

POLYETHYLENETEREPHTHALATE (PET) FILMS INTERACTIONS WITH LOW ENERGY OXYGEN IONS

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Investigations regarding mechanisms involved in surface modification of PET films subjected to the action of oxygen ions of relative low energies (100-500 eV) were realized. PET films of 25 μ biaxially drawing were concomitantly exposed to the action of positive ion beam delivered by a Kaufman ion source and to dilute target plasma. X-ray photoelectron spectroscopy (XPS) measurements at different take off photoelectron angles (sampling depth x) were performed on ESCALAB Mk II. Theoretical model that describes atomic mixing and erosion in the case of PET samples exposed to positive low energy ions has been obtained on the bases of the models developed by Sigmund Grass-Mari and Collins.

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1. Introduction

The oxygen discharge plasma is known to have complex kinetics because of the large number of species which are additionally produced, such as metastable molecules and atoms, positive and negative ions. Oxygen plasmas are very successfully applied in multilayer lithography for microelectronic pattern definition and etching of semiconductors [1-6].

Ion beam induced epitaxial crystallization (IBIEC) process, described by Linnors [7] and Elliman [8] for silicon treated with different high energy ions, has been studied out in PET foils treated with oxygen ions of relative low energies, at high doses. This process is controlled by the ratio between the fluency of fast atomic and molecular oxygen ions and by the energy deposited during nuclear collisions.

This paper presents the results on the action of oxygen ion beams which induces surface modifications measured versus ion energy and fluency.

2. Experimental

The experimental device consists in two cylindrical vacuum chambers, separated by a negatively biased grid (stainless steel, 70% transparency, 90 mm in diameter), Fig. 1. The PET Terom® foils, 25 μ , biaxially drawing, were exposed to the action of a positive ion beam delivered by a Kaufmann ion source and, simultaneously, to a dilute target plasma. Both plasmas are produced at a pressure of 5×10^{-4} Torr. The parameters of the source plasma are [2]: density 9×10^8 cm^{-3} , electron temperature 3 eV, ion temperature 0.25 eV and for the target plasma: density 10^6 cm^{-3} , electron temperature 3.5 eV, ion temperature 0.25 eV. The target plasma prevent the expansion of the beam due to its own space charge and neutralize the surface positive charge due to the ion beam on the insulated polymer sample. The ion-beam plasma system consists of a low density plasma through which drifts a positive ion beam. The energy of the ion beam was in the range 100-500 eV

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and the treatments were realized at three ion fluencies [2,3,4,5] : the saturation regime $\phi_1=0.3\times 10^{16}$ ions/cm² (1 min exposure); the reimplantation regime for ions track: $\phi_2=1.5\times 10^{16}$ ions/cm² (5 min exposure) and $\phi_3=9.0\times 10^{16}$ ions/cm² (30 min exposure). The grid bias is $U_G = -100V$ and prevents the cross flow of the primary electrons between the two chambers. The anode of the target chamber is at ground potential and the anode of the source plasma is positively biased U , with respect to the ground. The ion beam energy is $E_i \approx eU$ [2]. The polymer sample placed at 60 mm from the separation grid (Fig. 1) was not cooled during the treatment. The untreated PET film used is an amorphous and chemically unhomogeneous material in a surface layer of about 100 Å thickness. For high fluencies at considered exposure time for each ϕ , thermal effects must be considered due to the radiation from the hot cathode of the target plasma and to the ion bombardment.

