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Effect of the molecular weight on the depth profiling of PMMA thin films using low energy Cs⁺ sputtering

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Abstract

In this work, we investigate the influence of the molecular weight of poly (methyl methacrylate) (PMMA) thin films coated on silicon wafer on the ToF SIMS (Time of Flight Secondary Ion Mass Spectrometry) sputtering mechanisms and kinetics during depth profiling using low energy monoatomic caesium ions. The sputtering yield volumes are determined as function of molecular weight, film thickness and beam energy. The results show that the sputtering yield volume decreases with increasing molecular weight M_w down to a threshold value below which it becomes nearly constant, as previously observed with argon cluster ions. The relevance of physical parameters such as the glass transition temperature T_g – determined here from ellipsometry measurements - and the entanglement of the polymer chains to account for this behaviour is discussed. The variation of the sputtering yield was also found to vary logarithmically with the primary beam energy. In addition, preliminary experiments carried out using a low molecular weight PMMA (4 kg/mol) evidenced a nano-confinement effect similar to that observed with argon cluster sputtering but of lower magnitude.

Keywords: ToF-SIMS– Polymers- Molecular Weight- Caesium- Energy- Depth Profiling.

Introduction

Owing to their unique mechanical and optical properties, polymeric materials are becoming widely used in the field of micro and nanotechnologies, for nano-impression and lithography applications or organic light emitting diodes, as an example. Their physical properties are controlled by polymer structural parameters such as molecular weight, polydispersity.... As the polymer surface's properties are basically governed by the molecular structure of the outermost layers, sensitive and depth-resolved analysis techniques are required for the design and development of such molecular systems for microelectronics.

Within this context, ToF SIMS characterisation technique emerged as a powerful tool to investigate the near-surface structures¹ and chemical composition² of polymers. One of the limits of polymer chemical depth profiling using ToF-SIMS arises from the chemical damage induced by the formation of free radicals leading to chain scissions and crosslinking. However, since the introduction of polyatomic ion sources, depth profiling with ToF-SIMS is increasingly used for polymers. With polyatomic ions, the energy per bombarding atom is low (in the range of a few eV per atom for a cluster source with a few keV energy) and close to the dissociation energy of the polymer chemical bonds^{3,4} which reduces the depth of the altered region and damage accumulation, thus preserving the molecular information⁵. The use of innovative argon Gas Clusters Ions Beams (GCIB) have proven to be one of the most efficient approach in soft etching and sputtering of fragile organic materials, the depth resolution of the analysis^{3,5,6} being improved by the reduction of the degradation and fragmentation of polymer chains.

Recently, Cristaudo⁴ *et al* published an investigation of the effects of the molecular weight of two linear amorphous polymers, Poly-methyl-methacrylate (PMMA) and Polystyrene (PS) deposited on silicon substrates, on the efficiency of the sputtering process using 10 keV argon clusters. This work showed that the sputtering yield volume is highly dependent on the molecular weight below a threshold value and then becomes constant for higher molecular weights. This behaviour was attributed by the authors to the variation of the glass transition (T_g) of the polymers with M_w . Seah *et al*⁷ showed afterwards that these data are fully consistent with the so-called universal sputtering equation⁸, an empirical equation describing the dependence of sputtering yield by argon clusters on energy, cluster size and materials chemical structure. This equation proved to be accurate for different types of organic (polystyrene (PS), polycarbonate (PC) and PMMA) and inorganic materials. More specifically, Seah *et al*⁷ ended by discussing the effects of molecular weight on the empirical parameter which reflects, in this equation, the bonding energy per atom required to eject the sputtered fragments. Seah *et al* attributed the dependency of this parameter on M_w to the contribution of end groups to the sputtering process.

The objective of the present work is to evaluate the ability of monoatomic caesium ions to improve the sensitivity of ToF-SIMS analysis to structural parameters of polymer thin films, remembering that the high sputtering yield induced by argon cluster ions⁹ sputtering is a limiting factor when it comes to nanometric thin films depth profiling.

When monoatomic primary ions penetrate the polymer with an energy ranging from hundreds to thousands of eV, an energy transfer occurs via recoil collision cascades which directly leads to sputtering and species ejection^{10,11}. The associated damage is further enhanced by the electronic excitations induced by the primary ions charge which results in fewer molecular ions and thus, in a limited access to a molecular information when depth profiling is carried out. However, investigations by Houssiau *et al*¹². Different polymers (polycarbonate, polystyrene or polymethacrylate) sputtering processes by low-energy caesium primary ions have demonstrated that molecular depth-profiling with monoatomic ions can be successfully performed on polymers while maintaining their chemical structure and fingerprint.

According to a second study by Houssiau *et al*¹³ that aimed to explain the mechanisms involved in the sputtering process of organic materials, molecular depth profiling using monoatomic Cs⁺ ion is relevant for three main reasons. (i) the lower the impact energy, the lower the damage it generates within the polymer, (ii) the formation and emission of anions is enhanced due to the electron exchange between the alkali and polymer fragments, (iii) the reaction between free radicals and implanted neutralized Cs⁰ prevents the crosslinking and chain degradations and preserves the molecular information¹³.

Furthermore, it is known that the quality of a depth profile is controlled by operating parameters such as primary ions energy, angle of incidence, experimental temperature and sample's topography. Previous findings^{14,15} stated that projectile parameters including energy, affect directly the physical and chemical processes taking place upon ion bombardment. The primary ions' energy defines the induced damage accumulation^{16,17} and thus the sputtering yields.

