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Material dependence of argon cluster ion sputter yield in polymers: Method and measurements of relative sputter yields for 19 polymers^{a)}

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There is a pressing need for reference data to allow sputter depth-profiling of polymers using cluster and polyatomic ion sources for the quantification of depth in XPS and SIMS. The authors have developed a new method of sputter rate measurement based on a combination of contact masking and white-light interferometry. This allowed us to measure sputter rates for 19 different polymers of technological significance, a much wider set of data than any available previously. The results show a much larger range of sputter yield than might previously have been expected. For example, the sputter yield of PMMA being more than ten times that of poly ether ether ketone when using argon ion clusters of around 4 eV/atom, with other polymers being widely distributed between these extremes. Without reference data for sputter rate this wide range could lead to major errors in depth estimation in sputter depth-profiling of polymer coatings, biomaterials, nanostructures, polymer electronic and polymer photovoltaic devices. © 2013 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4791669>]

I. INTRODUCTION

Rapid and exciting progress has been made in recent years in depth-profiling of polymers through the use of polyatomic and cluster ion beams.¹ There is a pressing need for reference data to allow sputter depth-profiling of polymers using cluster and polyatomic ion sources. These sources have become commercially available on XPS instruments in the last few years, and offer the prospect for the first time of low-damage depth profiles of materials of critical importance in tissue engineering, drug delivery systems, organic photovoltaics, organic light emitting diode displays, and printable electronics among many others. Argon cluster ion sources were originally developed for semiconductor processing,^{2,3} and advanced coatings,⁴ and subsequently the use of these sources for analytical applications was pioneered in SIMS.^{5,6} They are likely to be equally or even more useful in XPS,⁷ where for example sputter depth-profiling of organic semiconductors⁸ could, at least in principle, give access to defect and band bending measurements at interfaces. X-ray assisted cluster ion sputtering⁹ has been observed to be a large effect, but is not significant for a large number of polymers.

As with all other types of sputter depth-profiling, one obtains spectra as a function of sputtering time, whereas the technological application generally requires a depth scale in nanometers. As we shall see, the sputter yield varies greatly from one polymer matrix to another so that the depth scale of a depth profile can be very misleading unless reference data are available.

Few measurements of sputter rate have so far been made with argon cluster ion sources. Of these, the typical method is to prepare a thin film of polymer on a substrate such as a silicon wafer by spin-casting from solution in an organic

solvent, or by a physical vapor deposition method. The thickness of the film can be measured using an optical technique (often ellipsometry) or atomic force microscopy (AFM) at a step-edge. A sputter depth profile of the film then indicates how long it takes to remove the film by sputtering and reveal the underlying silicon. This works well if a researcher is interested in the sputter rate for an individual polymer of relevance to his or her work. However, it has a number of practical problems if it is to be used to compile a large data set on sputter rate for many polymers. The spin-casting requirements are often very different for different polymers, and low solubility can be a problem. Some polymers are sufficiently opaque as to make ellipsometry difficult, while others are sufficiently soft to make AFM measurements of film thickness unreliable unless performed with great care. Opacity can often be overcome by coating with a thin reflective film (for example, a sputtered gold coating) but the other issues above often prove much more of a problem. When dealing with novel polymer materials, or multilayers, in an analytical laboratory such as ours we are often presented with a material having an application in medical implants or organic electronics and asked to produce a depth profile: the client would not be happy to be told to spin-cast a thin film for calibration purposes.

II. EXPERIMENT: METHOD OF SPUTTER CRATER MEASUREMENT

We have developed a method that allows sputter rates to be measured for an arbitrary sample without spin-casting, provided the sample does not have unusually high surface roughness. Our method is based on a combination of techniques set out in an ISO Technical Report¹⁰ and a method used previously to measure polymer sputter rates by Zekonyte,¹¹ together with profilometry by noncontact white-light interferometry. A contact shadow mask is used during sputtering, leaving fine step-edges throughout the area of a sputter crater