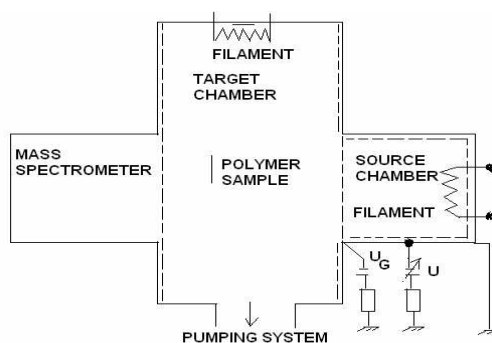
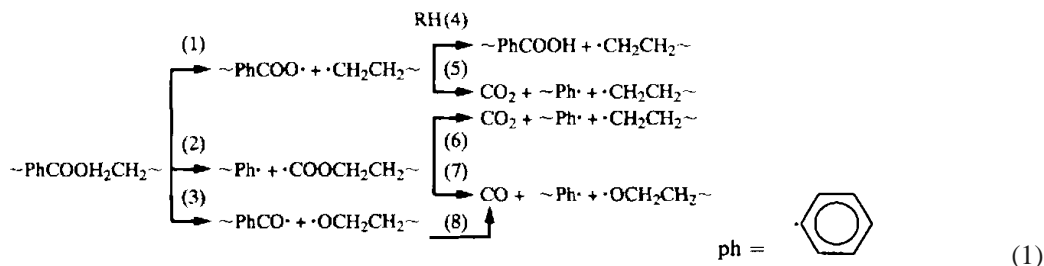


Fig. 1. Experimental device.

XPS measurements have been used to study the resulting modifications on the polymer surface. XPS analysis for this work was carried out using an photoelectron spectrometer VGS ESCALAB Mk II with Al K_α radiation (FWHM = 0.5 eV). The angle between the directions of the incident X-ray and that of the observations (fixed by analyzer entrance slit) was 50°. The angle α between the sample surface and the direction of observation was variable and the sampling depth is obtained from $x = 3l \sin\alpha$, where the inelastic mean free path for photoelectrons is $l = 26$ Å in polymers at 1200 eV mean energy.

3. Results

The first step in polymer chain scission reactions is [2]:



The oxygen ions have relative low energies and three situations were studied: at 100 eV, 300 eV and 500 eV. In Fig. 2 are presented the oxygen percentages θ_1 from the total atomic content obtained from XPS data versus sampling depth for the investigated ion energies and fluencies.

From Fig. 2 results that the oxygen percent from the total atomic content in the case of PET foils treated at 100 eV and 300 eV is lower than in the case of untreated sample. This dependence denotes more atomic oxygen in untreated samples compared with the treated samples. It is possible that different species of atomic and molecular oxygen to be eliminated in the treatment process, as it demonstrates formula (1).

For ions energy 500 eV, excepting fluency ϕ_2 at distances bigger than 45 Å, all percents of oxygen are higher than in the case of the untreated samples. This dependence denotes a reimplantation process [9] for all fluencies (excepting ϕ_2) at 500 eV.

From Fig. 2 it results that the highest oxygen percentages are obtained at 500eV, indicating a high speed in the sample surface consumption in the bombardment process.

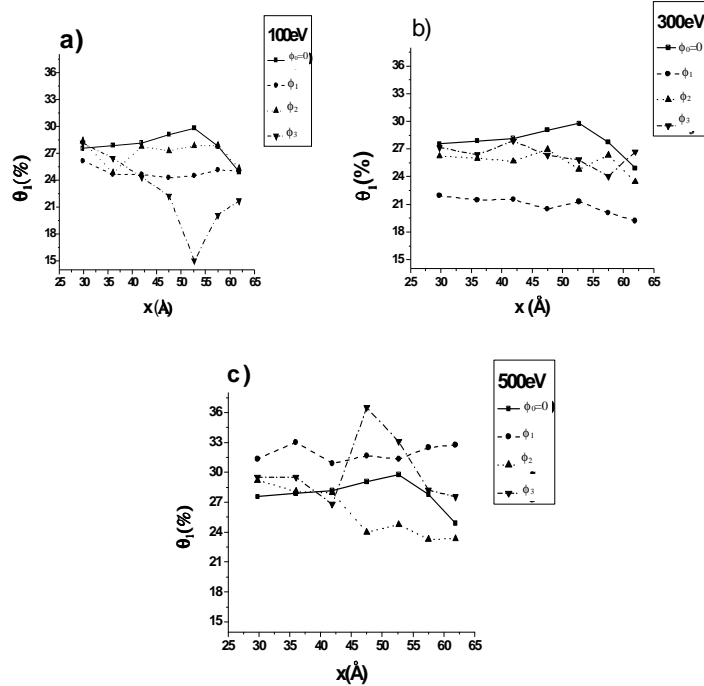


Fig. 2. The oxygen percentages θ_1 from the total atomic content obtained from XPS data versus sampling depth, x , at a) 100 eV; b) 300 eV; c) 500 eV. The curves for various ion fluency are given.

