Bulg. J. Phys. **40** (2013) 193–197

Optical Properties of Nano-Structured Material in Ion-Implanted Polymer*

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Abstract. Being of importance for applications of ion-implanted PMMA in integrated optics, optoelectronics and optical communication, we have studied the optical properties (controlled through the complex refractive index) of nano-structured material in silicon ion (Si^+) implanted polymethylmethacrylate (PMMA). PMMA was implanted with Si^+ ions accelerated to a relatively low energy of 50 keV at a high fluence of 3.2×10^{15} Si^+/cm^2. The carbon nano-clustered material in the ion-modified surface layer of Si^+-implanted PMMA of a thickness of about 100 nm was optically characterized by reflectance measurements, as well as by reflection ellipsometry at a wavelength of 632.8 nm (He-Ne laser).

PACS codes: 42.25.Gy, 61.72.uf, 78.20.Ci, 78.67.Sc, 78.68.+m

1 Introduction

Ion implantation is a powerful tool for local modification of the refractive index of polymers with the purpose of their practical application [1]. In particular, the ion-beam sensitivity of polymethyl methacrylate (PMMA) makes it possible to considerably modify the refractive index of this optically-transparent polymer. In practice, refractive index changes by light-ion implantation at low ion energy up to a few hundred keV with relatively small fluences (of an order of 10^{14}–10^{15} cm^{-2}) are sufficient to implement optical waveguiding structures in ion-implanted PMMA of importance for integrated optics, optoelectronics and optical communications [2-4]. Also, compact optical devices operating in transmittive and/or reflective mode based on ion-implanted PMMA have been reported [5].

*Talk given at the Second Bulgarian National Congress in Physics, Sofia, September 2013.

The increasing interest in ultra-thin layers, in which the refractive index is continuously varied (a gradient-index) in depth has stimulated a great effort in terms of characterization of ion-implanted PMMA by optical techniques, e.g. ellipsometry [2-4,6]. Reasonably, of paramount importance for optical applications of ion-implanted transparent polymer materials is the knowledge on their refractive index. Here, we report a study on the complex refractive index of nano-structured material in the near-surface (close to the surface) ion-modified layer of a thickness ~ 100 nm formed in PMMA by a low energy (50 keV) silicon (Si^+) ion implantation at a fluence of 3.2×10^{15} ions/cm^2.

2 Experimental

The sample used in this study was a plane-parallel PMMA plate of size 1×1 cm and thickness of 5 mm, implanted by 50 keV Si^+ ions with a fluence of 3.2×10^{15} cm^{-2}. Experimental details concerning the ion implantation have been given elsewhere [7]. Linearly polarized He-Ne laser beam (wavelength $\lambda = 632.8$ nm, beam diameter ~ 1 mm) was employed to perform measurements of reflectance of the ion-implanted surface of the sample versus the angle of incidence. The optical power incident on the ion-implanted sample was kept fixed at 0.9 mW. The reflected beam was measured with Ophir Nova II laser power meter with thermal head (Ophir Thermopile 3A). Reflection ellipsometry measurements were carried out by rotating analyzer PCSrotA-A/ null type ellipsometer [8] by illumination with He-Ne laser (power of 5 mW, beam diameter ~ 1 mm).

3 Results and Discussion

The spectroscopy analyses of considered Si^+-implanted PMMA [7,9] clearly indicated the presence of a carbonaceous layer located in the near-surface region of a thickness of less than 100 nm, and pointed toward the formation of nano-clustered structure of hydrogenated amorphous carbon (HAC) as a result from the ion implantation. As known, the modification of optical properties of ion-implanted materials is due to chemical and structural changes upon ion implantation [1]. For hydrocarbon polymers like PMMA, these changes include polymer decomposition, chain scissions accompanying with formation of double bonds, loss of hydrogen and hydrocarbons, light fragments outgassing and densification of remaining material,. As a result, a well defined subsurface layer from a more compacted material with carbonaceous structure having conjugated double bonds is formed that actually leads to increased refractive index. Monte-Carlo simulations of the spatial distribution of the deposited energy in the depth indicated that the projected range of 50 keV Si^+ ions in PMMA should be rather short, hence the refractive index change of this optically transparent ion-implanted polymer is expected to be close to the surface.

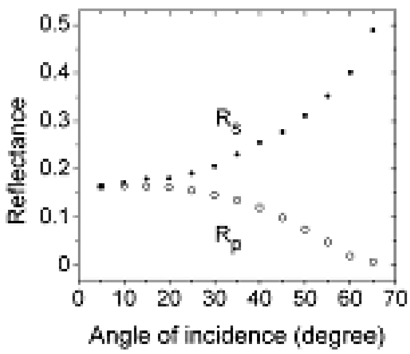

Figure 1: Experimental data for reflectance of Si^+-implanted PMMA measured with linearly polarized He-Ne laser beam (wavelength $\lambda = 632.8$ nm) by two orthogonal polarizations: *s* (solid circles) and *p* (open circles) versus the incidence angle.

