



Optical properties and oxidation of carbonized and cross-linked structures formed in polycarbonate by plasma immersion ion implantation



E. Kosobrodova^{a,*}, A. Kondyurin^a, W. Chrzanowski^{b,c}, D.G. McCulloch^d, D.R. McKenzie^a, M.M.M. Bilek^a

^a Department of Applied Plasma and Physics, School of Physics, University of Sydney, NSW 2006, Australia

^b Faculty of Pharmacy, University of Sydney, NSW 2006, Australia

^c Department of Nanobiomedical Science & BK21 PLUS NBM Global Research, Center for Regenerative Medicine, Dankook University, Cheonan 330-714, Republic of Korea

^d School of Applied Sciences, RMIT University, Melbourne, Victoria 3001, Australia

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ABSTRACT

At ion fluences higher than $5 \cdot 10^{15}$ ions/cm², plasma immersion ion implantation (PIII) of polycarbonate (PC) results in a formation of a carbonized surface layer. The thickness of this layer is close to the depth of ion penetration. A comparison of PIII treated, spin-coated PC films with pre-treatment thicknesses designed to match and exceed the carbonized layer thickness is employed to study the properties of the carbonised layer independently from the less modified underlying structure. At ion fluencies higher than 10^{16} ions/cm², the thinner PC film is completely transformed into an amorphous carbon-like material with no traces of the initial PC structure. The thicker films, however, incorporated two layers: a top carbonised layer and a cross-linked layer below. Compared to the two-layered PC film, the completely carbonized layer was found to have a much higher concentration of C=O bonds and much lower concentration of O–H bonds after exposure to atmospheric oxygen. The refractive index of the thicker PC films PIII treated with high ion fluencies is close to the refractive index of diamond-like carbon. Anomalous dispersion of the refractive index of the thicker PC films is observed after formation of the carbonised layer. The refractive index of the thinner PC film has normal dispersion at all ion fluences. At ion fluences of $2 \cdot 10^{16}$ ions/cm², both PC films were found to have the same etching rate as polystyrene. Washing in dichloromethane had no effect on the carbonised layer but affected the underlying material in the case of the thicker PC films leading to a wrinkled structure up to ion fluences of $2 \cdot 10^{16}$ ions/cm². At this and higher fluence, areas of an ordered island-like structure were observed.

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1. Introduction

Ion implantation dramatically changes the structure and properties of polymers resulting in a decrease of permeability [1,2], an increase of conductivity [3], hardness [4] and refractive index [5,6]. Other changes include an improvement of their adhesion properties [7], wear resistance [4], chemical resistance [8] and biocompatibility [9,10]. The degree of structural transformation and the surface chemistry of an ion implanted polymer can be regulated by the choice of appropriate ion implantation treatment parameters and storage conditions [11,12].

The structural transformations in PIII treated polymers can be divided into three main stages depending on ion the fluence. For PIII conducted at 20 kV these stages are (1) at ion fluences of less than

10^{14} ions/cm², the structural defects are low and concentrated mainly in latent ion track areas; (2) at ion fluences of 10^{14} – 10^{16} ions/cm², carbonised clusters are formed and their size and number increase with ion fluence and (3) at ion fluencies higher than 10^{16} ions/cm², a layer of amorphous carbon-like material is formed [11–14]. In the first two stages, the modified layer still contains fragments of the original polymer structure, so that the surface chemistry and properties of the PIII treated polymer are dependent also on the chemistry and structure of the initial polymer. In the third and final stage, most polymers have similar optical constants and surface chemistry [5,15,16] regardless of the starting structure. The formation of carbonised clusters is observed in a surface layer with a thickness approximately equal to the depth of ion penetration [13]. The presence of the carbonised structure has been confirmed by UV and Raman spectroscopy [17] and X-ray scattering [18].

Migration of radicals into the bulk material and their subsequent reactions result in the formation of an extended modified layer with

* Corresponding author. Tel.: +61 447510407.

E-mail address: elenak@physics.usyd.edu.au (E. Kosobrodova).

a thickness of about 1 μm [13]. The radical reactions can cause both cross-linking and chain scission in the modified layer. The efficiency of each process depends on the chemistry of the polymer. For example, cross-linking dominates in polystyrene (PS) [11] while chain scission prevails in poly(methyl methacrylate) (PMMA) [19]. After PIII treatment, cross-linking was observed in both PS and PMMA. However, the degree of cross-linking was different and the rate of thickness decrease of PMMA increased almost linearly with ion fluence while in the case of PS the rate of thickness reduction reached saturation after 10^{16} ions/cm² [5,16]. The presence of a cross-linked structure was demonstrated by washing of the ion implanted polymers in solvents that dissolve the unmodified polymer but do not dissolve the modified structure [8].

If after the PIII treatment, the modified polymer is exposed to atmospheric gases, its surface chemistry continues to change due to post-treatment oxidation [13]. In the case when the film thickness is comparable to the depth of ion penetration, not only the ion fluence and storage conditions, but also the film thickness itself affects the rate of oxidation of the PIII treated polymer. In our previous paper [12], we suggested that, oxidation of the carbonised and cross-linked layers follows different pathways and formation of O–H groups is more probable in the cross-linked structure than in the carbonised layer due to a significantly higher concentration of hydrogen in the cross-linked structure compared to the carbonised layer.

