Accepted Manuscript

Full Length Article

Effect of nanoconfinement on the sputter yield in ultrathin polymeric films: Experiments and model

Vanina Cristaudo, Claude Poleunis, Arnaud Delcorte

PII:	S0169-4332(18)30701-3
DOI:	https://doi.org/10.1016/j.apsusc.2018.03.041
Reference:	APSUSC 38789
To appear in:	Applied Surface Science
Received Date:	25 October 2017
Revised Date:	13 February 2018
Accepted Date:	5 March 2018



Please cite this article as: V. Cristaudo, C. Poleunis, A. Delcorte, Effect of nanoconfinement on the sputter yield in ultrathin polymeric films: Experiments and model, *Applied Surface Science* (2018), doi: https://doi.org/10.1016/j.apsusc.2018.03.041

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Effect of nanoconfinement on the sputter yield in ultrathin polymeric films: Experiments and model

Vanina Cristaudo^{a,b,*}, Claude Poleunis^b, and Arnaud Delcorte^b

^a National Physical Laboratory, Hampton Road, TW11 0LW Teddington, United Kingdom
 ^b Université catholique de Louvain, Institute of Condensed Matter and Nanosciences, 1 Place
 Louis Pasteur box L4.01.10, B-1348 Louvain-la-Neuve, Belgium

*Corresponding author:

E-mail address: vanina.cristaudo@npl.co.uk (V. Cristaudo)

Phone: +44 2089436161

Co-authors:

E-mail address: claude.poleunis@uclouvain.be (C. Poleunis) E-mail address: arnaud.delcorte@uclouvain.be (A. Delcorte)

1

ABSTRACT

This fundamental contribution on secondary ion mass spectrometry (SIMS) polymer depthprofiling by large argon clusters investigates the dependence of the sputter yield volume (Y) on the thickness (d) of ultrathin films as a function of the substrate nature, i.e. hard vs soft. For this purpose, thin films of polystyrene (PS) oligomers (~4,000 amu) are spin-coated, respectively, onto silicon and poly (methyl methacrylate) supports and, then, bombarded by 10 keV Ar_{3000}^+ ions. The investigated thickness ranges from 15 to 230 nm. Additionally, the influence of the polymer molecular weight on Y(d) for PS thin films on Si is explored. The sputtering efficiency is found to be strongly dependent on the overlayer thickness, only in the case of the silicon substrate. A simple phenomenological model is proposed for the description of the thickness influence on the sputtering yield. Molecular dynamics (MD) simulations conducted on amorphous films of polyethylene-like oligomers of increasing thickness (from 2 to 20 nm), under comparable cluster bombardment conditions, predict a significant increase of the sputtering yield for ultrathin layers on hard substrates, induced by energy confinement in the polymer, and support our phenomenological model.

Keywords: ToF-SIMS; polymer depth-profiling; polystyrene (PS); poly (methyl methacrylate) (PMMA); substrate effect; polymer molecular weight

1. Introduction

For a long time, SIMS was limited to the surface analysis of polymers, due to the loss of distinctive structure-related information during the erosion of the sample with monoatomic projectiles [1]. In the late 1990s, the advent of cluster-SIMS [2] paved the way for the molecular depth-profiling of polymer materials, and more generally of organics, thanks to the utilization of cluster ions like SF_5^+ and C_{60}^+ for sputtering. However, it was not until the development of massive Ar cluster ion beams (i.e. 5-10 keV $Ar_{500-5000}^+$) as sputter sources [3] that molecular depth-profiling of polymers could be performed universally, including even aromatic polymers (e.g. polystyrene) [4,5,6], where the more traditional fullerene ion beams failed (unless combined to nitric oxide dosing, sample cooling or sample rotation) [7,8,9,10]. In order to explain the greater success of massive Ar cluster ion sputtering of organic/polymer surfaces in cluster-SIMS, an extensive body of theoretical studies using MD simulations was conducted [11,12,13]. Simulations pointed out the minimal molecular degradation and fragmentation induced by the massive cluster impact (closer to the concept of desorption), compared to that of smaller polyatomic projectiles (like C_{60}) [14]. The main results of the theoretical studies are discussed in review articles [11,13,15].

Several theoretical and experimental studies were devoted specifically to the investigation of the effects of the Ar cluster energy and nuclearity on the energy deposition and fragmentation of organic solids. In 2013, two empirical equations were developed, independently by Seah [16] and Cumpson et al. [17], to estimate sputter yields by fitting their few parameters to the existing experimental data. Seah's universal equation was applied successfully to data sets concerning inorganics and some polymer materials (polystyrene (PS), poly (methyl methacrylate) (PMMA), and polycarbonate (PC)), with high molecular weight and polydisperse [16]. However, a study conducted in our laboratory in 2014 pointed out the influence of the polymerization degree on the sputtering efficiency of two model polymers,

namely PS and PMMA, that should be taken into account when comparing sputter yields [18]. In particular, experiments show that, at a given energy per atom, the sputter yield quickly decreases with increasing molecular weight (M_w) and becomes constant above ~60,000 amu. In 2015, Seah evaluated the effect of the molecular weight or the end-group density on the fit parameters of the "universal" sputtering equation [19]. The sputtering yields and their dependence on the molecular weight have also been predicted by molecular dynamics simulations [20]. An accurate estimation of the sputter yield of polymer materials is extremely important for the quantification and prediction of their depth-profiles and, to our best knowledge, the polymer-substrate interfacial effects on the sputtering efficiency upon massive Ar cluster bombardment have not been experimentally investigated yet. In the literature, only a few works can be found on computational investigations of the energy deposition pathways and the efficiency of ejection in organic solids as a function of the overlayer thickness [21,22].

In this fundamental contribution, the two previous model polymers - PS and PMMA - were chosen [18], since they exemplify two opposite degradation mechanisms occuring under ionic bombardment. Indeed, polystyrene undergoes mainly cross-linking reactions upon irradiation (type 1 polymer), that slow down the erosion process [23]. On the contrary, polyacrylate prevalently undergoes chain scission reactions (type II polymer), which enhance the sputtering efficiency [23]. Additionally, these two polymers interact differently with the silicon substrate used for the deposition in ultrathin films. In the conception of the model systems of this investigation, the aforementioned influence of the molecular weight [18] was taken into account. Thin layers of low molecular weight PS and PMMA of different thicknesses, spin-coated onto two different substrates (silicon and polymer), were bombarded by a 10 keV Ar_{3000}^+ ion beam in order to measure the thickness dependence of the sputter yield. In the remaining of the article, silicon will be defined as a "hard" material and the

polymers, as "soft" materials. Indeed, polymers plastically deform much more easily under an applied stress than silicon, and our simulations will show that the energy spent in plastic deformation is key to explain the different behaviours of these materials. The differences in hardness of the materials are due in part to their stiffness, which is directly related to their Young's moduli, which are reported in Table S1. The sputtering efficiency is found to be strongly dependent on the polymer overlayer thickness only for the hard substrate (silicon covered by native oxide). Then, a phenomenological model is elaborated to interpret the thickness dependence of the sputtering efficiency, and corroborated by MD simulations conducted with analogous samples and bombardment conditions.

