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X-ray enhanced sputter rates in argon cluster ion sputter-depth profiling of polymers^{a)}

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The authors have observed for the first time that x-ray exposure of certain polymers of “degrading” type can greatly enhance the sputter rate of these polymers by gas cluster ion beam (GCIB) profiling. They have observed craters of similar dimensions to the x-ray spot well within the perimeter of sputter craters, indicating that x-rays can assist GCIB sputtering very significantly. This can be a major source of the loss of depth-resolution in sputter depth profiles of polymers. The authors have measured experimentally sputter craters in 14 different polymers by white-light interferometry. The results show that x-ray exposure can introduce much more topography than might previously have been expected, through both thermal and direct x-ray degradation and cross-linking. Within the region exposed to x-rays, the response of the polymer surface depends on its chemistry, with degrading (also known as type II) polymers being susceptible to large increases in sputter rate in some cases. For example, this leads to a sputter rate increase of a factor of 3 in poly-L-lactic acid (PLLA) compared to cluster-ion sputtering in the absence of x rays under typical experimental conditions. By comparison, crosslinking (also known as type I) polymers show either the same sputter rate or a reduced sputter rate due to crosslinking. The authors model this behavior using the bond scission parameter (G_S) and crosslinking parameter (G_X) used to model radiation damage in polymers. Agreement is good, allowing us to provide guidelines to assist in planning XPS depth-profiling experiments, in particular, for polymers such as PMMA and PLLA, where any requirement for uniform sputter rate is a more stringent limit to x-ray exposure than the requirement for the XPS spectra to represent chemical states quantitatively without damage. © 2013 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4793284>]

I. INTRODUCTION

In XPS depth-profiles of polymers by gas cluster ion beam (GCIB) in our laboratory, we have sometimes noticed that the x rays leave an additional crater inside the ion-beam crater. The aim of this work is a systematic study of the results of this damage and a characterization of which types of polymer are susceptible to it. Clearly any additional topography introduced by the x rays is of great significance and potentially very detrimental to depth-resolution. The response of the sample depends, to some extent, on the operating mode of the XPS instrument regarding x-ray spot size.

A. Types of x-ray induced sputter crater morphology

The symptoms of x-ray assisted sputtering depend on the design of XPS instrument. In most XPS instruments, the area of analysis is limited by either

- (1) the x-ray spot size on the sample (x-ray limited, “XL”) or
- (2) the analyzed area (within the area illuminated by x rays) defined by the electron optics, iris, apertures, and analyzer (we may call such instruments “analyzer limited” or “AL”).

This is illustrated schematically in Fig. 1.

The shape of crater that one would ideally like to achieve is shown schematically in Fig. 2(a). This crater has a broad, flat crater bottom that allows one to produce a depth-profile with very good depth-resolution. Now consider how, in principle, the x rays may modify the sputter rate. One can imagine mechanisms that may increase, decrease, or leave the sputter rate unchanged. Consider first instruments of XL type. Any increase or decrease in sputter rate in the immediate vicinity of the x-ray spot will cause a topographical feature there during sputtering. We can interpret this as an x-ray induced feature within the sputter crater. Figure 2(b) shows one possible schematic profile in which the elevated temperature in the vicinity of the x rays causes a higher sputter rate, leaving a “thermally assisted” crater within the main GCIB crater. For low energy monatomic argon sputtering, Zekonyte¹ showed a sharp increase (around a factor of 10) in sputtering rate in nanometers per second as polystyrene was heated close to its glass transition temperature. We can expect that this may be true of GCIB sputtering too. If we were to separate the x-ray exposure from the GCIB sputtering (perhaps by first exposing to x rays, then leaving the specimen to equilibrate, and only then performing the GCIB sputtering), then we should not expect to see a thermally assisted crater. Similarly if a particular polymer shows little increase in sputter rate with temperature over the temperature range induced by x-ray heating, or a sample is particularly thin and thermally conductive, then again no thermal feature will result.

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FIG. 1. (Color online) Schematic of analytical area in XPS instruments: (a) limited by x-ray spot size and (b) limited by the analyzer acceptance.

The region over which temperature is increased is typically larger than that directly exposed to x rays, due to thermal conduction, so the thermally assisted crater may be larger than the x-ray spot, forming a "U-shaped" x-ray thermally induced crater inside the larger GCIB-only one. In addition, we sometimes see a central feature due to the *direct* effect of the x rays on the chemistry of the polymer. If the principal direct effect of the x rays is, for example, to cause

crosslinking in the polymer then we may expect a lower sputter rate than in the surrounding region that is not exposed to x rays. This will result in a mound-like feature having roughly the same area as the x-ray spot. This is shown schematically in Fig. 2(c) and gives rise to this "W-shaped" x-ray assisted GCIB feature inside the main GCIB-only crater. Polyether ether ketone (PEEK) is a polymer that we have seen exhibit W-shaped x-ray assisted GCIB features.