In this paper, we study oxidation, optical properties, gel fraction formation, topography and etching of 65 and 163 nm PC films spin-coated on silicon wafers to gain a better understanding of the role of the carbonised structure in determining the properties of PIII treated PC. We compare rates at which thickness decreases and the optical constants of the PIII treated PC to those reported previously for PS, epoxy resin and PMMA [5,15,16] treated using the same PIII process. We analyse radical reactions that result in the formation of volatile products, cross-linking, degradation of aromatic rings and radical migration to explain the structural transformations observed by IR and X-ray absorption spectroscopy and water contact angle measurements of the PIII treated PC.

2. Methods and materials

Polycarbonate was purchased from Goodfellow Cambridge Limited, UK. Two solutions with 1% and 2% w/v concentrations were prepared in a mixture of dichloromethane, chloroform and toluene with 1:1:1 volume ratio. The solutions were spin-coated on (100) silicon (P-doped, 10^4 – $2 \cdot 10^4$ Ω cm, one side polished, 0.610–0.640 mm thickness, Topsisil, USA) using an SCS G3P-8 Spincoater with a speed of 2000 rpm. The silicon was washed for 20 s in mQ-water with ultrasound before PC spin-coating. The 1% films (65 nm) were less than half the thickness of the 2% films (163 nm) owing to the differences in viscosity which determines the thickness of spun films.

Inductively coupled radio frequency (RF) nitrogen plasma powered at 13.56 MHz was used as a source of ions for PIII. The base pressure of the vacuum system was 10^{-5} Torr (10^{-3} Pa) and the pressure of nitrogen during the implantation was $2 \cdot 10^{-3}$ Torr (0.27 Pa). The forward power was 100 W with reverse power of 12 W when matched.

The PC samples were placed on a stainless steel holder with a mesh made of the same material. The mesh was electrically connected to the holder and held in front of the sample parallel to its surface. The distance between the sample and the mesh was 5 cm. During RF plasma treatment, no voltage was applied to the sample holder. For the PIII, plasma ions were accelerated by the application of high voltage (20 kV) bias pulses of 20 μs duration at a frequency of 50 Hz and drawing an average current of 1.2 mA to the substrate holder and its mesh. The PC samples were

treated for 40–1600 s corresponding to ion implantation fluences of $5 \cdot 10^{14}$ – $2 \cdot 10^{16}$ ions/cm² and stored in air at room temperature. Eight samples (four for each PC concentration) were treated without ion acceleration for 80, 400, 800 and 1600 s.

The contact angles between the PC sample surfaces and de-ionized water were measured using a Kruss contact angle analyzer DS10 employing the sessile drop method. Transmission infra-red (IR) spectra were recorded 2 days after RF plasma and PIII treatments using a Bomem spectrometer. Difference spectra of a silicon wafer with and without PC film were analysed.

The thicknesses and optical constants of the spin-coated PC film were measured before and after RF plasma and PIII treatment using a Woollam M2000V spectroscopic ellipsometer. Ellipsometric data were collected for three angles of incidence: 65°, 70° and 75°. For 1% PC films (both RF plasma and PIII treatments, all treatment times) and 2% PC films (40 and 80 s PIII treatments and all times for RF plasma treatment), a three layer model was used to fit the data with the layers being: silicon, native silicon oxide, and a Cauchy layer for the PC film. For 2% PC films PIII treated for 200–1600 s, two Cauchy layers were required to adequately represent the PC film. The thickness and optical constants associated with the best fits were determined for each PC sample.

The topography of PC samples before and after rf plasma and PIII treatments was imaged using a Park System (Park System Corp., Suwon, South Korea) atomic force microscope (AFM) in tapping mode with a speed of 1 Hz and amplitude of 10 nm. The data were analysed using Gwyddion software [20].

X-ray absorption spectroscopy was performed on untreated and 800 s PIII treated PC using the soft X-ray beam line of the Australian Synchrotron. The near edge X-ray absorption fine structure (NEXAFS) on the C k-edge was recorded using the total electron yield (TEY), collected from the sample at each photon energy. The X-rays were polarised horizontally and the sample was tilted at an angle of 45° to the incoming beam. Variations in X-ray intensity with energy were extracted from the measured spectra using the signal generated from a standard gold covered grid. Contributions to the C NEXAFS from contamination in the beam line were determined by replacing the sample with a reference photodiode and collecting a spectrum which was then used to correct the spectra from the PC samples.

Both the 1% and 2% PC samples were washed three times in dichloromethane for 10 s, 1 min and 10 s and quickly rinsed in toluene to dissolve the PC which was not cross-linked by ion bombardment. After washing, all samples were photographed using a digital camera connected to an optical microscope (Axioplan 2 Imaging, Zeiss, Australia) equipped with 20 \times /0.22 HD DIC and 50 \times /0.55 HD DIC objectives (reflective light mode). Then, the thickness and topography of the samples were measured again.

3. Results

3.1. Optical constants

Refractive index (n) and extinction coefficient (k) of RF plasma and PIII treated and untreated PC films are shown in Fig. 1. The RF plasma treatment has a minimal effect on the optical properties of PC. The PIII treatment however results in significant increases of both n and k for both the 1% and the thicker 2% PC films. Everywhere further in the text, 1% and PC films will be referred as thin and thick PC films, respectively. The refractive index of PIII treated thin PC films has a maximum at 380 nm. Its intensity increases with increasing PIII treatment time, reaching a maximum of 2.22 at PIII treatment of 1200 s. A similar value of the refractive index was previously observed for PS [5], epoxy resin [15] and PMMA [16] PIII treated with high ion fluence (2.0–2.2 at 500 nm) and

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