In this study, we investigate the effects of molecular weight and confinement on the sputtering process of Poly(methyl methacrylate) (PMMA) thin films by monoatomic Cs⁺ ions. For that purpose, we especially focus on the sputtering yield of thin PMMA films with varying molecular weight (in the 4-1260 kg/mol range) and thicknesses (in the 90-180 nm range) as a function of the beam energy. These results will be compared with GCIB sputtering as studied by Cristaudo *et al*⁴.

Experimental

Materials and sample preparation

PMMA polymer pellets and powder with average molecular weights ranging from 4 to 1260 kg/mol were purchased from Sigma Aldrich Inc. and Polymer Source Inc. The polydispersity of the polymers provided by Sigma Aldrich Inc. were measured using Size Exclusion Chromatography analysis, since the purchaser did not provide them. The molecular weights and polydispersity indexes of all the used PMMA are given in Table 1. The polymers have been used without any further purification. They were dissolved in Toluene (Sigma Aldrich, purity: >99.71%) and spin-coated on pre-treated ($1 \times 1 \text{ cm}^2$) silicon substrates. Prior to use, the silicon substrates were successively cleaned in sulphuric and hydrofluoric acid and subsequently rinsed in deionized water. Then, Si samples were stored in plastic boxes until PMMA film deposition. Prior to spin-coating, silicon substrates were systematically sonicated in acetone and dried under N_2 flow. They were first spin-coated with pure solvent in order to enhance the wettability of the substrate by the polymer solution. The concentration of, rotational speed and acceleration were adjusted in order to achieve film thicknesses in the range 90-180 nm. The samples were thermally treated at 90°C for 30 minutes in air to remove solvent by evaporation.

A spectroscopic ellipsometer (UVISEL SE, Horiba-Jobin Yvon) was used to measure film thicknesses using a Cauchy equation to model the refractive index. Three measurements were made on each sample to check the sample surface thickness homogeneity, found to be in the 95% range.

Ellipsometry measurements of the glass transition temperature T_g of the thin PMMA films were performed using a M2000 ellipsometer (Woollam) equipped with an Instec heat cell. Temperature scans between 20°C to 150°C were carried out at a $5^\circ\text{C}/\text{min}$ rate while the refractive index of the film was continuously monitored. Below and above T_g , the refractive index was found to vary linearly with temperature with different slopes (results not shown). The glass transition temperature was identified from the intercept of these two linear relationships.

In addition, glass transition temperature measurements of the bulk PMMA polymers were carried out by Differential Scanning Calorimetry (DSC) at the same heating rate using a Q200 (TA Instruments) apparatus.

Depth profiling

Dual beam depth profiling has been performed on a ToF-SIMS instrument (ToF-SIMS 5, IONTOF GmbH, Münster, Germany). The sputtering has been performed using Cs⁺ ion sources with energies ranging from 250 to 1000 eV rastered over a 400×400 μm² area.

The negative secondary ions mass spectra collection, from a 80×80 μm² area centred in the middle of the sputtered crater, has been performed with (15 keV) bismuth ions Bi₃⁺, from negative secondary ions.

One challenge of ToF-SIMS polymer analysis is the charge accumulation at the sputtering interface resulting in changes in the energy distribution of the emitted secondary ions which degrades the mass resolution¹⁸. Taking into account the polymer insulating electrical properties, charge compensation, using a 20 V electron flood gun, was applied for all depth profiling measurements. The acquisition was made in the non-interlaced mode with a 1 second pause, in order to properly compensate the charges.

Results and Discussion

Negative ions acquisition mode has been chosen since Cs enhances highly negative ionization (and depress positive ionization); in addition the presence of oxygen, as an electronegative species prone to accept electrons, in the PMMA backbone will favour the formation of significant negative ions¹⁹. The ToF-SIMS depth profiles of the PMMA thin films for two molecular weights ($M_w = 20$ kg/mol and 100 kg/mol) obtained with 500 eV Cs⁺ are shown in Figure. 1, where some of the characteristic fragment ion signals are represented as function of the sputtering time.

A transient region, due to the Cs built up at the surface¹², is present during the early stages of both depth profiles and followed by an equilibrium regime where the intensity of the signal is nearly constant as a function of the sputtering time. Reflecting the polymer chemistry, the selected PMMA fragments CHO_2^- at $m/z=45$, $C_3H_3O^-$ at $m/z=55$, $C_4H_3O^-$ at $m/z=67$ and $C_5H_5^-$ at $m/z=65$, are comparatively stable and their intensities logically start to decrease when reaching the Si substrate. The stability of the characteristic signals in the beginning of the depth profiles implies a limited change of the polymer chemistry and chemical damage. This is consistent with a previous study by Houssiau *et al*^{12,20} which successfully performed molecular depth profiling of PMMA using Cs⁺ sputtering primary ions while preserving the fingerprint ions intensity in the spectrum.

For a given film thickness (100 nm), the time needed to reach the interface (measured as the time required to reach 50% of the total ²⁸Si signal) is different for both polymers (194 s for PMMA 100 kg/mol and 138 s for PMMA 20 kg/mol) which suggests a molecular weight dependent sputter rate. In order to further

evaluate the dependence of sputtering yields on molecular weight, the sputtering yield volume per primary ion (PI) expressed in nm^3/PI has been determined for the different samples. This parameter has been calculated from the sputter time (time required to reach 50% of the total Si⁻ signal), the film thickness, the sputtering analysis current and the sputtered area.