FIG. 2. Schematic cross-section through a GCIB sputter crater: (a) without x-ray exposure, (b) in which the x-ray spot has caused warming and an increased sputter rate, U-shaped in cross section, (c) in which (as well as a thermal feature) the x-ray beam has reduced the sputter rate in polymer directly exposed to the x rays, perhaps by crosslinking, and (d) in which (as well as a thermal feature) the x-ray beam has increased the sputter rate in polymer directly exposed to the x rays (by bond-scission in the polymer backbone).

FIG. 3. White-light interferometry fringes for an x-ray damage crater in PLLA. This was created by a nominally $30\text{ }\mu\text{m}$ diameter x-ray spot for 50 min, followed (after more than 1 h) separately by 50 min GCIB exposure.

In other polymers, the principal direct effect of the x rays may be to cause bond scission, reducing the molecular weight of the polymer and increasing the sputter yield. In these cases, we should expect another crater of roughly the size of the x-ray spot, as shown in Fig. 2(d), and gives rise to this “V-shaped” x-ray assisted GCIB feature inside the main GCIB-only crater. Poly-L-lactic acid (PLLA) is an example polymer seen to give rise to V-shaped x-ray induced GCIB features.

Therefore, in some cases, one can observe x-ray induced craters having considerable complexity of structure. These craters can be dominated by temperature some distance from the x-ray spot and by direct x-ray absorption processes close to it. In XL-type instruments in the region of the x-ray spot, the x-ray induced crater may be U, V, or W shaped

FIG. 4. (Color online) X-ray induced crater in PLLA, a degrading or “type II” polymer, measured by white-light interferometry. Note that the ion beam exposure is uniform over the region displayed here and occurred a few hours after x-ray exposure. The crater in the center is due to sputter-rate enhancement resulting from damage introduced by the x-ray exposure.

FIG. 5. Vertical section through the x-ray induced sputter crater shown in Fig. 4. Note that the roughness at the bottom of the crater is reduced compared to the roughness at the top.

according to the polymer under analysis and the degree of x-ray exposure. We have observed all of the above crater shapes in one polymer or another under a variety of instrument conditions. It is not surprising that these features occur, but what has surprised us is their scale. In some polymers, under quite normal XPS instrument conditions and depth profiles, the x-ray induced crater can be micrometers deep, indeed deeper than the main GCIB crater by a factor of 2 or more, whereas in other polymers, it does not occur at all. Often some of these features are present, but not others, such as a direct x-ray crater without a thermal crater around it. The full behavior is no doubt very complex, and a variety of these features occur to different extents for different polymers under different conditions. In some polymer samples with very flat surfaces, these structures are easy to see. In others, especially those samples having rough surfaces, the morphology of the sputter craters can be lost in the general roughness of the surface when measured by profilometry or scanning electron microscopy.

In the case of AL instruments, and provided x-ray illumination is relatively uniform over the analyzed area, the effect will be to increase (or decrease, according to the polymer type) the sputtering rate uniformly. This may be small in some cases, particularly if the x-ray exposure time or intensity is relatively small. However, in other cases, it may lead to a significant underestimate of the true depth of a feature in nanometers if reference data for sputter rate in the absence of x rays are used.

For XL instruments, in addition to this potential error in the depth scale, there can be a loss of depth resolution. In the

FIG. 6. W-shaped crater in PEEK, a crosslinking or type I polymer. We interpret this as a crosslinked column of similar cross-section to the x-ray spot, inside a region of thermally assisted sputtering approximately 0.25 mm in diameter and 80 nm deep.

absence of x rays, the sputter crater may have a flat bottom that would lead one to expect good depth resolution. However, the enhanced sputter rate in the vicinity of the x-ray spot creates a second, inner crater of similar size to the x-ray spot itself, which means XPS spectra include photoelectrons from sloping side-walls having a range of depth of origin. Examples of x-ray induced features are shown for two polymers in Figs. 3–6.