2. Experimental methods

2.1. Materials and sample structure

Polystyrene and poly (methyl methacrylate) standards for gel permeation chromatography (GPC) with relatively low molecular weight (M_w) of ~4,000 amu, and high molecular weight of ~60,000 for PS and 150,000 amu for PMMA, were purchased from Sigma-Aldrich Inc. and Scientific Polymer Products, Inc. An overview of the polymer materials employed for the sample preparation is reported in Table 1.

Polymer	$M_w (amu)^a$	$\mathbf{M}_{w}/\mathbf{M}_{n}^{\ b}$	Source	Polymer name
Polystyrene	4,330	1.04	Sigma-Aldrich Inc.	PS 4k
	61,800	1.07	Scientific Polymer Products, Inc.	PS 60k
Poly (methyl methacrylate)	4,200	1.06	Sigma-Aldrich Inc.	PMMA 4k
	150,000	n.d. ^c	Sigma-Aldrich Inc.	PMMA 150k

Table 1. Description of the employed polymers.

^a Molecular weight determined by GPC; ^b M_w/M_n, polydispersity; ^c n.d., not determined.

Polymer ultrathin films were deposited onto $1 \times 1 \text{ cm}^2$ silicon substrates covered by a native oxide layer, previously cleaned by sonication in isopropanol (VWR Chemicals, 99.9% purity) and dried under nitrogen flux. PS 4k, PS 60k and PMMA 4k solutions were prepared

in toluene (Sigma-Aldrich, purity \geq 99.71%) with a concentration ranging from 7 to 72 g/L for PS and PMMA with low M_w, and from 6 to 54 g/L for PS 60k. This low pressure vapor solvent is known for providing very smooth surface morphologies upon spin-coating of the selected polymers [24,25,26], an important requirement for the measurement of the sputter efficiency of ultrathin films. The solutions were then filtered using 0.2-µm Teflon filters to remove any non-dissolved particle and dust before their deposition on the Si supports. The solutions were spin-coated onto the silicon wafers at 5,000 rpm with an acceleration of 20,000 rpm/s for 60 s, in order to obtain polymer single-layers with thickness comprised between ~15 nm and ~230 nm. The quality of the PS 4k film series in terms of morphology and roughness as a function of the thickness was verified by atomic force microscopy (AFM) measurements. Very smooth morphologies are observed in the all thickness range (Figure S1). For instance, 3 x 3 µm² AFM images of the PS single-layers show typical average surface roughness (R_a) values around 0.3 nm (close to the roughness of the silicon wafer, R_a ~0.2 nm) [27], independently from the given film thickness.

The polymer films on Si represent three model systems of polymer single-layers of type I, PS 4k and PS 60k, and type II, PMMA 4k [23]. In the particular case of PS, the additional influence of M_w (i.e. 4,000 versus 60,000 amu) on the thickness dependence of the sputtering efficiency is investigated. Silicon is a hard, relatively hydrophilic substrate, since no treatment was done to remove the outermost native SiO_x layer of the semiconductor. In order to study the effect of the substrate nature on Y(d), i.e. hard vs soft, a fourth model system was conceived. In order to obtain a soft substrate, a relatively thick polymer layer was spin-coated onto Si, ensuring a very smooth interface, which is not the case with commercial polymer sheets. Some known constraints exist in the preparation of model polymer bilayers by spin-coating, which are listed here: 1) the bottom layer should have minimal solubility in the solvent used to deposit the top layer, 2) high quality of both top film surface and

polymer/polymer interface is required, and last but not least, 3) in the present study, a wide thickness range of the top layer is demanded. The work conducted by Ennis et al. provides an ideal system for this investigation: direct spin-coating of PS thin films onto PMMA [26]. Indeed, it results in very smooth surfaces, with roughness of the uppermost PS layer comparable to that obtained with the correspondent single-layers spin-coated from toluene, and sharp interfaces [26]. The roughness of the PMMA layer remains very low (<1 nm) also after the deposition of the upper layer [26]. The established protocol permits to play in windows of PS thickness of \sim 5-500 nm and M_w of \sim 4,000-190,000 amu, but it also requires PMMA with $M_w > 3,000$ amu. Thus, it was decided to spin-coat the same PS 4k of the singlelayers onto PMMA 150k (high M_w to avoid its dissolution in the selective solvent of the PS). A solution of PMMA 150k was prepared in toluene, filtered and spin-coated onto several clean Si wafers at room temperature. The samples were left to dry for 24 hours. Then, filtered solutions of increasing concentrations of PS 4k in 1-chloropentane (Aldrich Chemistry, 99% purity) were deposited onto the PMMA 150k layers. None of the polymers was annealed after deposition. In the first column of Table 2, the four model systems used in this investigation are schematized, where the polymer names in italic indicate the outermost layers whose thickness was varied.

Model system	Sample	Polymer film thickness ^a	
A) <i>PS 4k /</i> Si	A1	$17.5 \pm 0.0 \text{ nm}$	
	A2	$36.4\pm0.4\ nm$	
<u>PS 4k</u>	A3	$60.9 \pm 0.3 \text{ nm}$	
Si	A4	$87.8 \pm 0.1 \text{ nm}$	
	A5	$194.0\pm0.2~nm$	
B) <i>PMMA 4k /</i> Si	B1	$15.7\pm0.3~nm$	
	B2	$27.9 \pm 1.1 \text{ nm}$	
PMMA 4k	B3	$37.6 \pm 0.1 \text{ nm}$	
	B4	$56.3 \pm 0.2 \text{ nm}$	
51	B5	$89.7 \pm 0.1 \text{ nm}$	
	B6	$199.3 \pm 2.4 \text{ nm}$	
C) <u>PS 60k</u> / Si	C1	$16.1\pm0.4\ nm$	
	C2	$34.4 \pm 0.1 \text{ nm}$	Co
<u>PS 60k</u>	C3	$72.8 \pm 0.5 \text{ nm}$	
Si	C4	$130.9 \pm 0.3 \text{ nm}$	
	C5	$230.2\pm0.8~nm$	
Z) <u>PS 4k</u> / PMMA 150k / Si		• PS 4k layer: ^b	
	Z1	$27.5 \pm 0.4 \text{ nm}$	
	Z2	$67.3 \pm 4.0 \text{ nm}$	
	Z3	$92.1 \pm 1.8 \text{ nm}$	
PS 4k	Z4	$128.0 \pm 5.1 \text{ nm}$	
	Z5	$156.0 \pm 1.6 \text{ nm}$	
Si	Z6	$235.0 \pm 1.3 \text{ nm}$	
		• PMMA 150k layer: ^b	
	Z0	143.3 ± 1.2 nm (constant)	

Table 2. Description of the investigated model systems, sample names and related thickness values.