In Figure. 2, the sputtering yield (Y) volumes of two sets of PMMA thin films differing in their thicknesses and sputtered by Cs⁺ 500 eV, are presented as functions of logarithm of the molecular weight M_w . For film thicknesses in the range 90-120 nm, Y decreases with increasing molecular weight until a nearly constant value is achieved for M_w above about ~32 kg/mol. For thicknesses in the range 120-180 nm, the existence of a plateau region is less evident but there is a clear indication of a decreased sensitivity of Y on M_w above the 32 kg/mol threshold.

Although the energy deposited on the surface per projectile ion is in the range of 500 eV, much higher than the intermolecular binding energies which generates fragmentation²¹, the sensitivity of the sputtering yield to the chemical nature of the analysed material is preserved. As a matter of fact, for lower molecular masses with higher end-groups densities and shorter backbone monomer chains, Y is higher than for polymers with longer and heavier backbone chains. As stated by Seah *et al*⁸, the difference in the number of end-groups per unit volume between polymers with different molecular weights could explain the dependence of sputtering yield on the chemical structure of the PMMA films. Working on Cristaudo *et al*,⁴ data, Seah *et al*^{7,8} postulated that, when using polyatomic argon cluster ions to sputter polymer thin films, the increased number of end groups enhances the sputtering yields^{7,8}. Indeed, when the molecular weight increases the number of end-groups decreases.

An alternate discussion of these molecular weight effects was provided by Cristaudo *et al*⁴ who postulated that the known increase in the glass transition temperature of the polymers with their molecular weights²² could also account for the observed decrease in the sputtering yield with M_w . Indeed, T_g is a notably important physical property which governs the mobility of polymer chains. It is known to be essentially independent of the M_w , except for the region of low degrees of polymerization, where T_g increases with increasing M_w ²³⁻²⁵. The enhanced sputtering yield at low M_w could therefore be attributed to the enhanced translational mobility of the polymer chains as a result of their depressed T_g .

In order to evaluate the relevance of such an hypothesis for our polymer films, while taking into account nano-confinement effects which are known to shift the glass transition temperature of thin films from bulk values^{26,27}, ellipsometry measurements of the glass transition temperature of the thin films have been performed as function of the molecular weight (Figure 3). In addition, T_g data of the investigated bulk

PMMA polymers as measured by Differential Scanning Calorimetry (DSC) at the same heating rate are reported in Figure 3. In the range 10-100 kg/mol, it appears that the T_g of the thin films is slightly higher than that of bulk PMMA. Although the thickness-dependence of the T_g of thin films is still being debated, such an increase could be attributed to nano-confinement effects as experimental values seem to be reliable for films thicker than 15 nm²⁸.

The results presented in Figure. 3, indicate that T_g of the 100 nm thick PMMA films under investigation are actually dependent on the M_w , increasing dramatically from the lowest molecular weight to reach a steady value around a M_w of ~ 20 kg/mol. It should be noted that the measured values are slightly superior to the T_g of a bulk PMMA of infinite molecular weight ($\sim 108^\circ\text{C}$)^{29,30}, consistently with the effect of nano-confinement which are expected to limit the chain mobility, thus displacing the glass transition towards higher values²⁶.

In the present ToF-SIMS experiments, the observed molecular weight dependence of the sputtering yield could be accounted for by the enhanced mobility of the polymer chain only if the surface temperature of the films is increased locally above T_g by the ion beam. Although an accurate measurement of the local film surface temperature during sputtering is a difficult task, the occurrence of such T_g effects was indirectly assessed from measurements of the sputtering yield as a function of temperature. In Figure. 4, the sputtering yield volumes of PMMA 20 kg/mol and 100 kg/mol sputtered by 500 eV caesium ions at different temperatures are presented. It appears that the sputtering yield is nearly independent of temperature until a threshold value (96°C for 20 kg/mol and 100°C for 100 kg/mol) which is close to the measured T_g of the films under consideration. Above this threshold temperature, Y increases dramatically, probably as a result of enhanced free radical formation and chain mobility in the glass transition zone. Both effects are likely to enhance the depolymerisation mechanisms and boost material removal.

These results clearly demonstrate that glass transition effects are not involved in sputtering experiments carried out at room temperature. In other words, film temperature remains far below T_g during experiments at room temperature and the dependence of the sputtering yield on M_w can barely be accounted for by the molecular weight dependent T_g of the films. Instead, a dependency of the sputtering yield on the molecular weight between entanglements (M_e) could be considered. Amorphous polymer chains in the solid or melted states are known to be entangled as a result of the ability of the macromolecules to adopt random-coil conformations³¹. The so-called molecular weight between entanglements- M_e is defined as the average molar mass of the polymer segment in between two consecutive entanglements points. Below M_e , polymer chains are un-entangled and the polymer materials presents physical and mechanical properties which are drastically different form the entangled state. M_e is known to be dependent on the polymer's chemical

structure. For PMMA, the entanglement molecular weight M_e is around 11 kg/mol³¹, a value close to the critical molecular weight above which the sensitivity of Y on M_w was observed to decrease (Figure. 2). The enhancement of Y below M_e could therefore tentatively be attributed to an easier depolymerisation of the un-entangled polymer chains.

