mu g/cm^2$) were used as a backing material for the different targets. PVDF in powder form was obtained from Aldrich Chemical Co. The PVDF targets were prepared by dissolving the solid polymer in slightly heated acetone (10 $\mu g/\mu l$ concentration) and then spin-coating [2] around 40 μl of the solution on the backing. This resulted in an estimated PVDF target thickness of about 2000 Å. Synthetic fullerenes were prepared according to the Krätschmer et al. method [9]. The soot was extracted with benzene and the extract was purified by centrifugation. About 40 μl of the benzene solution was then deposited onto the backing and dried at room temperature, which resulted in an amorphous film of C_{60} and C_{70} fullerenes.

3. Results and discussion

The dependence of the yield, Y, for different ions from PVDF and synthetic fullerene targets as function of primary ion charge state, q, is presented in Fig. 2 and Table 1. It has been already demonstrated that the dependence of the yield and the primary ion charge state is of the form $Y \propto q^n$, where n ranges from 0.8 to 4.4 [21]. Using the same parametrisation, we have found that the exponent, n, for the yields of different ions from PVDF and synthetic fullerene targets as a function of charge state varies, and for the same primary ions it is different for the two different targets. In general the dependence on the charge state is better pronounced for secondary ions, ejected from synthetic fullerene targets. For example, the H^+ ion yield scales with $n = 1.1$ and 2.6 for PVDF and synthetic fullerenes, respectively. The yield dependence for the C_{60}^+ and C_{70}^+ ions ejected from the synthetic fullerene target is weak ($n = 0.3$), while there is no dependence of the yield on the projectile charge state for the same ions, ejected from PVDF. There is somewhat stronger influence on the yields of the primary ion charge state for atomic carbon and fluorine ions from PVDF ($n = 1.7$ and 1.5 respectively), compared to other secondary ions. On the other hand the exponent in the C^+ ion yield dependence from a synthetic fullerene target is 4.2. Since values around 4 for C^+ ion emission have been often reported in the literature [16,21], this indicates that the lower exponents we find for the emission of different ions from PVDF are not due to an instrumental error.

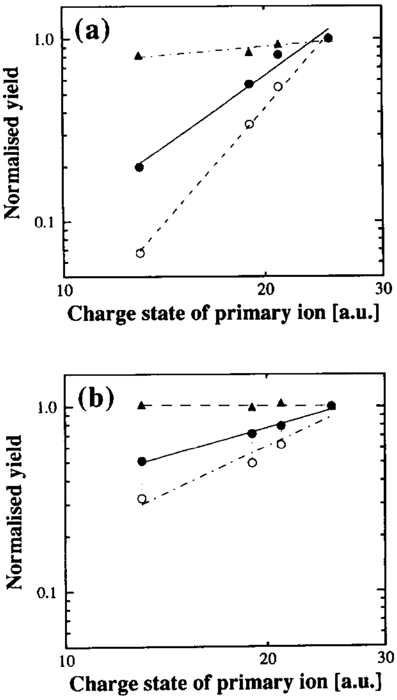

Fig. 2. (a) Log–log plot of the yield of H^+ (●), C^+ (○), and C_{60}^+ (▲) ejected from a synthetic fullerene target versus primary ion charge state. (b) Log–log plot of the yield of H^+ (●), C^+ (○), and C_{60}^+ (▲) ejected from a PVDF target versus primary ion charge state.

In order to provide an independent check for the validity of the experiment, i.e. whether we have employed incident MeV ions in different charge states and/or the target has not been modified during the experiment, spectra were recorded after the beam has passed through the carbon foil in front of the target (see experimental section above). A comparison of the

Table 1
Dependence of the positive secondary ion yield on the primary ion charge state for synthetic C_{60} and PVDF targets when irradiated with 72.3 MeV ^{127}I ions. The relation between the yield, Y, and the charge state, q, is $Y \propto q^n$, and the measured values of n are listed

Secondary ion	Target	
	Synthetic C_{60}	PVDF
H^+	2.6	1.0
H_2^+	2.5	0.8
C^+	4.2	1.7
C_2^+	3.0	1.8
C_3^+	3.2	1.4
C_4^+	3.1	1.3
C_5^+	1.6	0.7
C_6^+	0.2	0.6
F^+	–	1.5
F^{2+}	–	1.5
CH_3^+	1.5	0.3
$C_2H_3^+$	0.6	0.1
C_3H^+	2.5	0.9
$C_6H_2^+$	0.9	0.3
CF^+	–	0.8
C_{50}^+	–	0.0
C_{60}^+	0.3	0.0
C_{70}^+	0.2	0.0

yield for H^+ ions from PVDF with the carbon foil in the two different positions is given in Fig. 3. There is a clear dependence of the yield on the charge state with the foil retracted from the ion beam path, while with the foil intercepting the beam, this dependence vanishes. That result is a clear evidence that the incident MeV ions have different charge states, and a charge state equilibration is achieved after they pass through the foil. From these data it is also possible to deduce the equilibrium charge state of the primary ion in vacuum, which in this case (72.3 MeV ^{127}I) is about +21. This value is in good agreement with values determined by Brunelle et al. [22].

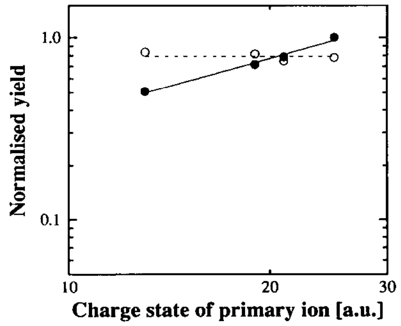

Fig. 3. A comparison of the yield of H^+ ejected from a PVDF target with the carbon foil before the target inserted into the beam path (○) and with carbon foil removed (•) for projectiles in different initial charge states (log–log plot).