^a Determined by spectroscopic ellipsometry

^b Determined by single-wavelength ellipsometry

2.2. Ellipsometry

A spectroscopic ellipsometer (SE) Uvisel from Horiba-Jobin-Yvon was used to measure the thickness of the PS and PMMA single-layers (systems A-B-C in Table 2), in the wavelength range 300-800 nm with intervals of 10 nm at an incidence angle of 70°. The measurements were carried out at least three times at different points of the sample to obtain an average thickness. The data acquisition and consecutive modeling were performed with the DeltaPsi2 software. The systems A-B-C were modelled by a 3-layers structure with a silicon substrate covered by a dielectric layer, with the optical constants of SiO₂ and fixed thickness of 1.70 nm, and on top the PMMA or PS layer. The dispersion formula used for the polymer layer is called "New Amorphous", and it is derived from Forouhi-Bloomer formulation [28,29]. The "New Amorphous" model works particularly well for amorphous polymers like PS and

PMMA and, more generally, for amorphous materials exhibiting an absorption in the visible and/or far ultraviolet (100-200 nm) range. The difference between the given model and the experimental data, indicated by the mean square error value (MSE), were in most of the cases below 1, showing an acceptable quality of the fitting. The results of the SE regression analysis of the polymer layers were also compared with those obtained from other models, i.e. Cauchy [30,31] and Classical (Lorentz). The comparison leads to no significant variations of the thickness values when changing the dispersion formula. A further verification of the quality of the data modelling consisted in the comparison of the post-calculated refractive index values at constant wavelength with those reported in the literature [32,33,34,35]. Additionally, the ellipsometry measurements were compared to the thickness estimations from AFM images of scratches [36] performed on the PS 4k single-layers, as shown in supporting information (Figure S2). For example, the measured step for sample A1 is 17.5 nm, in good agreement with the SE value of 17.5 ± 0.0 nm, while for sample A5 it is 198 nm (vs 194.0 ± 0.2 nm in SE).

In the case of the polymer bilayer (system Z), because of the very similar optical properties of PS 4k and PMMA 150k, the thickness was determined more accurately by a Digisel rotating compensator ellipsometer from Jobin-Yvon/Sofie Instruments (single-wavelength ellipsometer working at 632.8 nm), imposing the refractive index of the two materials. Firstly, the PMMA 150k single-layer of the Z-system series (sample Z0) was measured. Then, its thickness was assumed to remain unvaried after spin-coating of the upper PS layer, so that the topmost polymer layer was characterized. This procedure is validated by prior studies demonstrating that there is no significant reduction in the PMMA thickness or roughening after the deposition of the PS solution in 1-chloropentane [26]. Moreover, in order to validate this data treatment in ellipsometry, including the selection of refractive indices for PMMA and PS, sample Z2 was additionally analyzed by X-ray reflectivity (XRR). The total

thickness found by fitting was 210.0 nm, very close to the ellipsometry value of 143.3 nm + 67.3 nm = 210.6 nm. The results of the thickness measurements are summarized in Table 2.

2.3. ToF-SIMS molecular depth-profiling

The molecular depth-profiling experiments were performed using an ION-TOF TOF.SIMS 5 (Münster, Germany) instrument equipped with both Bi-LMIG (liquid metal ion gun) and Ar-GCIB (gas cluster ion beam) primary ion sources mounted at 45° to the surface normal. The secondary ions were collected by a reflectron-type time-of-flight analyzer perpendicular to the sample surface. The molecular depth-profiles, acquired in positive ion polarity, were obtained in non-interlaced dual ion beam mode. A 10 keV Ar₃₀₀₀⁺ cluster ion beam (0.3 nA, 0.1 nA and 0.05 nA) was employed to sputter a 600 x 600 μ m² area. All the argon cluster size distributions used to profile the different model systems showed a full width at half maximum (FWHM) below 2,000 atoms. The average energy per constituent atom was ~3.5 eV. A pulsed beam of 30 keV Bi₅⁺ ions (0.06 pA) was used to collect the mass spectra from a 200 x 200 μ m² area, concentric to the sputtered surface. A 20 eV electron flood gun was employed for charge compensation.

The model systems reported in Table 2 were analyzed with three different sputter currents of 0.3, 0.1 and 0.05 nA, depending on the thickness of the polymer (single- or bilayer) film deposited on the Si substrate. Especially for the thinnest films, the sputter current had to be lowered in order to record a reasonable number of scans along the polymer depth, so that an accurate determination of the polymer/Si interface was made possible. For the PS 4k/ PMMA 150k bilayer, all the SIMS measurements were acquired at the higher current, that is 0.3 nA. Indeed, in these erosion conditions it was feasible to profile in reasonable times thick layer systems as the one under investigation where, in addition, one of the polymer layer possess high M_w and relatively low sputter rate. Since the overall SIMS measurements

showed high reproducibility, generally only two profiles per sputter current were acquired. The detailed sputter conditions employed in this study can be found in supporting information (Table S2). No significant effect of the Ar cluster current is observed on the sputter yield volume. This concept is clear in the depth-profiles of the thinnest PS film (A1), acquired in the three different erosion conditions (Figure S3). The respective ratios of analysis dose (30 keV Bi_5^+ beam) to sputtering dose (10 keV Ar_{3000}^+ source) were calculated for these profiles. According to the literature, the ratio between the analysis and sputter doses excludes a significant contribution of the Bi_5^+ beam in the sputter yield Y [37]. Thus, along this work, all the Y values obtained for a given system and related to different sputter currents will be merged.

For single-layers on Si (samples A-C), the sputter yield volume Y ($nm^3/primary$ ion or nm^3/PI) was calculated as in reference [18]. First, the dose (ions/ nm^2) needed to reach the polymer/Si interface was determined (50% of the maximum intensity of the substrate signal – Si⁺, m/z = 28), as it can be observed in the depth-profiles displayed in Figure S3. Then, the measured thickness (nm) of the polymer single-layer was divided by this dose. The polymer/silicon interface position was determined by the SiOH⁺ ion signal (50% of its maximum intensity) as well. This signal relates to the presence of the native oxide layer on top the silicon substrate. Figure S4 shows the comparison between the two methods for the determination of the polymer/Si interface of PS 4k and PMMA 4k single-layers. In the case of the PS/PMMA bilayer on Si (sample Z), an analogous procedure was used for the polymer/polymer interface determination, taking into account characteristic ions of the "soft substrate" (PMMA 150k) that derive solely from the fragmentation of the polyacrylate, like for instance the ion C₂H₃O₂⁺ at m/z 59.