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that are straightforward to measure. We used white-light interferometry in place of contact profilometry and a specially designed photochemically etched mask. The masks were designed by us and fabricated in stainless-steel by photochemical etching (Photofabrication, St Neots, UK) from 100 μm thick metal foil. We designed this stainless-steel contact mask having twenty 150 μm wide rectangular slits, 0.8 cm in length, each separated by 100 μm bars. After etching, this results in a mask having self-supporting parallel bars about 100 μm wide and 150 μm apart. These dimensions were chosen to provide a sufficiently fine series of step-edges suitable for measurement across a sputter crater of dimensions of around 1–3 mm to suit the typical dimensions of typical argon cluster ion beam profiles and raster sizes. These grid masks were integrated into a larger and 0.5 mm thick frame, also fabricated in stainless-steel by photochemical etching, and which could be held on the surface of a sample in very close contact using a clip. No adhesives were used. All but a few of the polymers were as-received films obtained from Goodfellow Materials (Huntingdon, UK), the exceptions being polycaprolactone, which was drop cast by us at 65 °C from granules (MUTR, Waltham Cross, UK). The PETG sheet (Quinn Plastics, Derrylin, Northern Ireland, UK) was made from SpectarTM resin (Eastman Chemical Company, Kingsport, Tennessee, USA) and Kapton film supplied by Advent Materials (Oxford, UK). Unfortunately, molecular weight information is not available from the suppliers, though we expect these materials to have a form similar to those in normal industrial usage: They are not the result of unusual polymer syntheses.

In each case, the long axis of the apertures in the mask was aligned with the direction of the incident argon cluster ions in the plane of the sample—in other words, we sputtered along the trenches formed by the mask. The angle of incidence of argon clusters in this work was 58° from the surface normal. Prior to applying the mask, the only treatment of the polymer surface was a wipe using a lint-free tissue containing ethanol.

Mesh-shadowing is particularly useful in our application of polymer sputter rate measurement compared to other applications to craters in inorganic materials, because sputter rates from metals such as stainless-steel using Ar cluster or polyatomic ions are typically very small. Therefore, little damage was done to the mesh in the process of sputtering the polymers below it, and one can effectively regard the sputtering from the metal surface of the mask as negligible.

Stylus profilometry can be difficult and slow for sputter craters in polymers, some of which can be soft enough to be deformed or scratched by the stylus unless conditions are carefully optimized. Therefore instead we used a white-light interferometer, a Zygo Newview 5000 (Zygo, Middlefield, CT, USA) which provides a noncontact profiling method. The z-axis was calibrated using a step-height standard artifact (VLSI Standards, San Jose, California, Model SHS-1.8QC, Ser. No. 4343-39-22) traceable to dimensional standards at the US National Institute for Science and Technology (NIST). Most measurements were performed with a Michelson 2.5 $\times$ objective lens containing

a Michelson interferometer with a perpendicular reference arm but in some cases it was necessary to switch to a Mirau 10 $\times$ or a Mirau 50 $\times$, containing both a Mirau interferometer, in order to obtain good fringe patterns from which the crater depth could be measured. The profilometer provides an additional magnification control that ranges from 0.4 $\times$ to 2.0 $\times$, which was adjusted at convenience. The use of higher magnification settings and objectives was normally made necessary by the need for the instrument to resolve a complex narrow fringes pattern produced by high surface roughness.

The argon cluster ion sputtering was performed using the Thermo Scientific MAGCIS gun on our K-Alpha XPS instrument (Thermo Scientific, East Grinstead, UK) at 4000 eV cluster ion energy and using Wien filter settings that the manufacturer has observed to lead to clusters of approximately 1000 atoms with a wide size distribution. All sputtering was performed at ambient temperature without cooling, and flood gun used in each case to assist in neutralizing surface charges. No x rays were used during sputtering so as to avoid x-ray enhancement;⁹ however, a sample of XPS spectra at other points on the polymer surface showed that charge stability was achieved during sputtering. A square raster of 1 $\times$ 1 mm² in the plane of the sample was applied to improve the flatness of the crater bottom. No rotation of the sample was performed when masks were used. Rotation would have improved the uniformity of the crater further, but was difficult given the need to align the sputter direction with the linear apertures in the contact mask. In a few cases, notably PMMA, we saw the development of topography at the bottom of the deepest craters that made the formation of interference fringes difficult, so sputter times were typically limited so as to give craters no more than a few micrometers in depth. An example of white-light interferometry measurements is shown in Fig. 1.

