

## **STRUCTURE OF BULK AND THIN FILMS OF POLY-METHYL-METHACRYLATE (PMMA) POLYMER PREPARED BY PULSED LASER DEPOSITION**

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Homogeneous thin films have been obtained by UV-excimer pulsed laser deposition from a PMMA bulk material. The structure of films is at variance with the structure of the bulk polymer. The size of the ordered domains, as well as the structural features, evidenced by X-ray diffraction in the deposited films, depend on the fluence of the ultraviolet laser pulse used in the ablation process and on the temperature of the substrate. The radial distribution functions of the bulk PMMA material and thin films show differences in the short range order ascribed to the breaking of the polymer chains and monomer dissociation during deposition process.

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### **1. Introduction**

The interest in polymer materials has grown continuously in the last years. Various methods for preparation of thin polymer films emerged. New techniques for producing polymer particles of controlled composition and size [1] have been developed. Nanoparticles of polymers embedded in bulk materials or in thin films may show unusual properties due to size reduction to the point where the critical length scale of physical phenomena become comparable to or larger than the size of the structure itself.

The use of laser-based methods for thin film preparation [2], formation of optoelectronic structures [3] or inscription of optical information [4] opens new application possibilities.

The Pulsed Laser Deposition (PLD) method is one of the most simple and powerful procedures for preparing thin films from organic polymers. Nevertheless, the polymerized structure is not maintained in the deposited films. Usually a large size distribution of polymer fragments and various radicals occur. The polymer fragmentation during ablation and subsequent deposition leads to a new structure which can be exploited for applications. The understanding of the process and its full control is still challenging for physicists and electronic engineers.

Poly-methyl-methacrylate (PMMA) polymer is well-known and was widely studied both in bulk and thin film forms. Pressure-induced enhancement of photo-luminescence was observed in films of PMMA doped with CdS and CdSe nanocrystals, prepared by casting from chloroform solution [5].

Excimer laser ablation is an efficient technique for deposition of PMMA films. The PMMA, taylored as thin film, is an excellent material for many applications: chemical sensing, lithography, holography, data display and storage, etc...

In this paper we report the structural results obtained on thin films of PMMA prepared by pulsed laser deposition on silicon wafers in comparison with the PMMA bulk material.

## 2. Experimental method

Thin films of PMMA have been deposited by PLD using a KrF<sup>\*</sup> excimer laser (the wavelength of the emitted UV pulse is 248 nm, the pulse duration is  $\geq 20$  ns, the repetition rate is 1 Hz and the maximum output energy is 85 mJ/pulse). The pulses were focused on the target through a MgF<sub>2</sub> cylindrical lens (focal length: 30 cm). The incidence angle to the target was 45°. The laser spot was set within 4.2 and 6.4 mm<sup>2</sup> and the incident fluence varied roughly in the range 0.8 - 1.6 J/cm<sup>2</sup>.

The target material was a PMMA pellet 15×15×2 mm<sup>3</sup> made from high purity ICI DIAKON powder and moulded at 190 °C. The holder with the PMMA target was placed in stainless vacuum chamber, which was subsequently evacuated down to  $1 - 7 \times 10^{-3}$  Pa. The target was rotated with the frequency of 0.4 rot/min during PLD process. The substrate for film deposition was a [100] oriented silicon wafer mounted on a molybdenum heating block, parallel to the target surface and situated at a distance of 2 - 5 cm. The number of pulses applied for a film deposition ranged from 10 000 to 30 000. A special heating device was used in order to keep the deposition substrate at a pre-selected temperature in the range 100-200 °C.

## 3. Structural results

### 3.1. X-ray diffraction

The X-ray diffraction patterns were recorded in the diffractometric method. A computer-driven TUR M-62 diffractometer equipped with a copper target tube and proportional counter was used in the measurements. The diagrams were obtained by registering the scattered X-ray quanta within the range 2-32° and at an angle step of 0.02° ( $\vartheta$ ) with the measuring time of half a minute per angular position.