3. Results

The depth-profiling experiments conducted on all the model systems with thickness of several tens of nm show a high stability of the polymer structure-related fragments (such as $C_2H_3O_2^+$, $C_3H_7O^+$, $C_4H_5O^+$, $C_5H_9O_2^+$ (protonated repeat unit), $C_6H_{11}O_2^+$ in the case of the PMMA, and $C_6H_5^+$, $C_7H_7^+$, $C_8H_9^+$ (protonated repeat unit), $C_9H_7^+$, $C_{13}H_9^+$, $C_{15}H_{13}^+$ in the case of the PS) down to the Si interface. This observation indicates the retention of the molecular information in the depth-profiling of type I and II polymers, a characteristic feature of large Ar cluster ion sputtering, as already reported in the SIMS literature [4]. Furthermore, even the thinnest polymer films cover the Si supports uniformly, as demonstrated by the absence of the substrate signals at the surface of the specimens in the depth-profiles (cf. Figure S3) [38].

3.1. Effect of the layer thickness on the sputter yield

Figure 1 shows the variation of the sputter yield volume Y for the model system "<u>PS 4k</u> / Si", where the thickness of the polystyrene layer is varied from ~17 nm to 194 nm (see the black symbols related to the left y-scale). The graph of Figure 1 reports the thickness d on the left y-axis and Y on the right y-axis, both as a common function of the sputter dose at the polymer/substrate interface (D in x-scale). A linear fit of d(D) has been performed imposing a zero intercept and passing by the last point representing a bulk-like PS layer. An adjusted Rsquare value of 0.9983 was found, indicating the quality of the linear regression. The equation d = b×D, reported in the graph of Figure 1, represents the ideal situation of linearity, where the correlation coefficient b = 67.2 nm³/PI constitutes the sputter yield volume of the bulk material (Y_{bulk}). The related linear fits of all the investigated systems are shown in Figure S5. However, the experimental d(D) data deviates from linearity below ~90 nm, which explains the asymptotic trend of Y(D) described by the following analytical function y = a - b×c^x (in

the present case: $Y = 65.4 + 36.6 \times 0.115^{D}$). The data could also be reasonably fit with a linear function assuming an offset at the origin, but this is not physically meaningful since the sputtered thickness must tend to zero for a dose of 0 ions/nm².



Figure 1. Thickness (d) and sputter yield volume (Y) of the PS 4k single-layers as a function of the sputter dose needed to reach the polymer/silicon interface. The data points indicated by open triangles, open squares and solid triangles (black for d and blue for Y) refer to the different 10 keV Ar_{3000}^+ ion currents of 0.3 nA, 0.1 nA and 0.05 nA, respectively. The fitted curves of d and Y as a function of D (dose) are also reported.

D represents the "sputter dose" variable and the asymptote $a = 65.4 \text{ nm}^3/\text{PI}$ corresponds to the Y value of the bulk material (very close to that obtained by linear regression). In qualitative terms, Y decreases with increasing d till reaching a plateau around 90 nm. The sputter yield volumes (for 0.3 nA) vary from 88 nm³/PI at 17 nm to 67 nm³/PI at 194 nm (value close to the "bulk" material), that corresponds to an overall $\Delta Y(d)$ variation of ~23%. This points out a dependence of Y on the thickness in the nanoscale range (from a few nm to tens of nm). However, the quantification of $\Delta Y(d)$ depends significantly on the specific technique employed for the determination of d. This justifies the choice of reporting Y (as well as d) as a

function of the dose. The plot of Y as a function of d for the "<u>*PS 4k*</u> / Si" thin films, as well as for the other model systems, can be found in Figure S6.

Figure 2 shows the case of the model system "<u>PMMA 4k</u> / Si", where the thickness of the polymer layer is varied from 16 nm to 199 nm. As was the case for PS 4k, the loss of linearity between d and D indicates an effect of the thickness on Y, that is noticeable below ~90 nm. The evolution of the sputter yield volume is once again asymptotic, going from 103 nm³/PI at 16 nm to 80 nm³/PI at 199 nm (see the blue open triangles), which corresponds to a variation of ~22% based on spectroscopic ellipsometry estimation. The trend of Y as a function of the sputter dose follows the equation: $Y = 79.9 + 41.6 \times 0.0349^{D}$, where the Y_{bulk} value is 79.9 nm³/PI. Our results show that Y of PMMA 4k single-layers is generally higher than Y of PS 4k of a factor ~1.2, in agreement with the literature [16] (see Figure 1 and 2). This is explained by the different degradation behaviour of the two polymers upon ionic bombardment [23], that favors the sputtering of the polyacrylate compared to that of the polystyrene.



Figure 2. Thickness (d) and sputter yield volume (Y) of the PMMA 4k single-layers as a function of the sputter dose needed to reach the polymer/silicon interface. The data points indicated by open triangles and solid triangles (black for d and blue for Y) refer to the

different 10 keV Ar_{3000}^+ ion currents of 0.3 nA and 0.05 nA, respectively. The fitted curves of d and Y as a function of D (dose) are also reported.

3.2. Effect of the substrate nature on the thickness dependence of Y

In Figure 3, the model system "<u>PS 4k</u> / PMMA 150k / Si" (Z) is considered, where the 143-nm thick PMMA 150k layer constitutes a soft substrate and only the thickness of the topmost PS 4k layer is varied from 28 nm to 235 nm.



Figure 3. Thickness (d) and sputter yield volume (Y) of the uppermost PS 4k films in the bilayer model system (Z) as a function of the sputter dose needed to reach the polymer/polymer interface. The data points (open triangles) refer to a sputter beam current of 0.3 nA.

The linear regression on the data set d(D) of the uppermost PS 4k layer in the bilayer system points out a similar slope (within the experimental error) to that found for PS 4k single-layers spin-coated directly on the Si substrates. In this specific case, however, the sputter yield volume oscillates around an average value of ~73 nm³/PI (excluding the last point represented by a single measure), without any peculiar trend considering measurement uncertainties.

3.3. Effect of the polymer molecular weight on the thickness dependence of Y

The last case of study is represented by the polymer system "<u>PS 60k</u> / Si" depicted in Figure 4. Here, the influence of the M_w of the polystyrene on the thickness dependence of Y is investigated. Our previous study on the effect of the M_w on the sputtering efficiency highlighted that Y depends on M_w only for low polymerization degrees, while Y(M_w) is constant for M_w above ~60,000 amu [18].



Figure 4. Thickness (d) and sputter yield volume (Y) of the PS 60k single-layers as a function of the sputter dose needed to reach the polymer/silicon interface. All the measurements were performed with 10 keV Ar_{3000}^+ at 0.3 nA, with the exception of the 1st sample (0.1 nA). The fitted curves of d and Y as a function of D (dose) are reported.

Accordingly, higher doses were required to erode layers of PS 60k than layers of PS 4k of comparable thicknesses corresponding to lower sputter rates for the high M_w polymer. Figure 4 shows that the variation of Y as a function of the dose, in the given d range 16-230 nm, is around 14% for PS 60k. It is therefore notably reduced when compared to the PS 4k films, but still present. The experimental data can be fitted by the equation $Y = 43.2 + 10.6 \times 0.433^{D}$. The Y value in the bulk material is consequently estimated to be close to 43 nm³/PI. This finding

is confirmed with an additional sample of 366 nm (not shown). However, the decay of Y appears to be slower along the observed dose range, so that higher doses/thicknesses are needed to reach the Y_{bulk} value.

