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Effect of sputtering yield changes on the depth resolution in cluster beam depth-profiling of polymers

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The authors present the results of the simulation, by means of a recently introduced transport and reaction model, of the sputter depth profiling of delta layers in a polymer system that undergoes mild modification during the measurement, such as in the case of X-ray photoelectron spectroscopy profiling with large cluster ion beams. They find that, even in the absence of roughening and at constant beam-induced mixing effects, the variations of sputtering yield caused by sample damage produce non-negligible changes in depth resolution. *Published by the AVS.* https://doi.org/10.1116/1.5019698

I. INTRODUCTION

Thanks to the introduction of cluster beams (GCIBs), nowadays, it is possible to perform molecular depth profiles of polymeric materials. Successful profiles have been reported on a large variety of polymers by using either cluster-SIMS or X-ray photoelectron spectroscopy (XPS) coupled with GCIBs sputtering.[1–3] The depth resolution obtained when using GCIBs has been discussed in several papers. Recently, in the specific case of quantitative XPS/GCIB sputter profiles of polymers, it has been reported that the irradiation with x-rays can induce compositional changes that influence the quality of the analytical determination.[4,5] It is known that x-rays induce photochemical reactions in the polymeric compounds that lead to the break and/or formation of intra- and intermolecular chemical bonds.[4] The effects of these reactions can be merged in two classes: decomposition with the formation of low molecular weight degradation compounds or cross-linking between the chains with consequent increase in the average molecular weight. In the first case, photoinduced degradation, one could predict that the rate of erosion will tend to increase by accumulating irradiation. In the second case, photoinduced crosslinking, the increase in the molecular weight of the target is expected to negatively influence the magnitude of the volumetric sputtering yield. In cluster-SIMS depth profiling experiments, Cristaudo *et al.* found a decrease of volumetric sputtering yield in polymers with higher molecular weights with respect to polymers with lower molecular weights.[6] In particular, they show that the molecular weight and volumetric sputtering yield are inversely proportional to each other. In view of this, we can expect that, if the irradiation causes the formation of crosslinks, then the erosion rate will decrease accordingly. Recently, Smith *et al.* showed that prolonged x-ray exposure during depth profile of multilayers based on polystyrene (PS) and polyvinylpyrrolidone (PVP) influences the rate of erosion. In particular, the erosion rate of PS decreases with the exposure time, while the one of PVP increases slightly.[5] Analogously, during SIMS depth profiling of polystyrenelike polymers by means of C_{60} primary ions, the intensity of fragments characteristic of the original polymer is readily lost.[7] Moreover, experimental results show that polystyrenelike polymers exhibit a much lower sputtering than other polymers (such as acrylic polymers) due to the heavy ion-induced damage of the target, which leads to the progressive formation of carbonlike material.

Therefore, in order to study the consequences of the changes in the polymeric material during depth profiling on the quality of the analytical determination, it would be useful to be able to predict such effects by means of theoretical models. In this paper, we present a simulation of such physico-chemical processes through the application of a reaction and transport model we recently introduced for simulating sputtering also in the presence of beam-induced reactions. In this study, we highlight that the variation of sputtering yield along the profile, caused by irradiation, influences the depth resolution in a non-negligible way.

II. MODELING

Recently, we reported a strategy for simulating a D-SIMS experiment by means of the numerical resolution of an advection-diffusion-reaction differential equation.[8,9] In the present study, we apply the same approach for modeling the depth profiles performed using XPS and GCIB sputter beam, as a paradigmatic case of slow accumulation of irradiation-induced damage that causes changes in the sputtering yield of a polymeric material. In the model, the position of the bombarded surface is kept invariant, so that erosion process is represented as a "travel" of the underlying material toward the surface. The erosion rate is represented by the travel velocity of the inner target layers toward the surface. When the material moving toward the surface enters the altered layer, it is redistributed by ion-beam mixing. The partial differential equation describing the evolution of the relative concentration profile (expressed in atomic ratio) of a certain component (C) during a sputter profile experiment can be written as

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C) - \nabla \cdot (\mathbf{v} C), \tag{1}$$

where $\mathbf{v}$ is the velocity at which the inner material is moving toward the surface. The velocity $\mathbf{v}$ is equivalent to the erosion rate expressed in nm/s. If we express the flux ϕ of

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primary ions in ions $nm^{-2} s^{-1}$ and the volumetric sputtering yield **Y** in nm^3/s, we can write

$$\text{erosion rate}\left[\frac{\text{nm}}{\text{s}}\right] = Y\left[\frac{\text{nm}^3}{\text{ion}}\right] \cdot \varphi\left[\frac{\text{ion}}{\text{nm}^2 \cdot \text{s}}\right].$$

In other words, if the current density of erosion beam is kept constant, the velocity **v** is proportional to the volumetric sputtering yield.