The measured decay of Y as a function of the molecular weight using monoatomic ion sputtering is consistent with the results obtained using argon clusters on PMMA thin films⁴. However, the magnitude of the yields achieved when using monoatomic ions (Y varies from 0.4 nm³/PI to 0.75 nm³/PI) is one hundred times smaller than the values obtained with argon cluster ions by Cristaudo *et al*⁴ (Y varies from 20 nm³/PI to 110 nm³/PI). This can be explained by the difference in the sputtering mechanisms between monoatomic and polyatomic ions. On one hand, polyatomic ions bombard the target on a large scale with all the constitutive atoms penetrating collectively, thus constraining the resulting damage to a narrower volume and limiting the damage to the upper layers. On the other hand, monoatomic ions induce upon impact a collision cascade, penetrating farther in depth. In the case of monoatomic ions, the generation of large fragment ions along with oligomers requires that several cascades intersect and cross to produce high-efficient yield events, which is unlikely to happen^{10,16}. According to molecular dynamics (MD) simulations¹⁷, the use of polyatomic ions enhances the material removal as a result of the low energy density deposited on the surface, which justifies that higher sputtering yields are achieved with argon cluster ions than with caesium ions.

Effect of thickness on the mean sputtering yield

As shown in Figure.2, the dependence of Y on M_w follows the same decreasing trend whatever the film thickness. However, the magnitude of the sputtering yield is observed to decrease for thicker films in the whole investigated M_w range. Cristaudo *et al*³² have observed a similar thickness-dependence of the sputtering yield of PS and PMMA films on silicon wafers upon argon cluster ion bombardment. The observed thickness dependence of Y for polymer-based thin films was explained by the authors using a phenomenological model where the polymer film is supposed to be composed of two superimposed layers with different sputtering yields: (i) at distances from the substrate less than a critical value of a few nanometers, Y is at the highest due to a maximal contribution to the sputtering of the primary energy being back reflected into the polymer layer by the polymer/Si interface¹⁴ (ii) above this critical thickness, Y has the value which would be achieved with bulk polymers. As a result, the gradual increase in thickness of the film above the critical thickness mitigates the interface effects till its complete cancellation. Indeed,

Molecular dynamics carried out by Reznik *et al*³³ have shown that Y becomes independent of the thickness when it is much larger than the penetration depth of the projectile. However, when the polymer is not confined anymore by a dense substrate, the sputtering yield becomes independent of the thickness³².

Considering a similar reasoning, we tried to investigate the nano-confinement effect when using caesium monoatomic ions to bombard PMMA 4 kg/mol and 15 kg/mol thin films. These two materials were selected because the strongest changes in sputtering yield of PMMA films were found for low molecular mass. Accordingly, they were supposed to be the most appropriate systems to reveal film thinning effects. As shown in Figure. 5, whatever the primary beam energy used, the maximal sputtering yield is achieved for the lowest investigated film thickness (20 nm). Then Y decreases with thickness until a constant value is achieved around 70 nm for PMMA 4 kg/mol and 90 nm for PMMA 15 kg/mol. The threshold value for PMMA 4 kg/mol is slightly lower than that obtained on the same polymer by Cristaudo *et al*³² using 10 keV Ar_{3000}^+ . These results seem to indicate that, when using monoatomic ions, the thickness from which an effect can be observed in sputtering yield is slightly reduced. In other words, slightly thinner films can be addressed with Cs sputtering, in comparison to GCIB, before worrying about uncontrolled changes in sputtering yields. This difference is assumed to arise from the fact that we might expect a higher primary ions implantation in the Si substrate with monoatomic ions than with cluster ones, which limits the sputtering process for thinner films. These first results show a significant but limited difference between polymer thin films sputtering mechanisms using cluster or monoatomic ions. They clearly need to be completed with data for materials at higher molecular weights to have a clear overview of the dependence on molecular weight of the thickness-sputtering mechanisms relationship.

Effect of Cs⁺ ion energy

In order to get insights into the dependence on $Y(M_w)$ relationship on primary beam energy, depth profiling of PMMA thin films (>120 nm in thicknesses) has been performed at different Cs⁺ energies (250 eV, 500 eV and 1000 eV).

The depth profiles of PMMA ($M_w=54$ kg/mol) thin films displayed in Figure.6 show that there is a significant difference in the $C_3H_3O^-$ ion intensities depending on the beam energies. When profiling the polymer layer, the characteristic $C_3H_3O^-$ ion intensity is higher when reducing beam energy. Furthermore, the initial transient is more pronounced for higher energies. The transition between the $C_3H_3O^-$ and Si signals at the polymer/silicon interface is also narrower when the Cs⁺ ion energy is increased.

When sputtering with 1 keV Cs⁺, the polymer characteristic ion signal is unstable and unable to reach a steady-state value during the course of the sputtering process. Previous studies attributed this behaviour

to damage accumulation^{34,35} or ionisation³⁶ effects depending on the nature of the primary ion source. A lowered level of implanted Cs has also to be considered leading to less reactions with free radicals and subsequently less neutralization of polymeric chain degradation. In addition, increasing energy deteriorates the depth profiles quality due to induced roughness at the bottom of the crater. Indeed, Atomic Force Microscopy (AFM) measurements over a 1 μm^2 area (not shown in this paper) indicated that the rms roughness was respectively 0.23 nm, 1.29 nm and 2.49 nm for the virgin PMMA film and the craters sputtered at 500 eV and 1 keV. These changes were found to be independent on the molecular weight. The change in the sputtering yield volume with the primary beam energy for the different molecular weight films is shown in figure7. As expected, the overall sputtering yield increases with the energy of the ion beam, while the observed decrease in Y with M_w is preserved. In order to quantify these effects, experimental data were fitted to the following empirical equation initially developed for argon sputtering^{5,8}

$$Y = Y_0 + \frac{\alpha}{M_w^n} \quad (1)$$

Where Y_0 is the sputtering yield of a PMMA polymer of infinite molecular weight, n is an empirical parameter quantifying the dependence of the sputtering yield on the molecular weight and α is a constant. The values of the fitting parameters n (Table.2) indicates that the sensitivity of the sputtering yield to M_w is enhanced at 1keV, which could reflect a change in the sputtering mechanisms as compared to 250 and 500 eV.