In conclusion of this section, Figure 5 summarizes the fitted curves Y(d) of the two investigated model polymers, PS and PMMA, deposited on the two different supports, i.e. hard (Si) and soft (PMMA 150k). The influence of the M_w can be also derived from the comparison between PS 4k and PS 60k. Hence, this last figure illustrates the behaviors of all the proposed model systems, and will be used as a basis for the discussion of the underlying physics.



Figure 5. Fitted curves (analytical function: $y = a - b \times c^x$) of the sputter yield volume as a function of the film thickness for the Si-supported PS 4k, PMMA 4k and PS 60k single-layers, and the Y trend (dotted red line) of the topmost layer of the PS 4k / PMMA 150k bilayer.

4. Discussion

The two model polymers chosen to conduct this investigation differ in their degradation behaviour under keV ion bombardment [23], as well as in the interfacial interactions that they

establish with the untreated silicon supports. Indeed, the methyl methacrylate units are attracted to the native silicon oxide, forming H-bonds with the substrate. Conversely, in the case of PS, only weak Van der Waals interactions are created with the native Si oxide substrate [26,39]. One could think that these enthalpic contributions can at least partly explain the Y-enhancement observed for the thinnest polymer films in Figure 5. Apparently, this is the case for the nanoconfinement effect of the glass transition temperature observed for the two polymers, as extensively reported in the literature [40,41,42,43]. However, if the interfacial interactions of the two investigated polymers were a relevant parameter in the thickness dependence of Y, one should expect a different response of these two model systems to the modification of the silicon surface. For instance, the polymer-substrate interactions can be drastically changed for the PMMA chains by switching a native silicon oxide covered support to a H-terminated Si surface (by means of wet etching with HF aqueous solution) [44]. In doing so, one induces a more pronounced reduction of the attractive interactions between the methyl methacrylate units with the Si-H terminated surface, compared to the polystyrene chains. This procedure was tested and our experiments conducted on PMMA 4k and PS 4k single-layer spin-coated onto H-terminated silicon wafers indicate that Y decreases with increasing d in the same extent for both polymer systems, as was the case for SiO₂ surfaces (not shown). These results show that our depth-profiling experiments are not primarily sensitive to the variations of the polymer-substrate interactions and, very likely, small related differences in sputter efficiency lay within the experimental error of the Y estimation. Thus, our experiments rather suggest a mechanistic nature of the Y behaviour as a function of the film thickness, as already indicated by molecular dynamics (MD) computer simulations on other types of organic systems and projectiles.

In this respect, MD simulations have been carried out by Rzeznik and co-workers (2008) to gain microscopic insights into the sputtering of polystyrene tetramer (PS4) monolayers on

Ag induced by large Ar cluster projectiles [21]. The ion bombardment of the organic overlayer was performed with clusters composed of hundreds to 29,000 Ar atoms having kinetic energy per atom in the range 0.1-40 eV/atom. These simulations have shown a distinct physics of ejection by large and slow clusters compared to atomic projectiles and small clusters [45]. The organic molecules were ejected not in consequence of a direct interaction with individual substrate atoms, which was the case for atomic and small cluster bombardment, but by a collective motion of the recovering substrate [21] At the light of this novel ejection physics with large Ar clusters, Rzeznik et al. have conducted simulations (2009) to elucidate the sputtering of a denser, thicker and well organized system represented by Langmuir-Blodgett (LB) multilayers of bariated molecules of arachidic acid [22]. In that case, the sputtering yield with increasing overlayer thickness goes through a maximum, then decreases, and finally becomes constant as the LB layer becomes thicker (bulk regime). This behavior is explained by a competition between signal enhancement due to the increasing number of molecules contained in the organic overlayer, and the signal decrease due to lowering of the amount of the primary energy being back-reflected into the organic layer by the organic/metal interface [22]. The sputtering yield is independent of the thickness when the latter is much larger than the penetration depth of the projectile. Though the interaction of large Ar clusters and fullerenes with organic materials upon impact show other important differences, a similar behavior has been evidenced in cluster depth-profiling of cholesterol films sputtered with 40 keV C_{60}^{+} , in which the erosion rate increases as the organic-substrate interface is approached [46]. In all the observed cases, even with atomic projectiles [47], stiffer and more cohesive substrates tend to reflect more energy than softer ones, but the detailed mechanisms are different.

4.1. Model for the thickness dependence of the sputter yield

Based on the insights provided by the simulations [21,22], a phenomenological model is here proposed to explain the thickness dependence of Y for polymer-based thin films.

The measured sputter yield Y is actually an averaging over the local sputtering yields Y_z (z is the distance from the interface) over the sputtered layer thickness d, expressed as follows:

$$Y(d) = \frac{\int_{d}^{0} Y_{z} d(z)}{d}$$

(1)

In our model, we consider a simplified case where the polymer film (single-layer system) is composed by two layers, so the name "2-layers model". The first one is located at the interface with the hard substrate (e.g. silicon) and undergoes the Y-enhancement effect due to the Ar_n^+ sputtering. The second one sits on top, with a bulk value of the sputtering yield (Y_{bulk}). Accordingly there will be a critical thickness (d_{interface}) in the range of the first nanometers of the overlayer, where Y_z assumes the highest value ($Y_{interface}$), due to a maximal contribution to the sputtering of the primary energy being back-reflected into the polymer layer by the polymer/Si interface [48]. At distances from the substrate larger than d_{interface}, Y_z will have the value Y_{bulk} . Under these assumptions, Equation (1) becomes:

$$Y = \frac{d_{interface}}{d} Y_{interface} + \frac{d - d_{interface}}{d} Y_{bulk}$$
(2)

where Y_{tot} , d_{tot} and Y_{bulk} are determined experimentally, whereas $d_{interface}$ and the related

 $Y_{interface}$ are estimated by fitting. Figure 6.a depicts Equation (2) for the PS 4k single-layer, by using the characteristic parameters of the given system ($Y_{bulk} = 65.4 \text{ nm}^3/\text{PI}$ for d = 194 nm shown in Figure 1). Based on the 2-layers model, d_{interface} and Y_{interface} are 3 nm and 200 nm³/PI, respectively. This simple model using only two extreme values of Y describes the observations qualitatively. A more refined description of the gradual transition of Y(d) from $Y_{interface}$ (200 nm³/PI) to Y_{bulk} (65.4 nm³/PI) should lead to a more accurate fit.



Figure 6. a) 2-layers model applied to the experimental data set for the " $\underline{PS \ 4k}$ / Si" system (solid line), and b) MD simulations conducted on an amorphous film of polyethylene-like oligomers of increasing thickness (from 2 to 20 nm) onto a hard substrate.