Since during the analytical scan, x-ray induced chemistry is triggered on, **v** is not constant in time, because Y changes. In our calculations, we assume that **v** varies according to the following expression:

$$v = (v_0 - v_\infty)e^{-(t/k)} + v_\infty, \tag{2}$$

where $\mathbf{v_0}$ is the erosion rate at time $t = 0$ and $\mathbf{v}_\infty$ is at the erosion rate after an exposure to x-rays long enough to induce a steady state photochemical modification of the polymer. By changing the decay parameter **k**, one can simulate varying x-ray induced modification rate. The higher is **k**, the slower is the change in the erosion rate. It must be stressed that the functional dependence of **v** on irradiation time, reported in Eq. (2), was chosen as an exemplifying case, in order to check how a variation of **v** can influence the depth profile. The choice is also justified, *a posteriori*, by the fact that it fits with the experimental data reported in Refs. 4 and 5.

The quantity **D** in Eq. (1) is a function that takes into account the ion-beam induced mixing in the altered layer region. In the present simulation, surface roughening is neglected. The mixing term **D** in Eq. (1) is related to the ion-beam induced motion of particles in the collision cascade, which can be described by analogy with the self-diffusivity process. Strictly speaking, we should consider the lateral component to the diffusion. In a first approach, however, we can neglect the lateral component; thus, the model is reduced to a unidimensional one, along the traveling direction **z** (normal to the surface plane). For the sake of simplicity, we consider that, following the relocations caused by the erosion beam, the relocated atoms' positions are distributed according to a normal distribution with a variance $\boldsymbol{\sigma}^2$. By analogy with the unidimensional random walk model for diffusion, we assume that the mixing term **D** is related to **σ** according to the relationship

$$D = \frac{\sigma^2}{2t}. \tag{3}$$

Thus, the units of **D** are (nm^2/s). Since the mixing process takes place only in the portion of material involved in the interaction with the erosion beam, in all the simulated profiles, we use a simple depth dependence for **D**,

$$D(z) = \frac{\sigma^2}{2\Delta t} erfc\left(\frac{z - 3\sigma}{\sigma\sqrt{2}}\right), \tag{4}$$

where Δt is the duration of a single simulation step.

During a XPS sputter profile, the analysis cycles alternate with the erosion cycles. For the reconstruction of the depth profile, the model simulates the intensity (I) of the photoelectrons taking into account their inelastic mean free path **λ**,

$$I \propto \int_{z=0}^{z=\infty} C \cdot e^{-z/(\lambda\cos(\theta))}, \tag{5}$$

where **θ** is the take-off angle of photoelectrons.

The relation between I and **C** is expressed by Eq. (5). The parameter **v** is related to **k** according to Eq. (2). Since *C* and **v** are correlated according to Eq. (1), there exists a dependence of I from **k**. Here, we use a numerical approach to investigate this relationship.

III. EXPERIMENT

Numerical resolution of the equation involved in the proposed model was performed by means of a Python™-based script (v2.7), developed on purpose by using the FIPY LIBRARY. FIPY is finite volume partial differential equation solver developed by NIST (Version 3.1.3-dev2-g11937196).[10] We simulated the XPS depth profiles of six delta-layers (10 nm-thickness and spaced 100 nm each other). Sputtering area and beam current are assumed constant during the simulation. More details about the code are given in the supplementary material.[11]

IV. RESULTS AND DISCUSSION

Figure 1 shows the results of the simulations of the depth profile experiment of six delta layers. In each simulation, the instantaneous erosion rate varies according to the equation reported in each box, and it is plotted with dashed lines. For the sake of simplicity, we assume that each delta-layer has the same properties of the matrix in terms of sputtering yield and radiation induced chemistry. In the simulated profiles (intensity versus sputtering time) the delta-layers' signals appear as bell-shaped features, with a width that varies according to the erosion rate. Due to the variable erosion rate along the profile, it is difficult to extract information about possible variations in depth resolution along the depth. To this purpose, the same profiles of Fig. 1 are reported in Fig. 2 in terms of intensity versus depth. Unlike in the experimental case, where the time-to-depth conversion could be a difficult task in the presence of a nonconstant sputtering rate, in the case of the simulation this conversion is straightforward, since the instantaneous erosion rate is known.