In figure.8, the sputtering yield volume has been reported as a function of the logarithm of the primary ion beam energy. Whatever the molecular weight, this plot tends to suggest the existence on an energy threshold below which Y vanishes. The value of this threshold and its dependency on the molecular weight would, however, requires further investigations.

Conclusions

In this work, we investigated the specificity of caesium monoatomic ions when it comes to organic materials depth profiling in terms of sensitivity to structural parameters, specifically the molecular weight. Actually, a dependence of caesium sputtering yields on molecular weight was evidenced with some similarities with cluster ions sputtering⁴. Indeed, it decreases with increasing molecular weight until a threshold Mw value around (32 kg/mol) which is slightly higher than the one obtained with argon clusters (20 kg/mol). However, compared to previous studies of PMMA with argon clusters the sputtering yields are 10 to 100 times smaller which is potentially advantageous by giving suitable period of time for the depth profiling of very thin polymer multilayers.

In addition, from an investigation of the temperature-dependence of the sputtering yield, we have concluded that these dependence of the sputtering yield on molecular weight relationship at room temperature cannot be related to the M_w dependence of the PMMA glass transition temperature. Instead, the hypothesis is that the sputtering yield is enhanced below the entanglement molecular weight.

It was also evidenced that the ion beam energy doesn't change the overall way the sputtering yields varies with M_w . However, an explicit logarithmic dependence of Y on beam energy has been evidenced with parameters slightly dependent on the molecular weight. The variation of Y with the primary ion energy not only indicates changes in the ion-solid interactions at higher energies but also reveals the existence of a threshold energy below which sputtering seems to cease. This threshold, below which sputtering would no longer be possible, is found to be slightly dependent on the chemical structure of the polymer. Furthermore, the fitting of the variations of Y with M_w , reveals a sensitivity to the molecular weight of greater magnitude at higher energies.

Finally, the influence of the thickness of the studied film has been explored. It provided relevant elements in qualifying the differences in polymer sputtering mechanisms between monoatomic and cluster ions. This preliminary study, performed on 4 and 15 kg/mol PMMA films put into evidence a nano-confinement effect less pronounced than the one observed when using argon clusters³². The intensity of the phenomenon is much lower and begins for thinner layers than recorded with argon clusters. And the effect seems especially weak at low Cs^+ energy (250 eV) where it was seen to be limited to a doubling of sputtering yields. It's worth nothing this observation since it makes in regard to GCIB, low energy caesium sputtering promising for depth profiling of very thin polymeric layers on dense substrates. However these results have to be generalized and completed with further investigations for higher molecular masses, other types of polymers in order to confirm, potentially, the limited nano-confinement effect when using monoatomic ions compared to polyatomic ions.

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Tables

Table 1. Molecular characteristics of the studied PMMA polymers

| M_w (kg/mol) ^a | I_p ^b | Supplying source |
|-----------------------------|--------------------|------------------|
| 1 260 | 1.16 | Polymer Source |
| 356* | 1.4 | Sigma Aldrich |
| 107* | 1.05 | Sigma Aldrich |
| 54 | 1.09 | Polymer Source |
| 32 | 1.09 | Polymer Source |
| 15* | 1.02 | Sigma Aldrich |
| 7.5* | 1.04 | Sigma Aldrich |
| 4.2* | 1.7 | Sigma Aldrich |

^a M_w : Mass average molar mass

^b I_p : Polydispersity index = M_w/M_n

*: Polydispersity measured by Steric Exclusion Chromatography (SEC)

Table 2. Values of the fitting parameters of equation (1) giving the sputtering yield Y as a function of the molecular weight M_w for thin films with thicknesses in the range 120-180 nm.

| Energy (eV) | Y_0 | α | n |
|-------------|-------|----------|------|
| 250 | 0.13 | 0.12 | 0.33 |
| 500 | 0.48 | 0.27 | 0.33 |
| 1000 | 0.78 | 0.42 | 0.45 |