In order to validate our phenomenological model, MD simulations were also performed. For this purpose, an amorphous molecular sample made of 1.4 kDa polyethylene-like molecules was modelled using a coarse-grained representation of CH_2 and CH_3 residues, as described elsewhere [20]. This model provided a quantitative description of Ar cluster sputtering of organic materials. In these new simulations, the top layer of the organic sample, with a total thickness d, was left free to move, mimicking the oligomer overlayer. In contrast, the bottom layer of the sample was made "rigid" by constraining the atoms to their initial positions. The thickness of the rigid layer was adjusted to obtain a free film thickness d

ranging between 2 and 15 nm (the total thickness of the model sample). For these simulations, a Langevin algorithm with a friction coefficient was applied to the atoms located at the four lateral sides of the box (1.5-nm thickness region) in order to adsorb the pressure waves traveling laterally, but not at the bottom of the free layer. This arrangement models an infinite film of thickness d on an infinitely hard substrate. Another set of simulations was also conducted using a damping zone at the bottom mimicking, in that case, a semi-infinite, bulk sample. Two different impact points were calculated for each film thickness.

Figure 6.b shows the calculated sputtered mass of polymer as a function of thickness d, which should model the value Y_z in Equation (1). As a reference point for the bulk value, the results obtained for the sample with a bottom damping zone were arbitrarily placed at a film thickness of 20 nm (larger than the thickness of the model system). The other data points correspond to the first set of sample described above, with only a rigid bottom layer below a free film of thickness d. The results show that the sputtered mass remains constant down to a film thickness of 7 nm. Under that thickness, the sputtered mass increases very steeply, up to a maximum value at 4 nm. Below 4 nm, down to the bare substrate, the sputtered mass decreases. The maximum, due to the back-scattering of the projectile atoms (and energy) by the substrate, corresponds to a sputtered mass that is ~4 times larger than the bulk value. For d < 4 nm, the sputtered mass becomes limited by the reduced quantity of material present in the ultrathin layer. A similar effect was observed in the bombardment of arachidic acid Langmuir-Blodgett layers by C_{60} and Ar_n clusters [22,45]. In our simulations, 10 keV Ar_{3000} projectiles induce craters that are approximately 10 nm deep in pure organic material, a depth that is reduced to the thickness d when it is lower than 10 nm. More details about the evolution of the crater shapes and sputtered material in these simulations can be found in reference [49]. Though the analytical model presented above uses a crude representation of the curve obtained in the MD simulations, with only two steps of sputter yield (one for the

ultrathin film regime and one for the bulk), the values of thickness and yield extracted for the layer with enhanced sputtering are in qualitative agreement with the MD results ($d_{interface} = 3$ nm and $Y_{interface} = 3 \times Y_{bulk}$, see Figure 6.a). These simulation results therefore support the interpretation and the simple model of sputtering including a layer with enhanced sputtering near the substrate, resulting from the confinement of the Ar cluster energy for ultrathin organic films on hard substrates.

The proposed model is confirmed by the study of the bilayer system "<u>PS 4k</u> / PMMA 150k / Si", where the energy deposited by the projectile in the uppermost PS layer is not confined anymore by a dense substrate like Si, but it is now dispersed in the underlying soft PMMA layer. Consequently, the nanoconfinement effect on the sputter yield volume disappears, as indicated by the red dotted line in Figure 5. Moreover, the comparison of the extrapolated ideal dependence of the sputter dose as a function of d (obtained by linear regression) shows that the cases of PS 4k deposited onto Si and PMMA 150k are substantially identical (see Figures 1 and 3, or Figure S5). Indeed, for PS 4k on Si the fitted Y_{bulk} value is 67.2 nm³/PI, while for PS4k on PMMA 150 k is 69.2 nm³/PI.

As further validation of the hypothesis done, the sputter yield of the PS 60k single-layer system is also found to be dependent on the film thickness (see orange solid line in Figure 5). Here, the influence of the higher M_w is reflected in smaller variations of Y vs d. This might be explained by the fact that at higher M_w , long portions of macromolecules remain still entangled to the polymer surface after each Ar cluster bombardment event, conversely to low M_w polymers, where the material volume energized in the ion impact is wiped out more effectively because there is no need to break covalent bonds [18,50]. An additional factor might intervene in the Y(d) behaviour of PS 60k compared to PS 4k, that is the lower interfacial (air/polymer) free volumes that characterize high M_w polymers with respect to the oligomers [51].

5. Conclusions

This study demonstrates a remarkable dependence of the sputter yield on the thickness of model polymer ultrathin films deposited onto a hard substrate (in this case silicon) under Ar cluster ion bombardment. To our best knowledge, it is the first time that a similar behavior is experimentally shown for polymer-based materials and especially oligomers. Indeed, previous investigations were carried out with different organic systems and cluster projectiles or by MD simulations. The thickness dependence of Y for PS 4k ultrathin layers on Si substrate was confirmed by two independent measurements of the film thickness, i.e. ellipsometry versus atomic force microscopy. The quantification of the phenomenon was based on the ellipsometric determination of the thickness ranging from ~15 nm to ~230 nm. Y shows a steep decay in the region below 90 nm for both PS 4k and PMMA 4k single-layers, then it reaches a constant bulk value. The absence of the Y(d) enhancement in the thin layer regime for PS 4k films onto a soft substrate leads to hypothesize a mechanistic nature of the observed phenomenon involving the reflection of the Ar cluster energy at the interface with the hard silicon substrate and its confinement in the polymer layer. A physical "2-layers" model was developed to describe the thickness dependence of Y, where the maximal sputter yield is located at a critical thickness of a few nm, depending on the energized volume by the primary ion impact (1st constant layer). Then, the gradual increase of d, by means of a 2nd hypothetical layer of increasing thickness, mitigates the interface effect till its complete cancellation around 90 nm, where the bulk value of Y is reached. MD results obtained on ultrathin layers of PE-like oligomers onto a hard substrate are in qualitative agreement with this model, supporting the mechanistic interpretation of the observed phenomenon. Additionally, an effect of the polymer M_w on the thickness dependence of Y is highlighted in the case of PS. Indeed,

an increase of M_w leads to a decrease of the substrate effect on the Y-enhancement for very thin films, due presumably to a higher degree of entanglements and a lower chain-end density. Further investigation could be undertaken, both in experiments and theoretical work, in order to elucidate the M_w impact on the trend of Y versus d. Finally, for accurate sputtering yield measurements on hard substrates, it is recommended to work with polymer films with a thickness above 100 nm for oligomers (PS 4k) and probably more for longer chains (PS 60k).

Appendix A: Supporting information

Figure S1: Tridimensional AFM images and related average surface roughness (R_a) versus the thickness of Si-supported PS 4k ultrathin films.

Figure S2: Tridimensional AFM images of a single edge of the incisions performed on the samples A1 and A5 of the PS 4k single-layer system for an estimation of the polymer film thickness.

Table S1: Young's moduli for the materials used in this paper.

Table S2: Sputter conditions employed for the different model systems analyzed by SIMS.

