Polycarbonate surface modified by argon cluster ion beams

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X-ray induced photoelectron spectroscopy and atomic force microscopy were used to gain detailed information on surface topography, composition and bonding among atoms in a near-surface region of untreated and modified polycarbonate surfaces by argon cluster and argon monomer ion irradiation. As a consequence of the cluster ion beam impingement on the polycarbonates, their surfaces become rough with polymer structure partially damaged. Surprisingly, the surface irradiated by argon monomer ions was found less rough but the polymer structure in a surface region completely lost its integrity and an amorphous (hydrogenated) carbon layer was formed. © *1999 American Vacuum Society.* [S0734-211X(99)02006-5]

Recently, a novel method of modification of solid surfaces has been developed and successfully used for study of cluster ion interactions with several inorganic solid targets.[1–4] Using Ar cluster ions, the sputtering yield was measured to be 10–1000 times higher, smoothing of metal and semiconductor surfaces was observed at the normal impact and an angular distribution of sputtered species deviated substantially from a cosine law[1–4] predicted for a monomer ion sputtering.[5] Results have indicated that the cluster irradiation process is quite different from that of monomer ions.

The bisphenol-A-polycarbonate $[-C_6H_4-C(CH_3)_2-C_6H_4-O-CO-O-]_n$, denoted as PC, supplied by Mitsubishi Engineering Plastics Co., was used as $25 \times 25 \times 2$ mm^3 samples. A reference PC surface was prepared by cutting a PC just before analysis. The ion irradiated surfaces were exposed to air before their analysis until stated otherwise.

Neutral argon clusters were generated by adiabatic expansion of compressed Ar gas through a narrow nozzle. Following ionization by electron bombardment, the cluster ion beam was focused, mass separated, accelerated to 20 keV and scanned to irradiated the PC uniformly. The mean cluster size reached 3000 atoms. A detailed description of the technique used can be found elsewhere.[1]

Photoelectron spectra were recorded by an ADES-400 (V.G. Scientific) electron spectrometer with Mg $K\alpha$ radiation (1254 eV). The spectrometer was calibrated by the Au $4f7/2$ line peaked at 84.0 eV [full width at half maximum (FWHM) of 1.0 at 20 eV pass energy]. Photoelectron spectra were charge corrected with respect to the lowest binding energy component of the C $1s$ line peaked at 284.5 eV. All samples were analyzed in as-received state, no sputter cleaning was used.

C and O atomic concentrations, summarized in Table I, were determined semiquantitatively within a model of a solid homogeneous in composition. Peak areas were corrected for photoelectron cross sections, asymmetry parameters, inelastic mean free paths and measured transmission function of the electron energy analyzer. Close agreement between the O/C ratio measured for the reference sample and the theoretical value indicates that the reference PC surface is representative of the PC.[6] The untreated PC surface exposed to air for an extended period of time possesses a higher oxygen content. Ar cluster ion irradiated PC surfaces exposed to air appear to be oxygen rich noticeably with respect to the reference PC. The sample surface modified by a dose of 1 $\times 10^{14}$ ions/cm^2 possessed the highest oxygen inclusion. Its O/C ratio reached 178% of the theoretical value. This correlates well with a degree of a surface roughness examined by atomic force microscopy (AFM). The *in situ* Ar monomer ion irradiated PC surface (10 keV, 1×10^{15} ions/cm^2, at normal incidence) consisted of C atoms only [and some H not seen by x-ray photoelectron spectroscopy (XPS)], no oxygen signal was observed.

High resolution C $1s$ and O $1s$ spectra of the untreated and Ar ion cluster irradiated PC surfaces are shown in Figs. 1 and 2. In agreement with the literature,[6–8] the C $1s$ peak of the reference sample has been resolved by four Gaussian components corresponding to the aromatic C (284.5 eV), the aliphatic C (285.0 eV), the C–O functional group (286.2 eV) and the C=O carbonyl function group (290.5 eV). The substantial differences among the C $1s$ spectra of pristine PC and Ar cluster ion irradiated surfaces are found in a region of

TABLE I. Oxygen and carbon atomic concentrations in at % at pristine and modified polycarbonate surfaces; R_a in nm is the average surface roughness.

