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Studies of PMMA sintering foils with and without coating by magnetron sputtering Pd

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ABSTRACT

Polymethylmethacrylate thin foils were prepared by using physical and chemical processes aimed at changing certain properties. The density and the optical properties were changed obtaining clear and opaque foils. DC magnetron sputtering method was used to cover the foils with thin metallic palladium layers. The high optical absorbent foils were obtained producing microstructured PMMA microbeads with and without thin metallic coatings. Rutherford Backscattering Spectroscopy, optical investigation and microscopy were employed to characterize the prepared foils useful in the field study of laser-matter interaction.

1. Introduction

The polymers treatment using physical and chemical processes [1] permits to obtain new materials with unique properties concerning their electrical conductivity, chemical solubility, mechanical and optical characteristics, porosity and composition, doping with nanoparticles and microstructures, appearing with unlimited and promising applications in fundamental research and industry [2,3]. Polymers are low cost and exhibit low density, high resistance to corrosion and high strength to weight ratio. Despite a distinctive dominant property of polymer, i.e. the electrical insulating, the interest in the substitution of semiconductors and metals with polymers motivated researchers to overcome this drawback using many techniques such as plasma treatment enhanced by chemical vapor deposition (CVD) [4], doping with different species and laser ion implantation [5]. A powerful technique, applied to polymers, that has gained much interest over other techniques due its high controllability of process parameters, to synthesize thin film with low impurities, is the magnetron sputtering. Although the modifications of polymers have been widely investigated [6], a new research area is focused on the production of porous materials exhibiting the pore size ranging between tens of micrometers [7] and hundreds of nanometers [8]. Recent studies on polymethylmetacrylate (PMMA) based nanoporous materials [9] report that the reduction of the pore size is responsible for the decreasing of the thermal conductivity as a consequence of both heat conduction transfer decreasing by means of the gas phase (Knudsen effect) and the enhancement of the solid matrix tortuosity [10]. Nowadays, great effort is focused to the realization of high optical absorption materials playing a key role in laser-matter interaction studies [11–12]. The present work is addressed to investigate the porosity of employed polymeric foils; to evaluate the quality of metallic layers deposited on the polymer and produced by magnetron sputtering as well as their structural characterization; to conduct optical analysis of clear and opaque PMMA films in the optical range from UV to visible and to the IR.

2. Materials and methods

Special foils of Polymethylmethacrylate (PMMA) were prepared at the Institute of Nuclear Physics, ASCR, Tandetron Laboratory, Rez, in the Czech Republic and used as received [13]. PMMA powder of high purity (99.98% purity) purchased from Goodfellow was dissolved in chloroform (CF). The solution was used to produce thin foils by the spin coating deposition technique. These foils, with different thickness, were used as polymeric matrix.

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The DC magnetron sputter deposition was employed to sputter, in high vacuum, solid targets of pure (99.9%) Pd, and to deposit thin metallic films (1–20 μm) on the exposed PMMA sheet surfaces. 1 keV Ar^+ ions at 10–100 μA produce metallic films onto the polymeric matrix which thickness depends on the ion current and sputtering time. The thin film deposition process was performed directly on different PMMA foils $10 \times 20\ mm^2$ and 7.5 μm thick. Previous depositions and evaluations of the obtained thickness provide a calibration curve to determine the appropriate experimental conditions to obtain the required thicknesses of the Pd films. For the present measurements, the same experimental conditions have been adopted to compare the different response affecting the clear and opaque PMMA due to their different densites. Pd thin films were prepared at the Institute for Nuclear Research, Hungarian Academy of Sciences (ATOMKI) by magnetron sputter deposition in a home-made magnetron sputter system equipped with two magnetron sources produced by Kurt J. Lesker Company.

During the deposition the substrate holder was held at room temperature with a positive potential and the target metallic material was held at negative potential. The pressure during the deposition was $3.7 \cdot 10^{-3}$ mbar produced by a turbo-molecular pump connected to a deposition chamber before introducing argon. The sputtering chamber consists of two identical commercially available planar sources with shutters positioned in the bottom plate of the stainless-steel vacuum chamber. Plasma discharge is maintained above the target. The distance between the target and the substrate was 18 cm, the angular position of the magnetrons were perpendicular to the surface of substrate and the Pd sputtering rate was 0.13 nm/s (with 40 W power). Before deposition, the target was cleaned using argon gas discharge plasma for 15 min. The deposition time was fixed to 6 min and 25 s for Pd.