Figures

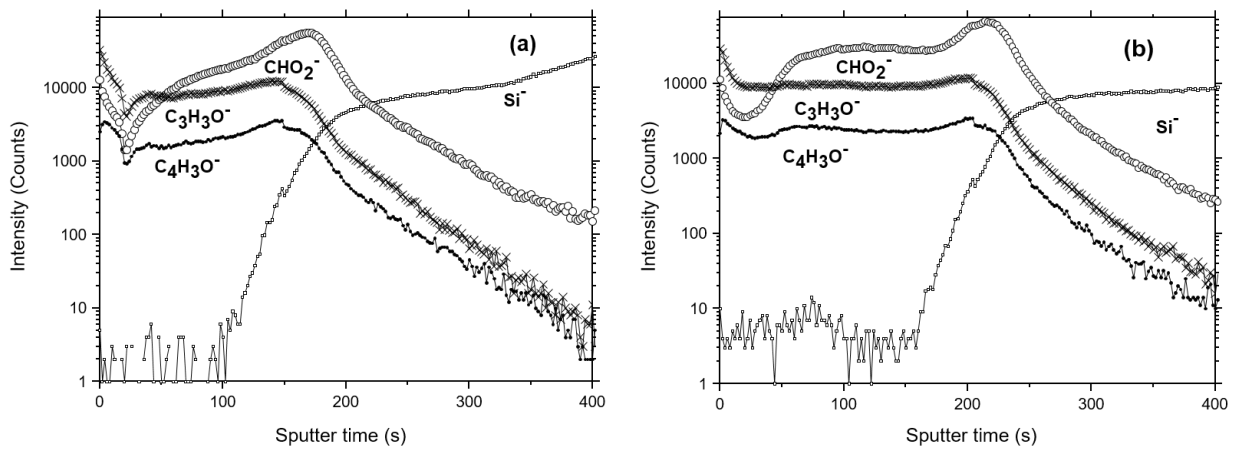


Figure 1. Negative ToF-SIMS depth profiles of PMMA (film thickness 100 nm) with different molecular weights: (a) 20 kg/mol; (b) 100 kg/mol (sputtering by 500 eV Cs⁺ ions).

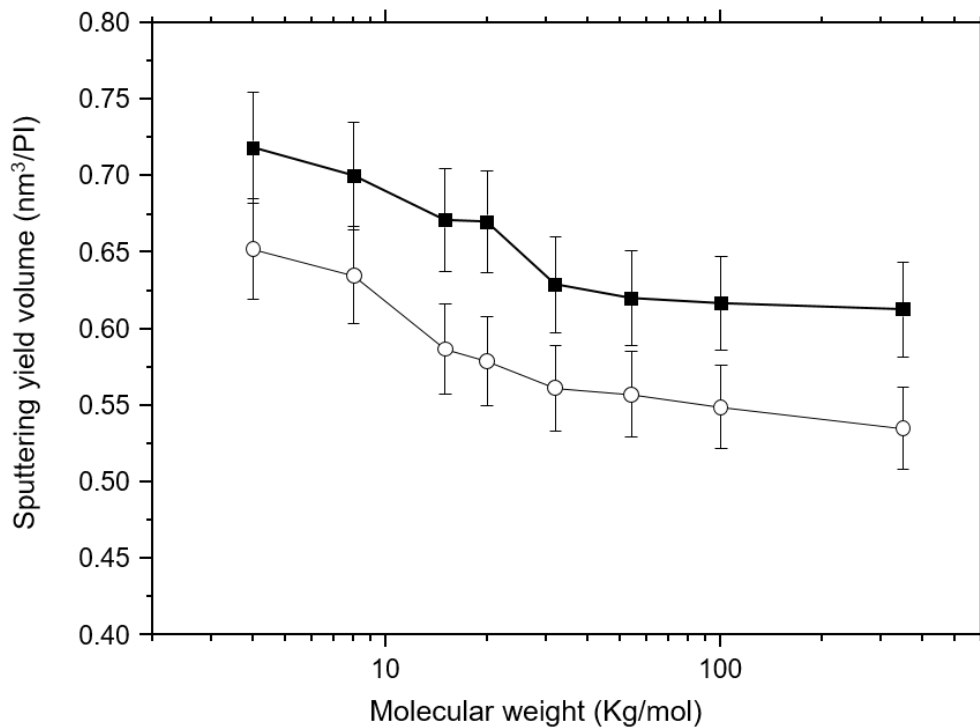


Figure 2. Sputtering yield volumes as function of molecular weight for two sets of PMMA thin films with different range of thickness : (■) 90-120 nm; (○) 120-180 nm (500 eV Cs⁺ ion sputtering).

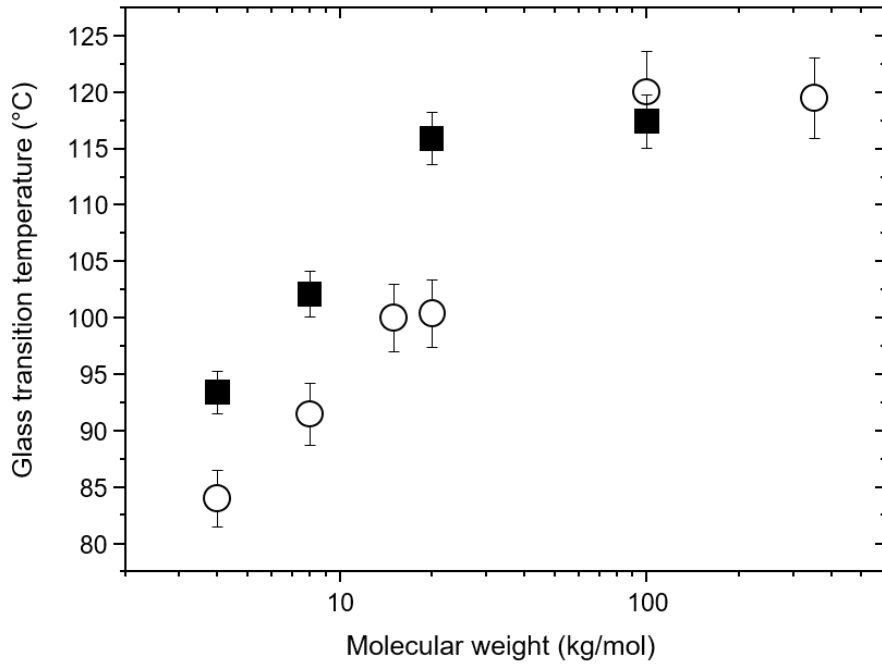


Figure 3. Glass transition temperatures of (■) PMMA thin films (thickness: 100 nm) and (○) bulk PMMA as a function of molecular weight, as measured by ellipsometry and DSC, respectively (5°C/min).