B. Polymer types

Winograd *et al.*² and Mahoney³ have reviewed the use of polyatomic and cluster ion sputter sources in SIMS. An important distinction has emerged in recent years in SIMS between two types of polymers. The first type comprises those polymers⁴ that undergo damage predominantly by crosslinking of the polymer chains, variously known as “crosslinking” or “type I” polymers.³ These are often difficult to depth-profile using a polyatomic ion such as C_{60} or coronene; it is thought because the ion-beam damage close to the surface introduces crosslinking that progressively impedes further sputtering. These may be called “self-sealing” materials. Of the suite of polymers of technological importance most seem to be of this self-sealing type. A large minority, however, respond to ion-induced damage predominantly by scission of bonds along the polymer backbone, gradually reducing the molecular mass of the polymer chains near the surface and thereby making sputter depth-profiling easier or at least not causing an unacceptable reduction in sputter rate with depth. These polymers are called variously “degrading” or type II polymers. In contrast to the “self-sealing” polymers, these may be called “self-opening” in a depth-profiling context. Generally, they are much easier to profile using polyatomic ions such as C_{60} or coronene because sputter rate is maintained even at depth. A promising feature of argon GCIB sources in both XPS and SIMS is that they appear to be capable of depth profiling both self-opening and self-sealing polymers.

We have found that the x-ray induced sputter craters discussed above can be correlated with the self-opening or self-sealing nature of the polymer matrix. If one assumes that the majority of the bond-scission or crosslinking is the result of free radical processes (such as Norrish I or II reaction⁵), then it should not come as a surprise that ions and x-ray photons both lead to either predominantly crosslinking or predominantly bond-scission in a particular polymer. The lifetime of free radicals can be long in these materials, much longer than photon absorption or the kinetic or even thermal effects of an ion cascade. Therefore, we should expect that the fate of these free radicals is only weakly dependent on what created them, and instead the local chemistry (and perhaps ambient temperature) dictates the relative probabilities of decay by inducing cross-linking or bond-scission. Many of the measurements of these rates of decay were made in the 1960s and 1970s in the context of attempts to use polymer irradiation on an industrial scale⁶ to improve their mechanical properties by crosslinking. Therefore, there is a good deal of published reference data available on the parameters

G_X and G_S that describe crosslinking and scission in polymers. These data provide a rough guide as to whether a particular polymer is likely to be of self-opening or self-sealing type. G_X is usually defined as the number of crosslinks created per 100 eV of radiant energy absorbed and G_S as the number of bond scissions in the polymer backbone per 100 eV of energy absorbed. For our application in XPS, with a monochromatic x-ray source of energy 1486 eV, this means that, on average, each x-ray photon introduces $14.86G_X$ crosslinks and $14.86G_S$ bond scissions in the polymer backbone. G_X is slightly below unity in many polymers, with a range between zero and about 2.5. Therefore, each XPS photon typically introduces an average of up to about 40 crosslinks each, with the value for a typical polymer being about 10. Charlesby summarized⁷ the main observations on the crosslinking of linear polymers as follows:

- (1) the degree of crosslinking is proportional to radiation dose;
- (2) it depends little on the type of high-energy radiation—sparsely ionizing (electrons, x rays, gamma rays) or highly ionizing (fast protons, alpha particles or fast neutrons);
- (3) it depends little on dose rate;
- (4) it does not require unsaturated or other more reactive groups;
- (5) with some exceptions (as in polymers containing aromatics), it does not vary greatly with chemical structure;
- (6) it does not vary greatly with temperature;
- (7) the efficiency of crosslinking, represented by G_X , is little influenced by molecular weight;
- (8) the G_X value for a polymer may, however, be greatly changed by the presence of certain additives in relatively small concentration.

As regards bond scission:

- (1) the number of bond scissions is proportional to radiation dose;
- (2) the bond scissions are randomly distributed.

Most of these observations date from around 60 years ago. Some are somewhat oversimplified, but nevertheless they are still useful.

C. Implications for sputter depth-profiling

In polymers where $G_X \gg G_S$ then the polymer is self-sealing or type I, and sputter rate *may* be reduced by x-ray induced polymer cross-linking. This occasionally leads to a central peak and a W-shaped x-ray induced crater, though in most polymers, the GCIB sputtering seems to have a virtually unchanged rate and no central peak is seen, giving a U-shaped thermal crater or no x-ray induced crater at all.

Polymers where $G_S \gg G_X$ are self-opening or type II. For these, the sputter rate may be increased by x-ray induced bond-scission, leading to V-shaped x-ray induced craters. If x-ray exposure is sufficiently small, or the polymer sufficiently resistant to x-ray induced free radicals causing either cross-linking or bond scission, then we may expect

U-shaped x-ray induced craters resulting from increased ion sputtering rates at the higher temperature in the vicinity of the x-ray spot, or no x-ray induced feature at all.