Sample	Modification	C	O	O/C	R_a
PC, theoretical		84.2	15.8	0.188	
PC, reference		83.8	16.2	0.194	
PC (*)[a]		80.6	19.4	0.241	0.3
PC+10^{14} Ar$^+$	clusters/cm^2 (*)	74.9	25.1	0.335	4.1
PC+10^{15} Ar$^+$	clusters/cm^2 (*)	76.3	23.7	0.311	3.8
PC+10^{15} Ar$^+$	monomers/cm^2	100.0	0	0	
PC+10^{15} Ar$^+$	monomers/cm^2 (#)[a]	90.7	9.3	0.103	0.5

[a]The sample surface was exposed to air under laboratory conditions for several weeks (*), for 2 h (#).
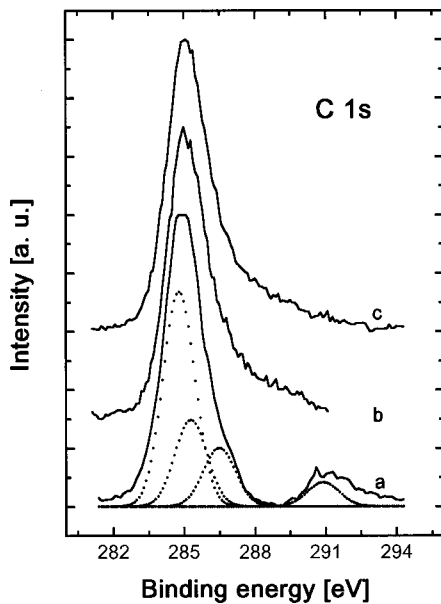
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FIG. 1. High resolution C 1*s* spectra. (a) The reference PC surface with the fit corresponding to the polymer structure (see Ref. 6), (b) the cluster ion irradiated PC surface at 20 keV with a dose of 1×10^{14} ions/cm^2, and (c) the cluster ion irradiated PC surface at 20 keV with a dose of 1×10^{15} ions/cm^2.

the C=O group. For irradiated surfaces, the intensity in this region is negligible indicating decarbonylation within 8–10 nm surface layer (XPS information depth). An increase in the signal intensity observed in between 287 and 289 eV (about 10% of the overall C 1*s* intensity) can be ascribed to C atoms bonded to −OH species. Curve fitting of the C 1*s* spectra of the irradiated PC surfaces revealed a decrease of the aromatic carbon intensity at 284.5 eV by about 50% and approximately the same increase of both the aliphatic at
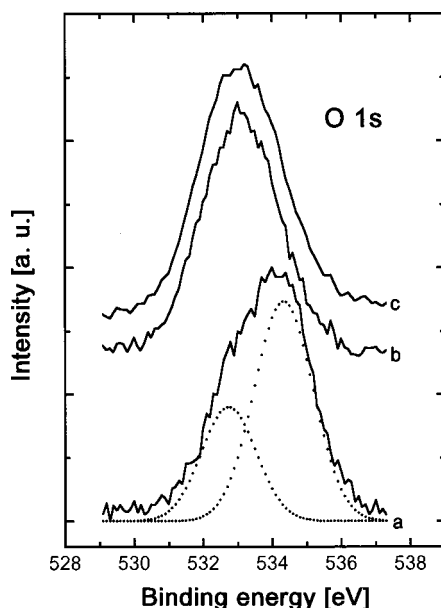
285.0 eV and the C–O functional group spectral intensity at 286.2 eV with respect to the expected values.

The O 1*s* peak of the pristine PC has been resolved in two components ascribed to oxygen in the C=O (532.4 eV) and in the C–O–C functional group (534.1 eV), in the expected 1:2 intensity ratio.[6] The irradiated sample surfaces show a peak centered at 533 eV with an undetermined number of components, due to the superposition of new species like (−OH) and −O–C in a vicinity of 533 eV.