Beam current in cluster ion sputtering is difficult to measure accurately due to the nonconducting nature of typical samples. Therefore, the relative sputter rate results we present in Table I are given relative to the sputter rate in Irganox 1010 under identical instrument conditions (but with sample rotation and without a mask). This is analogous to the practice for many years of quoting inorganic sputter rates relative to that of tantalum pentoxide reference materials. Certified reference materials consisting of 30 and 100 nm of tantalum pentoxide on tantalum are available commercially,¹² and the success of current interlaboratory comparisons of Irganox 1010-based multilayer reference material means that these will very likely shortly be commercially available too. This is appropriate to organic depth-profiling in the same way that the tantalum pentoxide reference materials have been appropriate for inorganics. We are grateful to Dr. Alex Shard of the National Physical Laboratory for samples of the FMOC/Irganox 1010 reference material developed there. Figure 2 shows the sputter depth profile through this reference material used to provide the relative sputter yields. This has rather fewer points in the depth profile than one might hope, given the clearly excellent depth resolution, but this was limited by the minimum period of computerized rotation of the sample, which made it necessary to have rather longer

FIG. 1. (Color online) (a) Topography map of a sputter crater on polystyrene obtained by white-light profilometry. (b) Linescan showing step-heights representative of crater depth.

TABLE I. Measured sputter rate relative to Irganox 1010 for 19 polymers for Ar cluster ions of energy 4000 eV and a typical cluster size of 1000 atoms.

Polymer	Acronym	Relative sputter yield (with respect to Irganox 1010)	Estimated uncertainty at one standard deviation
Cellulose acetate	CA	1.15	0.21
Poly methyl methacrylate	PMMA	1.02	0.19
Polystyrene	PS	0.87	0.17
Poly(vinyl chloride)	PVC	0.60	0.13
Polypropylene	PP	0.44	0.11
Poly-L-lactic acid	PLLA	0.44	0.10
Polycarbonate	PC	0.43	0.10
Poly chloro trifluoroethylene	PCTFE	0.39	0.10
Polyvinylidene fluoride	PVDF	0.31	0.09
Poly tetra fluoro ethylene	PTFE	0.30	0.09
Low density polyethylene	LDPE	0.29	0.08
Poly caprolactone	PCL	0.29	0.08
Nylon 6,6	Nylon	0.23	0.08
Acrylonitrile-methyl acrylate copolymer	Barex	0.21	0.07
Polyethylene terephthalate glycol-modified	PETG	0.22	0.07
Polyethylene naphthalate	PEN	0.16	0.06
Poly(ethylene terephthalate)	PET	0.15	0.06
Polyethersulphone	PES	0.14	0.05
Polyether ether ketone	PEEK	0.08	0.03

Fig. 2. GCIB sputter depth profile of FMOC/Irganox 1010 reference material under the same instrumental conditions (cluster ion energy 4000 eV, cluster ion size around 1000 atoms) as for the other polymer measurements in this work.

sputter intervals between successive fluorine narrowscan spectra than we would have liked. Nevertheless, the overly discrete nature of the depth profile in Fig. 2 does not lead to a significant additional uncertainty to the values of Table I, since the uniformity of crater bottom (measured by white-light interferometry) is the major contribution to uncertainty in these sputter rates. A number of repeat measurements were made as a check of repeatability and in order to estimate this accuracy. Three measurements of PS, PMMA, and CA were made, and the standard deviation used to estimate the accuracy of all the polymer relative sputter rates. Beam currents were recorded before and after measurements, and corrections made for the small beam current instability this indicated. A final set of measurements was performed with PMMA, PS, and directly with the NPL reference material.

A few polymers proved difficult to measure using our method, generally due to problems with forming good fringes in white-light interferometry arising from a combination of

- (1) surface roughness in the original as-received sample,
- (2) light-scattering within opaque polymer material.

In particular though we successfully formed sputter craters in polyoxymethylene and polyhydroxybutyrate that were visible to the naked eye, the measurements from these surfaces had large uncertainties, and data for these polymers are not presented in Table I. We plan to return to these polymers in the future and extend the table of measurements to include them, as well as add measurements for all these polymers at higher argon cluster ion energies and a range of cluster size. The main uncertainty in these measurements is in the white-light interferometry, in the measurement of the crater depth, particularly for crater profiles that have some residual nonuniformity. In future, this may be reduced by sputtering from both directions aligned with the mask slits rather than just one, even though full rotation of the sample is not possible in this method.