In instruments of AL type, both x rays and ion beam are approximately uniform over the area of analysis, so that one will not typically see a distinct x-ray induced crater within the area under analysis. Instead, one may expect sputter rate in the analytical area to depend on both ion beam current and accumulated x-ray exposure. In cases of self-opening polymers, this may lead to an apparent increase in sputter rate with depth. For self-sealing polymers, we may expect an apparent reduction in sputter-rate with depth as increasing accumulated x-ray exposure causes increased cross-linking and progressively lower sputter rate, even with constant ion beam current. Of course many other effects can cause reduced sputter rate with depth, so it may be easy to misinterpret x-ray induced slowing of the depth-profile as being due to some other effects.

II. EXPERIMENT

A. Effect on depth resolution during depth-profiling

To investigate the effect of the morphology of the x-ray induced sputter feature on depth resolution, we performed a depth-profile on a new potential XPS reference material kindly sent to us by Dr. Alex Shard of the National Physical Laboratory (NPL). This consists of four thin layers of 9-fluorenylmethoxycarbonyl (FMO) at known depths within a matrix of Irganox 1010 deposited on a silicon substrate. These should appear as near “delta-doped” layers within a depth profile. This material is similar to previous Irganox-based reference materials from NPL (Ref. 8) but is particularly useful for XPS as the fluorine content of the FMO makes these layers easy to distinguish. Sample rotation was used to ensure the crater bottom was as flat and uniform as possible and to discourage the appearance of sputter-induced topography. The x-ray spot size was set to $100\text{ }\mu\text{m}$ nominally and the GCIB raster to a $1\text{ mm} \times 1\text{ mm}$ square. The argon cluster ion sputtering was performed using the Thermo Electron MAGCIS gun on our K-Alpha XPS instrument (Thermo Scientific, East Grinstead, UK). A sample of XPS spectra showed that charge stability was achieved at the polymer surfaces.

We performed two depth profiles on the NPL FMO-in-Irganox reference material. The first involved extensive acquisition of spectra from C 1s, F 1s, and widescan regions, totaling 257 min. An excellent feature of this reference material is that, being a thin organic film, one can see visible interference colors change as the depth profile progresses (provided, as in this case, one has an optical microscope focused on the sample *in situ*). After the second FMO layer appeared in the depth-profile, it became clear from interference colors of the optical image that there was an x-ray induced topographical feature at the x-ray spot location, and the depth-profile was terminated after a total of 257 min of x-ray exposure. The final-state optical micrograph is shown in Fig. 7, where the x-ray induced feature can be seen clearly

Fig. 7. (Color online) Optical micrograph of the surface of an Irganox 1010/FMO reference material specimen after x-ray and GCIB depth profiling. Colored interference fringes make the x-ray induced feature of this specimen particularly clear.

at the center of the rotationally symmetric crater near the corner of the specimen.

In the second depth-profile at a different location on the specimen, only snapshot (parallel energy-acquisition) spectra of the F 1s region were recorded, taking only 4 s for each spectrum. The results of both depth-profiles are presented in Fig. 8, where the F 1s peak intensities are plotted. This figure shows two buried layers rich in fluorine, as expected. However, depth-resolution is significantly degraded by long x-ray exposure (continuous line) compared to the snapshot depth profile (dashed line). We attribute this to the development of varying-height topography within the area of analysis defined by the x-ray spot, caused by a varying degree of x-ray assisted (or inhibited) GCIB sputtering within that area. Figure 8 shows a schematic cross-section through the sputter crater inset at the top right; this shows the sputter crater for large (continuous line) and small x-ray exposures (dashed line). To verify this

Fig. 8. Reduction in depth resolution resulting from x-ray damage during argon cluster ion sputter-depth profiling. The dashed line shows F 1s peak intensity for short x-ray exposure and the continuous line for x-ray exposure totaling 257 min. Clearly prolonged x-ray exposure reduces depth-resolution but increases overall sputter rate by about 40% in this case. Inset at the top right is a schematic diagram showing the expected cross-section through the two sputter craters, again dashed for short exposure and continuous for long exposure.

interpretation, we measured the topography of the long-acquisition crater. We used a white-light interferometer, a Zygo Newview 5000 (Zygo Corporation, Middlefield, CT). The z axis was calibrated using a step-height standard artifact⁹ traceable to dimensional standards at the U.S. National Institute for Science and Technology. The interference colors that are so helpful when viewing this material by eye caused problems in the interferometer. Therefore, we deposited around 10 nm of gold on the surface by sputtering, using a sputter coater regularly used to prepare nonconducting samples for electron microscopy. This coating ensured good reflection from the top surface of the sample, giving the results shown in Fig. 9. We interpret this as a W-shaped x-ray induced GCIB sputtering feature. The x-ray spot size was nominally 100 μm , leading to a central peak of around 60 nm in height and 140 μm diameter, within a valley of around 80 nm in height and 700 μm diameter resulting from, we believe, enhanced sputtering due to local x-ray heating.