A careful analysis of the results of Fig. 2 shows that: (1) the width of the delta-layer signals increases with increasing depth; (2) at a fixed depth, the width is larger when the erosion rate is lower; (3) the apparent position of the delta layers is anticipated with respect to the actual one, the effect being larger for lower erosion rates. All the above is consistent with a degradation of depth resolution along the depth when the erosion rate is not constant.

A quantitative evaluation of such effect is reported in Fig. 3, where the apparent full width at half maximum (FWHM) of the delta layers is plotted as a function of depth, in simulations in which the erosion rate changes according to Eq. (2) for several **k** values. There is a clear indication that depth

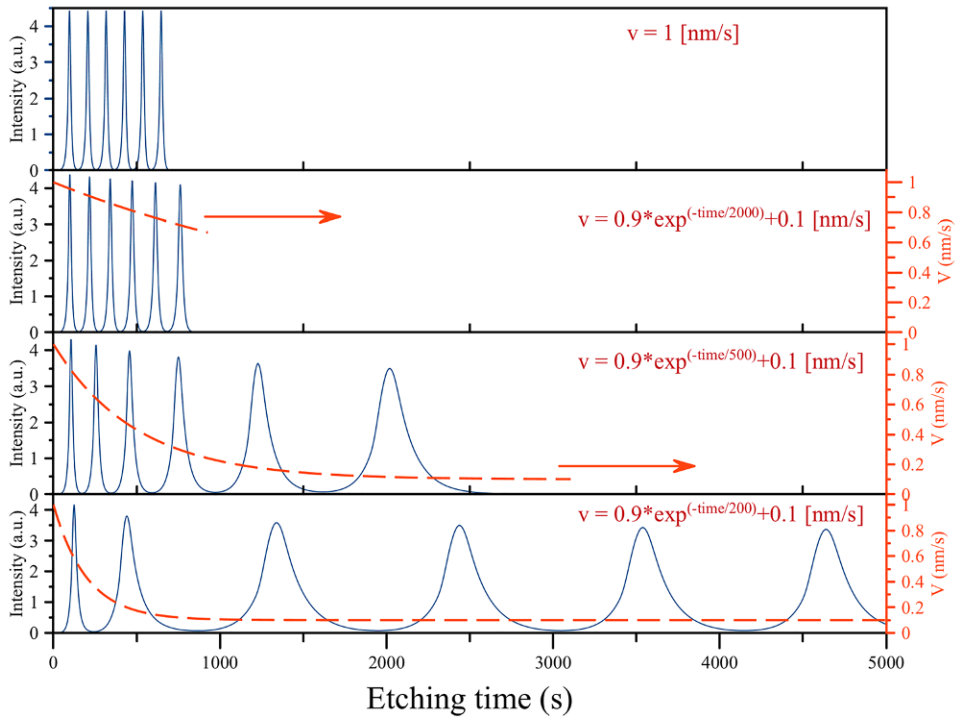

FIG. 1. (Color online) Simulated depth profiles of six delta layers (continuous lines). Erosion rates change with time (dashed lines) as indicated by the reported equations.

resolution decreases with depth (unless v is constant) and it worsens faster for lower **k** values, i.e., when the erosion rate gradient is higher. It is worth to remark that such effect on depth resolution does not depend on the mixing parameter D (which is kept constant) nor on the roughness (that is ignored in the model). It is related only to the change, along the depth, of the volumetric sputtering yield of the material, which in the XPS sputter depth profiles is caused by the exposure to x-rays. The previsions of the model are in agreement with the experimental XPS sputter depth profile results, recently published by Smith *et al.* on PS/PVP multilayers.[5] In these experiments, authors sputter the sample with a GCIB (which minimizes ion beam damage) and reduce the development of surface topography by means of sample rotation. However, they observe that a degradation of depth resolution occurs, caused by x-ray induced damage, which is more pronounced for longer exposures to x-rays. In view of