III. RESULTS AND DISCUSSION

A. Measured polymer relative sputter yields

Relative sputter rate measurements are presented in Table I. It is surprising that there is such a wide range of relative sputter rate (or, equivalently, sputter yield per ion) in these materials. The high sputter yield for PMMA may be related

TABLE II. Measured sputter rate ratio for PMMA to PEEK, PET, and PP at three values of energy-per-atom of incident argon cluster ions.

Argon cluster energy (eV)	Nominal mean cluster size (atoms)	Average energy-per-atom (eV)	Measured sputter rate ratio		
			PMMA/PEEK	PMMA/PET	PMMA/PP
4000	2000	2	10.8	7.1	2.0
6000	2000	3	11.0	7.3	3.0
4000	1000	4	12.8	6.8	2.3

to its tendency to depolymerize or “unzip” on damage. This is known to occur in thermal degradation of PMMA.¹³ Effects of free-radical processes during sputtering and the degree of crystallinity of the polymer are also important, and we have in development a semiempirical theory to describe these trends in gas cluster ion beam (GCIB) polymer sputter yield that we expect to publish in due course.

The values in Table I can be compared with the sputter rates seen in previous work. Lee *et al.*¹⁴ observe a roughly linear relationship in Irganox 1010 between sputter volume per ion and cluster ion energy between 8 and 17 keV for cluster ions of size 500–1000 atoms. Extrapolation of their measurements to 4 keV would give a sputter yield volume of around 26.2 nm³/ion. Ninomiya *et al.*¹⁵ present data for spun-cast films of three polymers, PMMA, PS, and PC using 5.5 keV cluster ions of around 700 atoms. They measured sputtered yields of 30, 20, and 8.4 nm³/ion for PMMA, PS, and PC, respectively. From these two works we should therefore expect sputter rates, relative to Irganox 1010, of around 1.15, 0.76, and 0.32 for PMMA, PS, and PC, respectively. Our measured values of 1.02, 0.87, and 0.43, respectively, at least show a similar trend. Our values indeed agree quite well given the differences in the experimental conditions.

B. Absence of an ion energy threshold effect

The energy of gas cluster ions used in Table I is 4000 eV, meaning that, on average, each of the approximately 1000 atoms in each cluster has approximately 4 eV of energy. This is close to the bond energies of many carbon bonds so that one may suspect that the wide variation of sputter rate seen in Table I may be due to 4 eV being close to a threshold energy at which PMMA (for example) will sputter easily whereas poly ether ether ketone (PEEK) (for example) will not. The threshold may be above 4 eV per atom for some polymers, and below for others. At energies-per-atom slightly higher (or lower) than this one might expect greater similarity of sputter yield across the set of polymers, as the energy-per-atom is now above (or below) this threshold for all of them. Although we have not yet made systematic measurements of sputter yield at different energies across this whole polymer set, we have made some measurements in which there seems to be *no significant threshold effect of this kind* within the energy range currently available to us.

Due to some power supply limitations in our instrument the range of energy-per-atom available to us is quite small, though we expect to increase this in future. Table II shows results for 2, 3, and 4 eV-per-atom sputter rate measurements,

in particular the relative sputter rates for PMMA/PEEK, PMMA/PET, and PMMA/PP. We have selected 4000 eV clusters having 2000 atoms to give 2 eV/atom, 6000 eV clusters having 2000 atoms to give 3 eV/atom, and 4000 eV clusters of 1000 atoms to give 4 eV per atom. Table II shows that these relative sputter rates are fairly constant over this range of energy-per-atom for these three polymer pairs. If there really were a threshold then one would expect a smaller ratio of sputter yield to appear in one or more of these measurements, and a much larger variation of these ratios as a function of energy-per-atom. The conclusion, which needs validation for a wider range of energy-per-atom, must be that the material dependence of sputter yield is *not* a strong function of energy-per-atom for these polymers over this energy range. The wide range of sputter rate seen across the polymers listed in Table I is therefore unlikely to become much narrower due to any threshold effect, and indeed the relative sputter rates seem to remain approximately the same in the range 2–4 eV/atom.

IV. CONCLUSIONS

We have developed a method for relatively rapid measurement of cluster ion sputter rate in as-received polymer materials. By this method, we have measured values for relative sputter yield for 19 polymers of technological importance. The wide range of sputter yields, greater than a factor of 10 between, for example, PMMA and PEEK, is much greater than might have previously been expected. This wide range does not appear to be an energy “threshold” effect that would disappear at any energy-per-atom values between 2 and 4 eV.

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