B. X-ray induced crater measurements

We have measured argon GCIB craters in 14 different polymers to assess how the susceptibility to x-ray assisted sputtering may depend on the chemistry of the polymer. The aim is to provide guidelines to assist in planning XPS depth-profiling experiments, in particular, the x-ray exposure limits that may apply in the analysis of particular polymers.

For each polymer, three separate sputter craters were formed, plus an additional sample to confirm particular results and ensure the measurements are repeatable. In particular, for each polymer, we formed GCIB sputter craters by

- (1) 3000 s simultaneous GCIB and x-ray exposure,
- (2) 3000 s x-ray exposure, followed by a cooling period of at least 1 h, followed by 3000 s of separate GCIB sputtering without x rays, and
- (3) 3000 s GCIB sputtering alone.

This allows us to separate thermal effects caused by the x-ray exposure from direct x-ray induced changes to the

polymer chemistry that will persist after the temperature of the sample returns to ambient.

Sputter craters were formed in our Thermo Scientific K-Alpha instrument, which is of XL type. This has a monochromated Al $K\alpha$ x-ray source having an x-ray energy of 1486 eV. The GCIB source is a Thermo Scientific MAGCIS gun, which throughout this work we operated at a beam energy of 4000 eV in “small cluster” mode, meaning a broad distribution of argon cluster size centered around 1000 atoms per cluster. The GCIB gun is placed at 58° to the surface normal. A 1 mm $\times$ 1 mm raster scan of the cluster ions in the plane of the sample was used, and the x-ray spot size was set to a nominal 30 μm , i.e., well within the area of the cluster ion crater. Details of the polymer samples are given in Table I, including reference data on polymer response to radiation taken from Mahoney³ and Berejka and Cleland.¹⁰ Polymer glass transition temperature, T_g , is an important parameter for understanding the general trend in behavior as we shall see. Values for T_g in Table I are taken from the OUP Polymer Handbook.⁴

III. RESULTS AND DISCUSSION

A. Modeling of x-ray assisted GCIB sputtering

We should expect that the additional sputter rate observed will increase with the propensity of the polymer concerned to degrade by a molecular-mass reducing route. Figure 10, developed from a diagram by Makuuchi and Cheng,⁶ shows in a very schematic way how one may expect polymer microstructure to develop during irradiation. We would expect that self-opening polymers, i.e., cases in which $G_X \ll G_S$ would lead to increased sputter rates, whereas self-sealing polymers, i.e., cases in which $G_X \gg G_S$ may lead to a reduction in GCIB sputter rate.

There are reasons to guess that both the thermal and direct x-ray induced GCIB sputter features depend on the glass transition temperature of the polymer, though via very different mechanisms. We first discuss these mechanisms qualitatively.

Fig. 9. (Color online) (a) Topographic map of x-ray assisted sputter feature in Irganox 1010/FMOC reference material. Areas where surface roughness has made fringe measurement difficult are left black in this plot; nevertheless, there is a clear central peak in a larger thermally induced crater. (b) Three-dimensional view of the x-ray induced sputter feature shown in (a).

TABLE I. Polymer films from which sputter crater topography measurements were made. Also listed here are the polymer type from Mahoney (type I or II) and Berejka and Cleland (S = scission; X = crosslinking, O = neutral). Glass transition temperatures are taken from the OUP Polymer Handbook (Ref. 4).

Polymer	Acronym	Radiation response type		Glass transition temperature (K)
		Mahoney (Ref. 3)	Berejka and Cleland (Ref. 10)	
High density polyethylene	HDPE	I	X	140–160
Polyvinylidene fluoride	PVDF	I	X	213
Nylon 6,6	Nylon6,6	I		320–330
Poly-L-lactic acid	PLLA	II		326–377
Polyvinylchloride	PVC	I	S/X	344–371
Polyethylene terephthalate	PET	II	O	342–388
Polystyrene	PS	I	O	373
Cellulose triacetate	CA			273–473
Poly methyl methacrylate	PMMA	II	S	379–387
Polyether ether ketone	PEEK			415–425
Polychlorotrifluoroethylene	PCTFE	II	S	423
Polycarbonate	PC	I	O	423
Polyethersulphone	PES			498
Polyimide	PI (kapton)	I		633–683

1. Thermal feature

Suppose the ambient temperature is T , and this is increased by ΔT under the heating action of the x-rays. Clearly ΔT depends on the thermal conductivity in the vicinity of the x-ray exposure and, for example, the thickness of the polymer film and what material supports it. Nevertheless, we might normally expect a T of around 290 K, and a ΔT of a few tens of Kelvin, though this will usually be very difficult to measure *in situ*. If $T + \Delta T$ approaches T_g , then sputter rate may increase substantially due to increased mobility of the polymer chains allowing rearrangement to reveal more vulnerable parts of the chain to the thin surface layer that undergoes GCIB sputtering. Therefore, we would expect a thermal sputter feature to be observed if $(T + \Delta T) \sim T_g$.