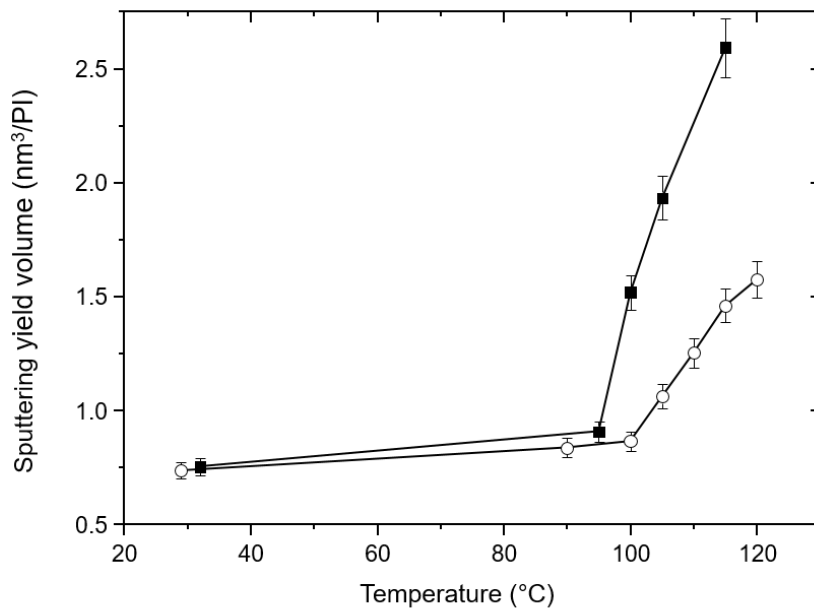


Figure 4. Sputtering yield volumes of PMMA thin films (■) 20 kg/mol and (○) 100 kg/mol as a function of temperature (film thickness: 100 nm).

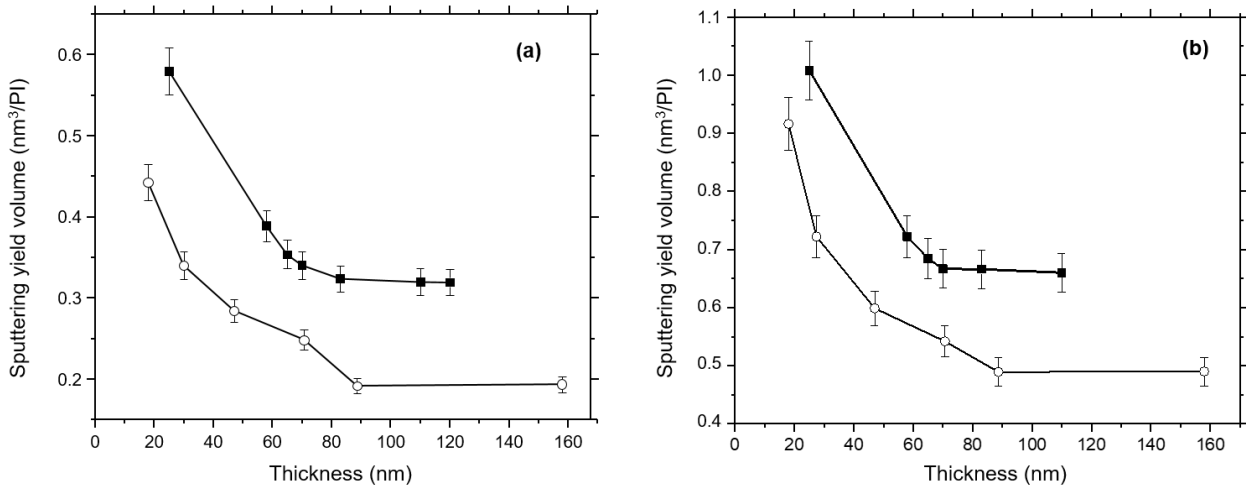


Figure 5. Sputtering yields of PMMA thin films (■) 4 kg/mol and (○) 15 kg/mol sputtered by Cs⁺ ions as function of film thickness at (a) 250eV and (b) 500eV.