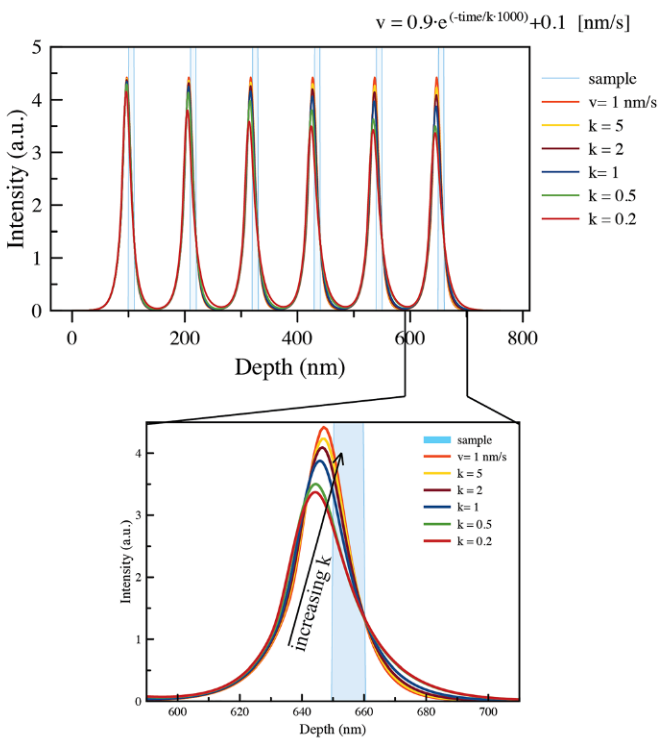

FIG. 2. (Color online) Depth calibrated profiles of six delta layers (the same in Fig. 1). The effect of damage accumulation on depth resolution and on apparent layer position is evidenced in the inset, where the region of the sixth delta layer is zoomed.

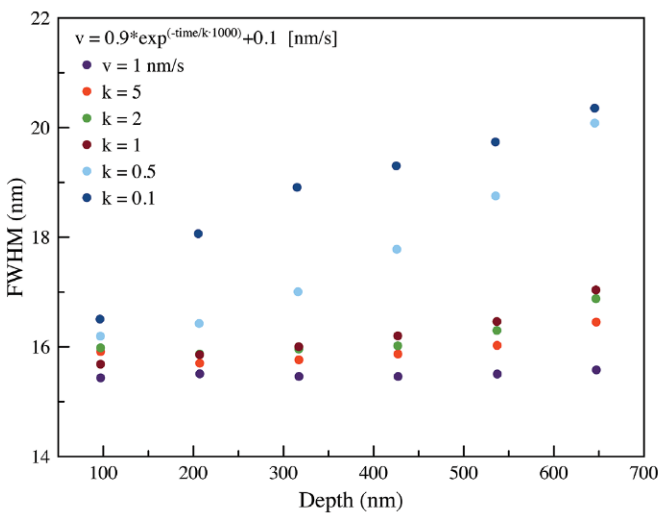

FIG. 3. (Color online) FWHM of delta layers as a function of depth, for different erosion rate changes.

the results of our simulations, we believe that such a degradation of resolution can be attributed to the decrease of sputtering yield of the polymer system, caused by x-ray induced crosslinking.

V. SUMMARY AND CONCLUSIONS

Our recently presented transport and reaction model for sputtering was applied to the simulation of the depth profile of a polymer system in conditions of moderate damage, such as those present in XPS experiments with GCIB sputtering. We simulated the profile of a series of delta layers located at increasing depth, in the hypothesis that the sputtering yield decreases due to x-ray induced damage. The simulations were performed keeping constant the beam mixing effects along the depth and excluding any roughening. In these idealized conditions, it is still possible to observe a degradation of resolution along the depth that must be related to the variation of the sputtering yield of the material caused by the accumulation of x-ray induced damage. These observations are in agreement with the recent experimental results by Smith *et al*.

We believe that the results of our simulations can be relevant also for the interpretation of SIMS depth profiles, since they indicate that a non-negligible contribution to depth resolution can be given—in addition to the well known roughening and mixing effects—by changes in sputtering yield connected to tiny chemical modifications of the polymer. Further investigations are ongoing to evaluate the effect, on depth resolution, of degradation reactions that could induce a sputtering yield increase.

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