FIG. 10. Schematic diagram indicating the structural responses that polymers have to radiation. In those polymers where crosslinking dominates, a dense network of crosslinks in a 3D structure is formed. Where bond scission dominates then low mass linear fragments are formed. In between, a mixed network of crosslinks and scissions leads to a complex mixed network.

Conversely, if $T \gg T_g$, i.e., the ambient temperature is already well above the glass transition temperature, or $(T + \Delta T) \ll T_g$, i.e., the x-rays do not raise the polymer temperature to near the glass transition temperature, then we would expect not to observe a thermal topographical feature because sputter rate inside and outside the x-ray heated region will be very similar.

2. Direct x-ray feature

The radiation induced crosslinking of two polymer chains depends on the close proximity of two free radicals, one on each chain. For temperatures very much lower than T_g , polymer chains are restricted to thermal vibration, but chains cannot rotate or move relative to one another. Within the lifetime of an x-ray induced free radical, it is unlikely to come within the required proximity of another free radical on another chain and form a crosslinking bond. Conversely, above T_g , the polymer becomes rubber-like, and chains move relative to one another. Within the lifetimes of two free radicals on two different chains, they are much more likely to come into close proximity and form a crosslink. Therefore, we might expect G_X to be related to T_g , and for G_X at the XPS analytical temperature to decrease monotonically with the increasing T_g of polymers in a set of samples. Figure 11 shows G_X plotted against T_g for a large number of polymers of technological significance, and indeed there is a trend, albeit with considerable scatter due to specific chemistry. We have plotted an exponential fit to this data in the figure, though this has no purpose except to guide the eye.

Figure 12 shows our measurements of x-ray sputter rate enhancement factors of the 14 polymers in Table II, plotted against their glass transition temperatures. We interpret this as follows (though given the complexity of this wide range of polymer morphologies and the challenging nature of the measurements, this is likely to be only a first approximation to the full behavior).

FIG. 11. (Color online) Effect of the glass transition temperature on G_X , comprising data from Fig. 2.11 of Makuuchi and Cheng (Ref. 6) and our own exponential fit.

Consider T_g as characterizing the mobility of polymer chains at around room temperature, the temperature at which the GCIB sputtering was performed. For polymers such as high density polyethylene (HDPE), with very low T_g ,⁴ these chains have high mobilities. Crosslinking being a binary process, two free radicals from two polymer chains need to come into close proximity to form a crosslinking bond. Therefore, the high chain mobilities of low T_g polymers aid crosslink formation, and we do not see any x-ray enhancement of sputter rate for these polymers. At the other extreme, for polymers of high T_g (such as PES, for example), the chain mobility is very low, and at room temperature, only thermal vibration around equilibrium positions are possible. This means crosslinking is not favored, and instead bond scission is the dominant fate for free radicals created by x-ray exposure. However, for these high T_g polymers, this does not aid sputtering rate; the density of scission events is still small compared to the total length of each polymer chain and the chain segments still immobile due to the non-covalent interactions that give the polymer chains a high T_g . Therefore, x-ray exposure does not increase sputter rate of polymers of high T_g (more than about 200 °C) or low T_g (less than about 60 °C). In the mid-range of glass transition temperature, however, much more interesting behavior can

TABLE II. Results of white-light interferometry measurement of x-ray induced GCIB sputter crater morphology.