Figure S3: SIMS molecular depth-profiles of the 17.5-nm thick PS 4k film on silicon acquired with three different 10 keV Ar_{3000}^+ currents: 0.3 nA, 0.1 nA and 0.05 nA.

Figure S4: Comparison of the Y calculation based, respectively, on the Si^+ and $SiOH^+$ ion signals for the PS 4k and PMMA 4k single-layers.

Figure S5: Summary of the linear fittings Y(d) for the different model systems described in Table 2.

Figure S6: Sputter yield volume (Y) versus thickness (d) of the Si-supported thin films of PS 4k, PMMA 4k, PS 60k, and Y of the uppermost PS 4k layer of the polymer bilayer system.

Notes

Conflicts of interest: none.

Acknowledgements

The authors acknowledge the Belgian Science Policy Office for funding this work through the Interuniversity Attraction Pole (IAP Phase VII, convention: P7/34 'Physical Chemistry of Plasma Surface Interactions'). The authors also acknowledge the Belgian 'Fonds National de la Recherche Scientifique' (FNRS) for financial support to purchase the ToF-SIMS instrument. V. Cristaudo thanks Professor Alain Jonas, Professor Bernard Nysten and Cécile D'Haese for the single-wavelength ellipsometry and AFM measurements, respectively. Finally, V. Cristaudo thanks Dr. Delphine Magnin for the XRR measurements.

References

[1] A. Benninghoven, The History of Static-SIMS – A Personal Perspective, Chapter 2 in ToF-SIMS: Materials Analysis by Mass Spectrometry, Second Edition, IM Publications LLP and SurfaceSpectra Limited: Chichester, 2013.

[2] C.M. Mahoney, Cluster secondary ion mass spectrometry of polymers and related materials, Mass Spectrom. Rev. 29 (2009) 247-293.

[3] I. Yamada, J. Matsuo, N. Toyoda, A. Kirkpatrick, Materials processing by gas cluster ion beams, Materials Science and Engineering: R: Reports 34 (2001) 231-295.

[4] S. Ninomiya, K. Ichiki, H. Yamada, Y. Nakata, T. Seki, T. Aoki, J. Matsuo, Precise and fast secondary ion mass spectrometry depth profiling of polymer materials with large Ar cluster ion beams, Rapid Communications in Mass Spectrometry 23 (2009) 1601-1606.

[5] T. Mouhib, C. Poleunis, R. Möllers, E. Niehuis, P. Defrance, P. Bertrand, A. Delcorte, Organic depth profiling of C_{60} and C_{60} /phthalocyanine layers using argon clusters, Surface and Interface Analysis 45 (2013) 163-166.

[6] D. Rading, R. Moellers, H.-G. Cramer, E. Niehuis, Dual beam depth profiling of polymer materials: Comparison of C_{60} and Ar cluster ion beams for sputtering, Surface and Interface Analysis 45 (2013) 171-174.

[7] R. Havelund, A. Licciardello, J. Bailey, N. Tuccitto, D. Sapuppo, I.S. Gilmore, J.S. Sharp, J.L.S. Lee, T. Mouhib, A. Delcorte, Improving secondary ion mass spectrometry C_{60}^{n+} sputter depth profiling of challenging polymers with nitric oxide gas dosing, Analytical Chemistry 85 (2013) 5064-5070.

[8] T. Terlier, G. Zappalà, C. Marie, D. Léonard, J.P. Barnes, A. Licciardello, ToF-SIMS depth profiling of PS-b-PMMA block copolymers using Ar_n^+ , C_{60}^{++} , and Cs^+ sputtering ions, Analytical Chemistry 89 (2017) 6984-6991.

[9] G. Zappalà, V. Motta, N. Tuccitto, S. Vitale, A. Torrisi, A. Licciardello, Nitric oxide assisted C_{60} secondary ion mass spectrometry for molecular depth profiling of polyelectrolyte multilayers, Rapid Communications in Mass Spectrometry 29 (2015) 2204-2210.

[10] R. Möllers, N. Tuccitto, V. Torrisi, E. Niehuis, A. Licciardello, Chemical effects in C_{60} irradiation of polymers, Applied Surface Science 252 (2006) 6509-6512.

[11] B.J. Garrison, Z. Postawa, Computational view of surface based organic mass spectrometry, Mass Spectrometry Reviews 27 (2008) 289-315.

[12] A. Delcorte, O.A. Restrepo, B. Czerwinski, Cluster SIMS of Organic Materials: Theoretical Insights, Chapter 2 in Cluster Secondary Ion Mass Spectrometry: Principles and Applications, First Edition, John Wiley & Sons: New Jersey, 2013.

[13] A. Delcorte, V. Cristaudo, V. Lebec, B. Czerwinski, Sputtering of polymers by keV clusters: Microscopic views of the molecular dynamics, International Journal of Mass Spectrometry 370 (2014) 29-38.

[14] B. Czerwinski, Z. Postawa, B.J. Garrison, A. Delcorte, Molecular dynamics study of polystyrene bond-breaking and crosslinking under C_{60} and Ar_n cluster bombardment, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 303 (2013) 23-27.

[15] T. Aoki, Molecular dynamics simulations of cluster impacts on solid targets: Implantation, surface modification, and sputtering, Journal of Computational Electronics 13 (2014) 108-121.

[16] M.P. Seah, Universal equation for argon gas cluster sputtering yields, The Journal of Physical Chemistry C 117 (2013) 12622-12632.

[17] P.J. Cumpson, J.F. Portoles, A.J. Barlow, N. Sano, Accurate argon cluster-ion sputter yields: Measured yields and effect of the sputter threshold in practical depth-profiling by X-ray photoelectron spectroscopy and secondary ion mass spectrometry, Journal of Applied Physics 114 (2013) 124313.

[18] V. Cristaudo, C. Poleunis, B. Czerwinski, A. Delcorte, Ar cluster sputtering of polymers: Effects of cluster size and molecular weights, Surface and Interface Analysis 46 (2014) 79-82.

[19] M.P. Seah, Argon cluster size-dependence of sputtering yields of polymers: Molecular weights and the universal equation, Surface and Interface Analysis 47 (2015) 169-172.

[20] A. Delcorte, M. Debongnie, Macromolecular sample sputtering by large Ar and CH_4 clusters: Elucidating chain size and projectile effects with molecular dynamics, The Journal of Physical Chemistry C 119 (2015) 25868-25879.

[21] L. Rzeznik, B. Czerwinski, B.J. Garrison, N. Winograd, Z. Postawa, Microscopic insight into the sputtering of thin polystyrene films on Ag {111} induced by large and slow Ar clusters, The Journal of Physical Chemistry C 112 (2008) 521-531.

[22] L. Rzeznik, R. Paruch, B. Czerwinski, B.J. Garrison, Z. Postawa, Sputtering of thin films of bariated molecules of arachidic acid by large noble gas clusters, Vacuum 83 (2009) S155-S158.

[23] A. Chapiro, Radiation Chemistry of Polymeric Systems, John Wiley and Sons: New York & London, 1962, p. 712.