4. Discussion. Theoretical model

On the bases of theoretical models developed by Sigmund Grass-Mari and Collins [1] for high energy ions bombardment, a model that describes atomic mixing and erosion in the case of PET samples exposed to positive low energy ions has been obtained. The model was applied previously to describe the variation of the carbon percentage θ_2 from the total atomic content [10]. In this article

was found a correlation between the oxygen percentage θ_1 and its variation versus fluency $\frac{\Delta\theta_1}{\Delta\Phi}$ and

distance $\frac{\Delta\theta_1}{\Delta x}$.

A linear dependence of the type:

$$\frac{\Delta\theta_1}{\Delta\Phi} = C_1 \frac{\Delta\theta_1}{\Delta x} + C_2 \theta_1 + C_0 \quad (2)$$

was tested, where $C_1 = u + q$ (u denotes the surface recession speed and q is the collective current of particles of all species towards the surface across an arbitrary plane P). In the initial model, parameters C_2 and C_0 have some physical meaning. They are expressed in function of q and q_1 : $C_2 = \frac{\partial q}{\partial x}$, $C_0 = \frac{\partial q_1}{\partial x}$ (q_1 - for current of oxygen particles). Using data from Fig. 2, the coefficients C_1 , C_2 , C_0 from (2) were statistically estimated (Fig. 3). Because a multilinear relation of the type (2) has been found, it results that the model developed in [1] is applicable for fitting the experimental data regarding bombardment with low energy ions. The values of coefficients $C_1, C_2,$

C_0 were determined and displayed graphically on Fig. 3. The coefficient C_0 is always negative. This means that the values of q_l decrease proportional with the increase of sample depth x . It results that condition (3) is accomplished.

$$q_1 = C_0 x + const. \quad (3)$$

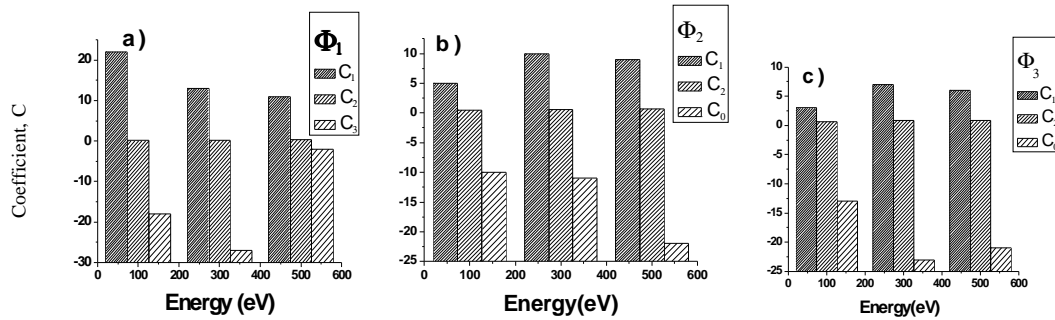


Fig. 3. Coefficients for theoretical model at ion fluencies: a) $\phi_1=0.3 \times 10^{16}$ ions/cm²; b) $\phi_2=1.5 \times 10^{16}$ ions/cm² and c) $\phi_3=9.0 \times 10^{16}$ ions/cm².

Small positive values obtained for coefficient C_1 means that the collective current q toward the surface is higher than the corrosion speed.

It was demonstrated [10] that θ_2 (the carbon percentage from the total atomic content) is a continuous function of ϕ and the atomic mixing model can be applied to the PET samples bombarded with ions of low energies. Because $\theta_1 = 1 - \theta_2$, it means that the oxygen percentage from the total atomic content is also a continuous function.

6. Conclusions

The oxygen percent from the total atomic content in the case of PET foils treated at 100 eV and 300 eV is lower than in the untreated sample, while for 500 eV excepting fluency ϕ_2 at distances larger than 45 Å, the situation is different.

This paper demonstrates that the theoretical model described by Sigmund Grass-Mari and Collins can be applied to the PET samples bombarded with ions of low energy. The model is applied with success to describe the variation of the oxygen percentage, θ_1 , from the total atomic content.

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