Polymer acronym	Mean T_g (K)	X-ray induced topography	Sputter feature depths (nm)				
			D_T	D_X	D_{CI}	D_T/D_{CI}	D_X/D_{CI}
HDPE	150	U	2507	0	476	5.3	0.0
PVDF	213	U	510	0	506	1.0	0.0
Nylon6,6	325	—	0	0	370	0.0	0.0
PLLA	351.5	V	0	1541	881	0.0	1.8
PVC	357.5	—	0	0	969	0.0	0.0
PET	365	—	0	0	238	0.0	0.0
PS	373	—	0	0	1193	0.0	0.0
CA	373	V	0	1171	1761	0.0	0.7
PMMA	383	V	62	575	801	0.1	0.7
PEEK	420	W	144	-103	128	1.1	-0.8
PCTFE	423	V	0	1264	635	0.0	2.0
PC	423	V	0	234	687	0.0	0.3
PES	498	—	0	0	220	0.0	0.0
PI (kapton)	658	—	0	0	174	0.0	0.0

occur. In this regime, there is enough chain mobility at room temperature to make G_X comparable with G_S in many polymers, and which is dominant depends on chemistry and structure in some detail. There is enough chain mobility to allow rearrangement of the surface during sputtering, so that x-ray induced bond scission—if it is the dominant process compared to crosslinking—can result in relatively low mass fragments being sputtered easily from the surface, then replaced by more low mass fragments. Within this mid-mobility range, x rays can enhance the GCIB sputter rate considerably, provided the particular polymer structure does not favor crosslinking.

3. Damage limit estimation

The practical consequence of the above work is that there is a limit to the total x-ray exposure we can apply to a polymer sample during depth-profiling by GCIB. This may be very different, either higher or lower, than the x-ray exposure that causes significant changes to the XPS spectra themselves. The important issue is how to tell when that limit has been reached or when one is in danger of exceeding it in a planned experiment. Direct measurements are difficult, because few XPS users have easy access to tools for measuring the morphology of sputter craters rapidly. Even fewer can measure x-ray intensity inside the XPS instrument directly. Therefore, a simple method of judging whether the damage limit will be reached would be very useful. We have examined the suitability of unplasticized polyvinylchloride (PVC) for this purpose. It is readily available and known to be sensitive to x-ray damage¹¹ in XPS. An interlaboratory comparison has shown it to be a suitable material for damage estimation in XPS (Ref. 12) (rather than polytetrafluoroethylene, for example) in part because it degrades by first-order kinetics under the conditions typical of XPS analysis. The

FIG. 12. X-ray sputter rate enhancement ratio and glass transition temperature for the 14 polymers in this study.

particular nature of this damage in PVC does not have a significant effect on GCIB sputter rate, but it does make substantial and easily measureable changes to the C 1s spectrum. Our aim is to be able to estimate the maximum permissible x-ray exposure time in a given depth-profile experiment by recording XPS spectra from a separate sample of PVC as they change over time of x-ray exposure. PVC x-ray damage is known to occur principally through the loss of pendent Cl atoms rather than scission of bonds in the $-C-C-$ backbone.¹³ Damage is known to depend on temperature,¹⁴ so for the purposes of this work, PVC spectra were all acquired without external heating or cooling. PVC has been used as an indicator of x-ray damage for many years,¹¹ but in the application here, one can view it slightly differently. Essentially, we are using the damage rate in a crosslinking (self-sealing or type I) polymer with easily XPS-identifiable side groups (chlorine atoms) to estimate the rate of damage in degrading (self-opening or type II) polymers, where there is no direct evidence in the XPS spectra of backbone bond scission having occurred. Results are plotted in Fig. 13 using the same x-ray conditions in the same instrument as the polymer measurements set out earlier. The damage is roughly exponential, at least over the first 200 min for both 100 and 30 μm nominal spot sizes. The time taken for Cl 2p peak intensity to fall to 90% of its original intensity is 31.8 min in the case of the 100 μm nominal spot and 100.6 min in the case of the 30 μm nominal spot. Let us call this the PVC90% damage time, $t_{\text{PVC90\%}}$. This then allows us to summarize results from Table III in terms of the PVC damage time. To ensure, for any particular polymer, that the x-rays do not increase sputter rate by more than 10%, one must not exceed an exposure time $t_{\text{SR10\%}}$, which is a fraction K of the PVC90% damage time, $t_{\text{PVC90\%}}$.

$$t_{\text{SR10\%}} = K t_{\text{PVC90\%}}. \quad (1)$$

For example, if on a particular XL XPS instrument the Cl 2p peak intensity falls to 90% of its original value after 60 min of x-ray exposure, then to ensure that the GCIB

FIG. 13. Measured Cl 2p peak intensity of unplasticized PVC under prolonged x-ray exposure.

TABLE III. Maximum x-ray exposure time (in units of the PVC 10% damage time) to ensure <10% difference in sputter depth due to x-ray exposure.