[24] C.B. Walsh, E.I. Franses, Ultrathin PMMA films spin-coated from toluene solutions, Thin Solid Films 429 (2003) 71-76.

[25] E. Mohajerani, F. Farajollahi, R. Mahzoon, S. Baghery, Morphological and thickness analysis for PMMA spin coated films, Journal of Optoelectronics and Advanced Materials 9 (2007) 3901-3906.

[26] D. Ennis, H. Betz, H. Ade, Direct spincasting of polystyrene thin films onto poly (methyl methacrylate), Journal of Polymer Science Part B: Polymer Physics 44 (2006) 3234-3244.

[27] T. Ohmi, M. Miyashita, M. Itano, T. Imaoka, I. Kawanabe, Dependence of thin-oxide films quality on surface microroughness, IEEE Transactions on Electron Devices 39 (1992) 537-545.

[28] Online Horiba technical notes: Forouhi-Bloomer alias Amorphous Dispersion Formula. http://www.horiba.com/fileadmin/uploads/Scientific/Downloads/OpticalSchool_CN/TN/ellips ometer/Forouhi-Bloomer_alias_Amorphous_Dispersion_Formula.pdf (accessed 23 October 2017)

[29] Online Horiba technical notes: New Amorphous Dispersion Formula. http://www.horiba.com/fileadmin/uploads/Scientific/Downloads/OpticalSchool_CN/TN/ellips ometer/New_Amorphous_Dispersion_Formula.pdf (accessed 23 October 2017)

[30] J.N. Hilfiker, R.A. Synowicki, C.L. Bungay, R. Carpio, Spectroscopic ellipsometry for polymer thin films, Solid State Technology 41 (1998) 101-107.

[31] H.M. El-Nasser, O.D. Ali, Effect of molecular weight and UV illumination on optical constants of PMMA thin films, Iranian Polymer Journal 19 (2010) 57-63.

[32] Website: refractiveindex.info.https://refractiveindex.info/?shelf=organic&book=polystyren&page=Sultanova (accessed 23 October 2017)

[33] Website: refractiveindex.info.

https://refractiveindex.info/?shelf=organic&book=poly(methyl_methacrylate)&page=Sultano va (accessed 23 October 2017)

[34] G. Beadie, M. Brindza, R.A. Flynn, A. Rosenberg, J.S. Shirk, Refractive index measurements of poly(methyl methacrylate) (PMMA) from 0.4-1.6 µm, Applied Optics 54 (2015) F139-F143.

[35] N. Sultanova, S. Kasarova, I. Nikolov, Dispersion properties of optical polymers, Acta Physica Polonica A 116 (2009) 585-587.

[36] R.F.M. Lobo, M.A. Pereira-da-Silva, M. Raposo, R.M. Faria, O.N. Oliveira Jr, M.A. Pereira-da-Silva, R.M. Faria, In situ thickness measurements of ultra-thin multilayer polymer films by atomic force microscopy, Nanotechnology 10 (1999) 389-393.

[37] A.G. Shard, R. Havelund, M.P. Seah, S.J. Spencer, I.S. Gilmore, N. Winograd, D. Mayo, T. Miyayama, E. Niehuis, D. Rading, R. Moellers, Argon cluster ion beams for organic depth profiling: Results from a VAMAS interlaboratory study, Analytical Chemistry 84 (2012) 7865-7873.

[38] A. Delcorte, P. Bertrand, X. Arys, A. Jonas, E. Wischerhoff, B. Mayer, A. Laschewsky, ToF-SIMS study of alternate polyelectrolyte thin films: Chemical surface characterization and molecular secondary ions sampling depth, Surface Science 366 (1999)149-165.

[39] S. Tardio, M.L. Abel, R.H. Carr, J.F. Watts, Polystyrene-silicon bonding through π electrons: A combined XPS and DFT study, Surface and Interface Analysis 48 (2016) 556-560.

[40] J.L. Keddie, R.A.L. Jones, R. Cory, Interface and surface effects on the glass-transition temperature in thin polymer films, Faraday Discussions 98 (1994) 219-230.

[41] J.L. Keddie, R.A.L. Jones, R. Cory, Size-dependent depression of the glass transition temperature in polymer films, Europhysics Letters 27 (1994) 59-64.

[42] R.D. Priestley, Effects of Nanoscale Confinement and Interfaces on the Structural Relaxation of Amorphous Polymers Monitored at the Molecular Scale by Fluorescence and Dielectric Spectroscopy. Ph.D. Thesis, Northwestern University, 2008.

[43] P. Rittigstein, The Glass Transition and Physical Aging Behavior of Polymer Nanocomposites Studied via Fluorescence. Ph.D. Thesis, Northwestern University, 2008.

[44] M. Grundner, H. Jacob, Investigations on hydrophilic and hydrophobic silicon (100) wafer surfaces by X-ray photoelectron and high-resolution electron energy loss-spectroscopy, Applied Physics A 39 (1986) 73-82.

[45] R. Paruch, L. Rzeznik, B. Czerwinski, B.J. Garrison, N. Winograd, Z. Postawa, Molecular dynamics simulations of sputtering of Langmuir-Blodgett multilayers by keV C_{60} projectiles, The Journal of Physical Chemistry C 113 (2009) 5641-5648.

[46] J. Kozole, A. Wucher, N. Winograd, Energy deposition during molecular depth profiling experiments with cluster ion beams, Analytical Chemistry 80 (2008) 5293-5301.

[47] S. Berg, I.V. Katardjiev, Preferential sputtering effects in thin film processing, Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 17 (1999) 1916-1925.

[48] N. Matsunami, Y. Yamamura, Y. Itikawa, N. Itoh, Y. Kazumata, S. Miyagawa, K. Morita, R. Shimizu, H. Tawara, Energy dependence of the ion-induced sputtering yields of monatomic solids, Atomic Data and Nuclear Data Tables 31 (1984) 1-80.

[49] A. Delcorte, K. Moshkunov, M. Debongnie, Relationships between crater and sputtered material characteristics in large gas cluster sputtering of polymers: Results from MD simulations, J. Vac. Sci. Technol. (2018), in press.

[50] A. Delcorte, O.A. Restrepo, K. Hamraoui, B. Czerwinski, Cluster impacts in organics: Microscopic models and universal sputtering curves, Surface and Interface Analysis 46 (2014) 46-50.

[51] W. Xia, D.D. Hsu, S. Keten, Molecular weight effects on the glass transition and confinement behavior of polymer thin films, Macromolecular Rapid Communications 2015, 36, 1422-1427.

Highlights

- The sputtering efficiency Y of polymers near the surface is dependent on that substrate. •
- The increase of Y for ultrathin layers on silicon is due to energy back-reflection. ٠
- A physical "2-layers" model is developed to describe the thickness dependence of Y. •
- The mechanistic interpretation of Y(d) is supported by molecular dynamics simulations. •
- The effect of the polymer M_w on the thickness dependence of Y is pointed out. •

pointee