The dependence of the yield of different ions as a function of charge state provides an important information on the mechanism of electronic sputtering of organic solids. While the radial dimensions of the nuclear track, formed as a result of the interaction of a swift heavy ion with a solid, correlate with the velocity of the projectile, its charge determines the energy density deposition along the track [14–22]. It has been established that depending on ion mass, ion velocity, and target properties, swift ions in different charge state undergo complex charge exchange processes (stripping or electron attachment) in the first 50 to 200 Å in the solid. Initially the ions reach the so-called "fast pre-equilibrium charge state" before equilibration (e.g. after around 150 Å for 0.5 MeV/u I ions penetrating C containing materials) [23]. The deposited energy density, which is a function of the charge state (q^2), would change in the first few tens of angströms along the track. Secondary ion yield versus charge state dependence allows estimates of the contribution to the sputtering process for different elements along the track [16,21,22]. The concepts of interaction and desorption depths have been invoked to incorporate the experimental findings in a phenomenological description of the electronic sputtering process. The mean interaction depth is the "effective" vertical projection length of that part of the ion track that contributes to the desorption (sputtering) event. A mean interaction depth of around zero is correlated to a very strong charge state dependence (e.g. $Y \propto q^{4.4}$ for C^+ ions as it has been found [21]) and vice versa. The mean interaction depth depends among other parameters on the mass, charge state and angle of incidence of the swift MeV ions, and for a coronene target ranges from 12 to 160 Å for Ne, Ar and Kr in charge states from +5 to +24 [21]. The yield of light ions that are emitted predominantly from the surface (including positive or negative atomic ions – H, C, O, Na, etc.), has a stronger dependence on the charge state, compared to molecular and molecule-related ions. It has been demonstrated for the latter that layers as deep as 200 Å from the surface may contribute to the ion desorption [21,22]. For instance, the yield of both positive and negative molecule-related ions from valine, ejected by swift ^{238}U ions in different charge states, scales as $Y \propto q^{0.85 \pm 0.15}$ [21].

The preferentially non-normal ejection of carbon clusters from a PVDF target back along the direction of the incoming MeV ion, and the stopping power dependence of the fullerene ion yield, strongly suggests that they are formed at very high energy densities in the infratrack plasma and are ejected by the axially expanding track core [1,2,27]. The interpretation of our main result in this study, namely that the yield of fullerene ions from PVDF is independent from the incident ion charge state, is that both energy and material along the infratrack from well below the target surface, contribute to the formation, ionisation and ejection process. The equilibration depth (reaching the "fast pre-equilibrium charge state") for 72.3 MeV ^{127}I ions in an organic solid is of the order of 150 Å [23]. Thus, by analogy to the direct electronic sputtering process, we may assume that the mean interaction depth, from which excited material contributes to the fullerene growth, is more than 150 Å. This assumption is in agreement with data on the dependence of the carbon cluster yield as a function of PVDF film thickness [2]. It has been found that the yield for C_{60} increases from 100 Å and saturates at around 300 Å (for an MeV ion incidence angle of 45°) [2]. The weak dependence of the H^+ ion emission from PVDF on the primary ion charge state may be correlated to differences in the MeV ion induced chemistry in that material (leading to e.g. fullerene formation and ejection) compared to other organic solids. For example, HF elimination (the main chemical path of MeV ion induced degradation of PVDF [28]) is exothermic and thus can influence H^+ ion emission by prolonging the infratrack plasma neutralization time. On the other hand, the dependence of the yield of ejected ions from the synthetic fullerene target as a function of the charge state suggests that this is predominantly a surface thermally induced process, as has been deduced previously from initial radial velocity distribution data [1,2].

The volume of PVDF, containing at least 60 C atoms, needed for formation of a C_{60} molecule, is around 2000 Å^3 (density of PVDF is 1.74). Since a C_{60} cluster can be imbedded in a cylinder with a diameter of at least 7.2 Å, that would correspond to a cylinder height (depth) around 50 Å. However, since larger clusters are ejected (at least up to C_{376}), and not all carbon atoms will be incorporated in a cluster, the excited material volume has to be larger. For the largest cluster observed, the volume has to be around 6.5 times larger, which (for a cluster with a diameter roughly 2.5 times the C_{60} diameter) gives the same height (50 Å) of the excited cylindrical volume. Taking into account the distance (150 Å) for reaching the pre-equilibrium charge state, it follows that material from depth of around 200 Å may be involved in fullerene formation. These estimates do not contradict the thickness dependence data [2] if one takes into account that the angle of incidence is 45°, so the MeV ion path in the solid will be accordingly extended (for 100 Å thickness the actual track length will be 140 Å). On the other hand, the estimated depth value of 200 Å may be somewhat lower, because the radial dimensions of the excited volume are probably larger. In a model assuming that the clusters are formed in the higher energy density plasma of the ion track core, the estimated radial dimensions of the excited region are of the order of 30 Å [27].

4. Conclusion

The charge state of the incident 73.2 MeV I ions does not influence the yield of high mass carbon cluster ions, electronically sputtered from PVDF. This experimental finding is an indication that the mean interaction depth for fullerene formation in electronic sputtering is bigger than the charge (pre-)equilibration length of 150 Å for the incident MeV ions in that material. Thus material in polymer layers that are deeper than the charge equilibration length in the solid, is excited to form fullerenes. The dependence of the yield on the charge state for ions, electronically sputtered from synthetic fullerene targets, demonstrates that these ions originate very close to the surface in possibly a thermal evaporation type process. Experiments are in progress to elucidate further these interesting experimental findings that may lead to better understanding of both nuclear track and fullerene formation in electronic sputtering.

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