Polymer	K
PLLA	0.03
PMMA	0.07
Cellulose acetate	0.07
PEEK	0.06
PCTFE	0.03
PC	0.17

sputter crater depth in polycarbonate (PC) varies by no more than 10% due to x-ray exposure, one must limit that exposure to 0.17 of 60 min, i.e., around 10 min. Expressing maximum exposure time in terms of the PVC90% damage time allows these figures to be used in any XPS instrument, even if the x-ray intensity of the x-ray source in that instrument is not known.

4. Effect of charge neutralizer

The effect of x-rays on the rate of GCIB sputtering is clear, since the size of the x-ray spot is known in XL-type instruments. However, the “thermal” crater could potentially result from not just thermal effects but damage introduced by the charge neutralizer (flood gun) used to maintain charge neutrality at the surface. In the XPS instrument used for this work, the neutralizer consists of a gun producing low energy electrons and argon ions. Though the x-ray feature is the main focus of this work, at the kind suggestion of one of the reviewers, we have made measurements indicative of the effect of the charge neutralizer.

We acquired a series of spectra from a single piece of unplasticized PVC film. The x-ray spot size was chosen to be 400 μm . Survey and narrowscan C 1s spectra were taken at each point (with flood gun on), then the x-ray spot was moved 1 mm away. The flood gun was then left on for a predetermined time between 30 and 3000 s, followed by repeating the original survey and C 1s spectra at the original point. Five points provided data for 30, 100, 300, 1000, and 3000 s of flood gun exposure, the narrowscan spectra shown in Fig. 14. There is some degradation of the material, especially at the longest exposure times, as evidenced by the reduction of the C 1s chemical state peak corresponding to carbon bound to chlorine. The sequence of five point measurements was then repeated in a new region of the film, this time with the flood gun off for the 30–3000 s exposure intervals. The x-ray gun was on throughout, and the flood gun was on during the acquisition of all of the spectra. Figure 15 shows the ratio of chlorine and hydrocarbon chemical states in the C 1s region after peak fitting, for flood gun on (filled circles) and flood gun off (open circles). There is evidence of degradation taking place as the chlorine-bound state decreases in intensity with time. There is considerable scatter in these results; nevertheless, similar degradation seems to occur even without the flood gun being on. This could be the result of heating by the x-ray spot or the small x-ray intensity at 1 mm

FIG. 14. Peak fits to the C 1s region for increasing exposure of PVC film to charge neutralizer (flood gun) as discussed in the text. There is a progressive loss of C*-Cl as time progresses, representing progressive surface damage to the PVC sample.

from the center of the x-ray spot (of nominal width 400 μm). Much more systematic data are needed to draw firm conclusions, but it would not seem that flood gun exposure is a dominant effect likely to cause the large thermal craters seen

FIG. 15. Ratio of peak intensity of C*-Cl to non-C*-C groups in PVC as a function of time interval exposed (filled circles) or not exposed (open circles) to the flood gun charge neutralizer.

in our measurements set out above, though it may be a contributory factor in some cases.

IV. CONCLUSIONS

- (1) For polymers of the degrading type, x-ray exposures of the type typical in XPS analysis can accelerate GCIB ion sputtering by large factors in the range 1 to around 3.
- (2) For polymers of the crosslinking type, little or no such acceleration is seen, at least within the limits of accuracy of our present work.
- (3) For both types of polymers, there may be a thermally accelerated sputtering effect, especially for polymers where the temperature reached in the analytical position approaches the polymer glass transition temperature. For most polymers, this thermal effect is not seen, perhaps due to the glass transition temperature being much higher or lower than the temperatures reached during analysis. Charge neutralizer (flood gun) damage may also contribute to this thermal effect.
- (4) It is good to blank the x rays (i.e., either switch them off or move the x-ray spot away from the area under analysis) if one can, whenever acquisition of XPS spectra is not in progress.
- (5) In addition, for some polymers, perhaps especially including those such as PMMA with glass transition temperatures that may be approached by x-ray induced heating, it may be beneficial to allow a cooling-period between blanking the x-rays and the subsequent ion beam raster scan.
- (6) In a few cases, x-ray assisted GCIB sputtering may be beneficial rather than a problem to be avoided. We observed PLLA and in some cases PMMA to show smoother surfaces in areas exposed to both x rays and ion beam compared to ion beam alone at the same depth. Therefore, depth resolution in a few cases may be enhanced by x-ray assisted GCIB sputtering, and total experimental time may be reduced by a factor of up to 3 or 4 in a few such cases.
- (7) A limit on the allowable x-ray exposure time for a particular polymer under particular instrument conditions may be estimated by measuring the damage rate of a sample of unplasticized PVC.
- (8) Clearly, a full description of the GCIB sputtering process must include effects such as depolymerization ("unzipping") and crystallinity as they affect G_X and G_S .

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