The optical characteristics of the PMMA foils, in terms of translucent or opaque appearance in the visible region, depend on the fast or slow cooling of the chloroform solution as a consequence of the solvent evaporation. In the first case very small beads are expected to appear in the clear PMMA foil while micrometric beads in the opaque one as discussed in the following section. Details on sample preparation and characterization are given in Ref. [13]. The trace analysis of heavier elements, film and interface thickness, atomic mixing effects of the layers and measurements of the hydrogen content were evaluated by Rutherford Backscattering Spectrometry (RBS) and Elastic Recoil Detection Analysis (ERDA) [14] measurements by using 2.0 MeV He^+ ions at Tandetron Lab [15], Nuclear Physics Institute of the ASCR, in the Czech Republic. During the RBS measurement the incoming helium ions arrive on the substrate at 0° then they are backscattered and detected at an angle of 170° by Ultra-Ortec PIPS detector placed below the incoming beam in the Cornell geometry. During the ERDA measurements the incoming beam angle is 75° and the scattering angle is 30°. The forward recoiled atoms (light elements, such as protons) are detected by a Canberra PD-25-12-100 AM detector fixed in plane with the incoming ion beam and covered by a 12 μm Mylar foil to avoid the detection of back-scattered He^+ ions. Both hydrogen and heavier ion distributions obtained by ERDA and RBS, respectively, are determined in absolute mode without any reference to a standard sample and taking into account all the parameters involved in particles-solid interaction and experimental configuration (stopping power, elastic recoil-cross section, kinematic and geometric factors, energy spreading). The measurements uncertainty generally are within 20% or less. Both RBS and ERDA spectra were detected, stored and transformed into concentration depth profiles by using the SIMNRA 6.06 code [16] software based on the cross-section data from IBANDL [17]. The typical He^+ ion current for each analysis was about 5.6 nA and the irradiation time maintained about ten minutes to avoid thermal degradation of the samples. The beam current is monitored before and during the irradiations using a Farady Cup so that the dose as a function of the time can be accurately calculated. It is know that hydrogen and other elements can desorb during helium irradiation using ERDA and RBS analysis. Our measurements have demonstrated that for a dose of about 3.1×10^{14} ions/cm^2, obtained during 4–5 min analysis beam time, the hydrogen outgassing is negligible (reduction of the order of 3%) but increasing this helium dose the hydrogen loss increases, in agreement with literature, as described in our previous article [14].

The evaluation of the porosity of the opaque PMMA was carried out using a software written employing MathLab code [18] enabling us to recognize the shape and the dimension of the porosity being into the polymer.

Optical properties in the spectral region from 250 to 1000 nm and measurements of absorption and transmission have been performed by using a Perkin-Elmer spectrometer.

3. Results

Two variants of PMMA foils have been used: the clear and the opaque one both obtained by application of our physical-chemical synthesis processes [13]. The density of PMMA polymers was measured in different ways. The first method concerns the different polymer density given in g/cm^3 and the second one, the superficial beads density.

The first method used the alpha particle energy loss in a known thickness of polymer by using a radioactive alpha source (Am-241, 5.48 MeV) and detecting the transmitted particle energy. This is a function of the massive stopping power (tabulated at 5.48 MeV) and of the polymer density. From the measure of the average transmitted energy was calculated the polymer density in terms of g/cm^3 finding that the clear PMMA has a higher density of the opaque one. The second method was performed using known thickness and surface area of the foils and accurate weight of the samples with a Mettler Toledo Micro-Balance with ±1 μg absolute accuracy. It depends on the measure of the film volume and mass and provide a density of 1.18 g/cm^3 for the clear PMMA and 0.75 g/cm^3 for the opaque PMMA, in agreement with the measurements of alpha energy loss. Such measurements are affected by an error of about 15%.

The morphological surface and the optical properties of the bulk of the prepared samples were investigated with microscopy and optical spectroscopies assisted by a software written and implemented by ourselves. One square of 600×650 pixels from the calibration picture has been used; inside this square there are 1299 squared holes with a side with a length of 6.25 μ. The average surface of each square, taking into account a Gaussian distribution of the surfaces, evaluated by MatLab is 164.4 ± 8.6 pixel corresponding to a real area of 39 μm^2 with an error of ± 2 μm^2. At this point the picture of opaque PMMA taken at the same conditions than the calibration one is studied. Inside a square of 600×650 pixels has been counted 1583 beads, corresponding to a density of 17,100 beads/mm^2. The average diameter of the beads is 4.56 μm. The analyzed surface of 92,496 μm^2 was covered by 1583 beads taking a total surface of 25,839 μm^2 corresponding to 28% of the total sample surface.

Fig. 1a, for example, shows an optical microscopy ×500 magnified of the pure opaque PMMA (Fig. 1b) rich in micrometric beads produced by the chemical attach in chloroform. Step by step, the MathLab code converts the image in a grey scale and, using a function based on a Otsu method, a global threshold (level) among white and black pixels is computed. An image of Cu mesh ×500

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