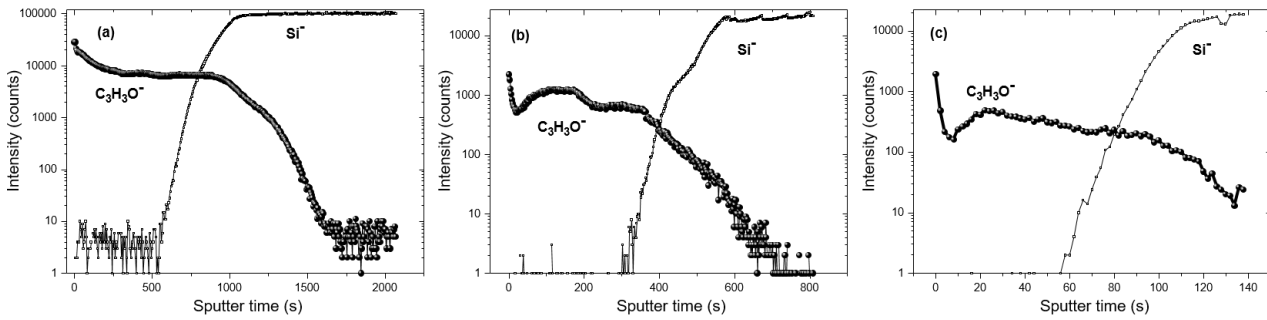


Figure 6. Depth profiles of C₃H₃O⁻ and Si⁻ ions of 120 nm PMMA thin films sputtered by Cs⁺ ions at different beam energies: (a) 250 eV; (b) 500 eV; (c) 1000 eV.

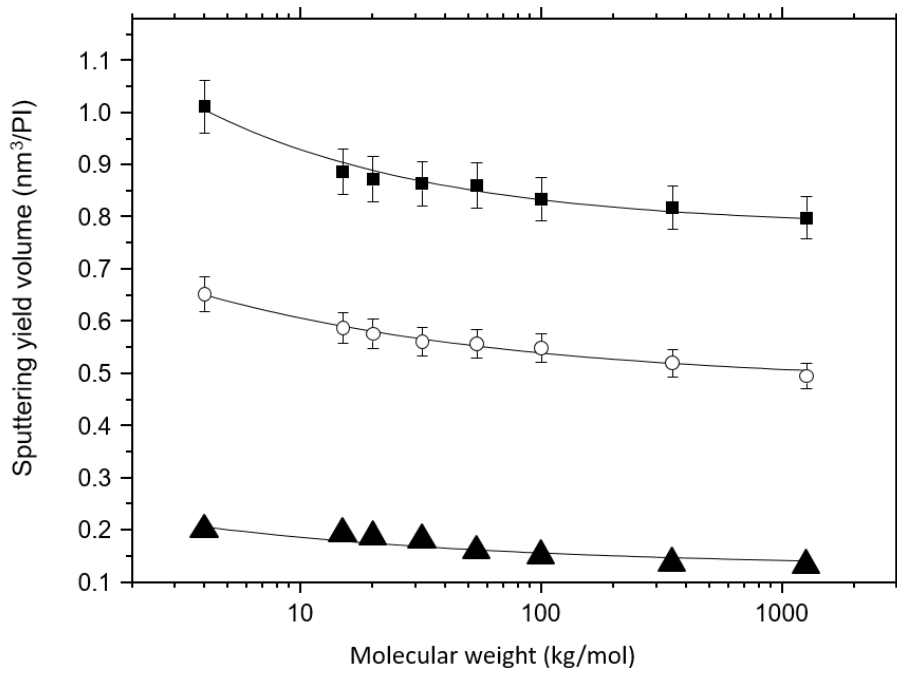


Figure 7. Sputtering yields of PMMA thin films as a function of molecular weight for different beam energies : (▲) 250 eV; (○) 500 eV; (■) 1000 eV (film thicknesses in the range 120-180 nm). Solids lines correspond to fits to equation (1).

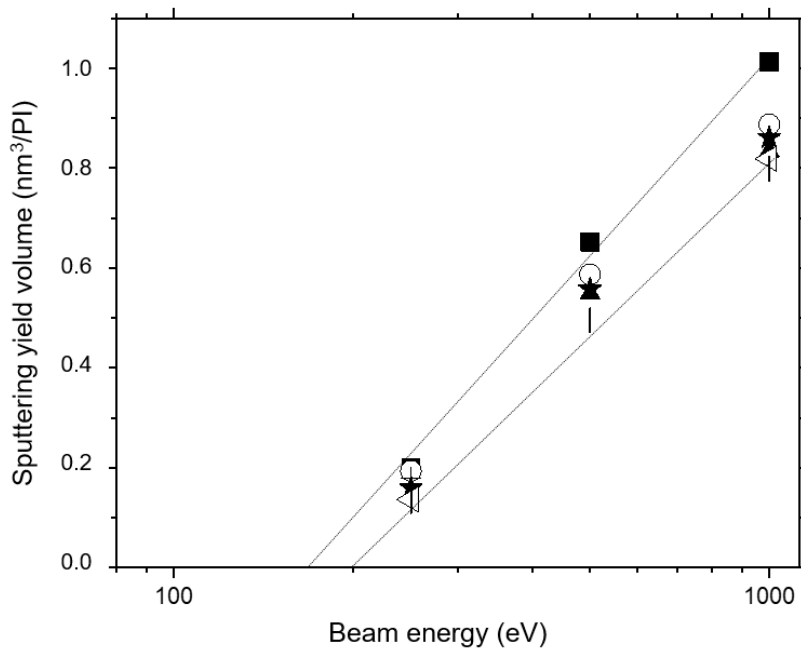


Figure 8. Sputtering yield volumes as a function of Cs⁺ beam energy for PMMA thin films with different molecular weight M_w (film thicknesses in the range 120-180 nm). (■) 4 kg/mol; (○) 15 kg/mol; (+) 32 kg/mol; (★) 54 kg/mol; (▲) 100 kg/mol; (◄) 350 kg/mol; (◊) 1260 kg/mol. Dotted lines are guides for the eye.