Surface topography was observed by atomic force microscopy (SPI-3700, Seiko Instruments). Typical AFM images are displayed in Fig. 3. Due to the normal incidence cluster ion irradiation, a surface roughness increased considerably by about 1 order (see Table I). The highest surface roughness was achieved for a dose of 1×10^{14} ions/cm^2. This corresponds to the highest oxygen content which occurred at the same sample surface. The AFM image of 30 keV Ar monomer ion irradiated PC at normal incidence, with a dose of 1×10^{15} ions/cm^2, is shown in Fig. 3(d). The treated surface is smoother compared to the cluster irradiated PC and slightly rougher than the pristine PC. Surfaces of inorganic solids irradiated by cluster ions at normal incidence become smooth.[1–4] The smoothing effect, simulated by molecular dynamic methods, has been explained by a collective momentum transfer of the cluster atoms during impact resulting in shallower lateral sputtering.[2] On the contrary, we have observed development of surface roughness as a consequence of Ar cluster ion interaction with PC targets. This behavior may be due to the very fast dissipation of cluster energy in the close proximity of every incident cluster. We expect quick evaporation of soft polymer material (with low thermal conductivity and melting point) from the impact area and its close vicinity. Consequently, huge craters markedly overlapping at higher doses should be formed. The less rough surface observed for Ar monomer ion irradiated PC
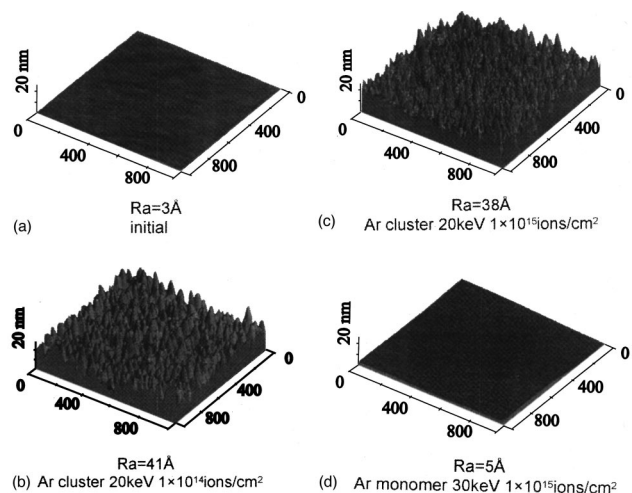

FIG. 2. High resolution O 1*s* spectra of the same samples as in Fig. 1.

FIG. 3. AFM images ($1 \times 1 \ \mu m^2$) on the pristine PC surface (a), Ar cluster ion irradiated PC surfaces at 1×10^{14} (b) and 1×10^{15} ions/cm^2 (c) and Ar monomer ion irradiated surface at 1×10^{15} ions/cm^2 (d). The average surface roughness (R_a) is given as an average of the modular difference between the height at each point and the average height.

surfaces at normal incidence could be connected with a complete dissociation and carbonization of a surface layer of the PC target, well documented by XPS results. Recently, similar behavior, namely the surface smoothing and carbonization, has been observed for N monomer ion beam modified polyimide surface studied by AFM. The irradiation to the fluences below 1×10^{15} cm^{-2} led to dramatic smoothing of the surface due to ion beam induced sputtering and surface compaction.[9]

In summary, Ar cluster ion irradiation of PC surfaces at the normal incident angle induced the following modification of the polymer surface: almost complete decarbonylation as well as partial fragmentation of aromatic rings occurred in a surface layer of 8–10 nm and the surface became rough. Ar monomer ion irradiation of PC surfaces led, in contrast to the Ar cluster ion irradiation, to a less rough surface but the polymer structure in the surface region was completely destroyed (carbonized) and *a*-C or *a*-C(H) surface layer was formed.

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