The in-depth spatial distribution (depth profile) of the refractive index of the material in the ion-modified surface layer formed in optically transparent polymer PMMA subjected to 50 keV Si^+ implantation was determined by calculations based on discrete multilayer model [10] and optical reflectance data (simple measurement of the optical reflection from the layer versus the incidence angle) (Figure 1). By that, both real (n) and imaginary (k) components of the complex refractive index were modeled in a geometry that includes a gradient of their in-depth spatial distribution. According to our calculations, both n and k have maximum values at the surface of Si^+-implanted PMMA (Figure 2). The relatively large positive change in the refractive index (over those of the substrate PMMA) upon implantation at present energy and fluence levels, is indicative of a significant modification of PMMA, related to HAC formation in the ion-modified layer. In depth, towards the end of the modified region, the values of both n and k gradually decrease up to the ones of the substrate PMMA (ellipsometric data: $n = 1.490$ and $k < 0.01$ measured at $\lambda = 632.8$ nm). Such a form, the monotonic distribution, the smoothed shape and the relatively small gradient of the simulated index depth profiles are reasonable having in mind that the variation of refractive index of the ion-modified material is controlled by the damage distribution.

Since the refractive index change in the ion-modified layer of the studied Si^+-implanted PMMA is close to the surface, well suited for its in-depth characterization is the application of reflection ellipsometry. Reasonably, we have compared the depth profiles of n and k simulated by the classical multilayer approach to those obtained from ellipsometry data. In the latter case, the (n, k) depth profiles of the ion-modified material in Si^+-implanted PMMA were calculated by employing Maxwell–Garnet effective medium approximation and sim-

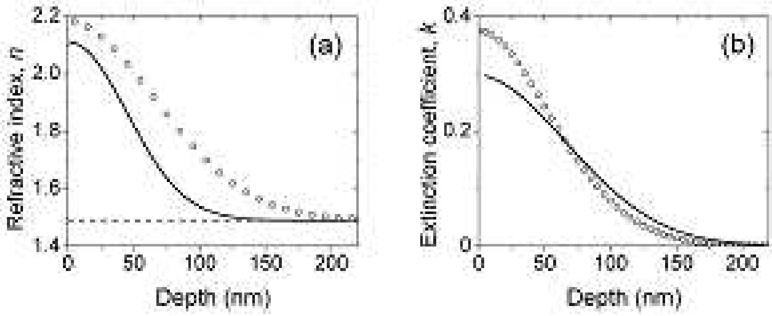

Figure 2: Depth profiles of n and k ($\lambda = 632.8$ nm) derived by: (a) multilayer model and photometry reflectance data (open circles), (b) multiangle-reflection ellipsometrical measurements of Si^{+}-implanted PMMA. The dashed line indicates the refractive index of non-implanted PMMA (in our case 1.490 determined by ellipsometric measurement at $\lambda = 632.8$ nm).

ulation based on multiangle reflection ellipsometry data obtained at the wavelength $\lambda = 632.8$ nm (He-Ne laser) [11]. The numerical results for the depth profiles of n and k are shown in Figure 2. As seen, they resemble the depth profiles derived by the multilayer approach. In total, the results for the depth profiles of n and k in Figure 2 show that Si^{+} ion implantation (in our case at an energy of 50 keV and at the fluence of 3.2×10^{15} Si^{+}/cm^{2}) of PMMA leads to a material modification of this polymer in a depth ~ 100 nm beneath the surface. This agrees well with the thickness of the ion-modified layer in the same Si^{+}-implanted PMMA sample estimated previously by application of other optical methods [9,11].

4 Conclusions

We report on characterization of the complex refractive index (at the wavelength of 632.8 nm) of PMMA subjected to an implantation with silicon ions at an energy of 50 keV and fluence of 3.2×10^{15} cm^{-2}. Being of interest for photonic integrated polymer components and optical circuits for telecommunication and sensor applications, the depth profile of the complex refractive index of the formed ion-implanted material was modelled numerically, based on experimental data obtained by reflectance photometry or ellipsometry. The ion-induced refractive index change in this optically-transparent ion-implanted polymer is close to the surface and is distributed in a depth region of about 100 nm. On the top surface, the refractive index reaches values up to 2.1–2.2 and 0.3–0.4, for the real and imaginary parts, respectively, and beneath the surface is gradually decreasing. The results for the index depth profile of the formed Si^{+}-implanted PMMA material would be useful for the application of optically-transparent ion-implanted polymers.

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