The following samples have been prepared and used in the investigations:

a) the target bulk sample of PMMA (symbol B); b) film deposited on silicon substrate held at room temperature, by using a laser fluence of 1.4 J/cm<sup>2</sup> and a number of 30000 laser pulses (symbol F<sub>1</sub>); c) film deposited on silicon substrate held at 200 °C, by using a laser fluence of 0.8 J/cm<sup>2</sup> and a number of 20000 laser pulses (symbol F<sub>2</sub>); d) film deposited on silicon substrate held at 200 °C, by using a laser fluence of 1.20 J/cm<sup>2</sup> and a number of 10000 laser pulses (symbol F<sub>3</sub>).

The X-ray diffraction patterns recorded on bulk PMMA and PMMA films deposited by PLD, are shown in Fig. 1a-d.

The bulk PMMA polymer exhibits a typical diagram of an amorphous polymer with large diffraction maxima that vanish at large diffraction angles (Fig. 1a). The first maximum situated at  $\sim 8^\circ$  ( $\vartheta$ ) is responsible for the packing of long polymer chains. The second maximum is mainly related to the effect of atom ordering inside the chains. The medium-range order configuration in the polymers influence the width and intensity of both first and second peak.

The film deposited at room temperature exhibits a different diffraction pattern, if compared to that of the bulk material. The striking modification is the increase of the intensity and narrowing of the second diffraction maximum, while the remaining part of the diagram exhibits only little changes (Fig. 1b). The films deposited at 200 °C differ in the width of the first maximum, while the second one remains practically identical (Fig. 1 c-d).

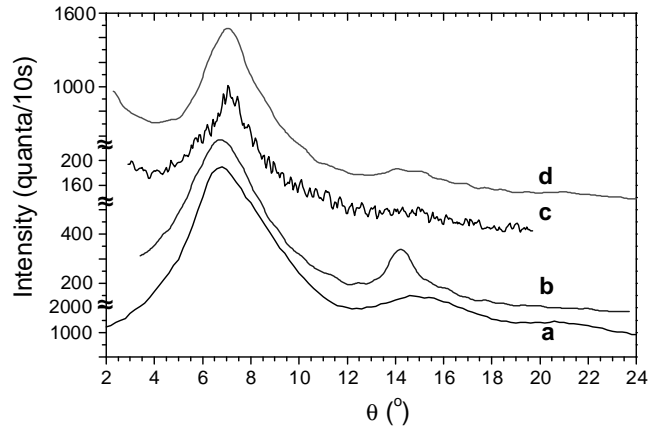


Fig. 1. The X-ray diffraction patterns of the bulk PMMA and the films deposited by PLD: (a) bulk PMMA; (b) thin film deposited at room temperature,  $F_1$  ( $\Phi = 1.4 \text{ J/cm}^2$ ); (c) thin film deposited at  $200^\circ\text{C}$ ,  $F_2$  ( $\Phi = 0.8 \text{ J/cm}^2$ ); (d) thin film deposited at  $200^\circ\text{C}$ ,  $F_3$  ( $\Phi = 1.2 \text{ J/cm}^2$ ).

### 3.2 Radial distribution functions

The Radial Distribution Function (RDF) for PMMA bulk polymer has been calculated starting from the X-ray diffraction pattern shown in Fig. 1a. Fig. 2 a-d, shows the results. The RDF (Fig. 2c) shows maxima corresponding to the mean distance calculated from the monomeric basic formula. The agreement between the value for the first order distance (deduced from the position of the first maximum in the differential RDF, which is situated at  $r_1=1.513 \text{ \AA}$ ) and the calculated one on the basis of the PMMA chemical formula ( $r_1=1.482 \text{ \AA}$ ) shows a short-range order in the amorphous bulk phase, in agreement with the molecular configuration of PMMA.

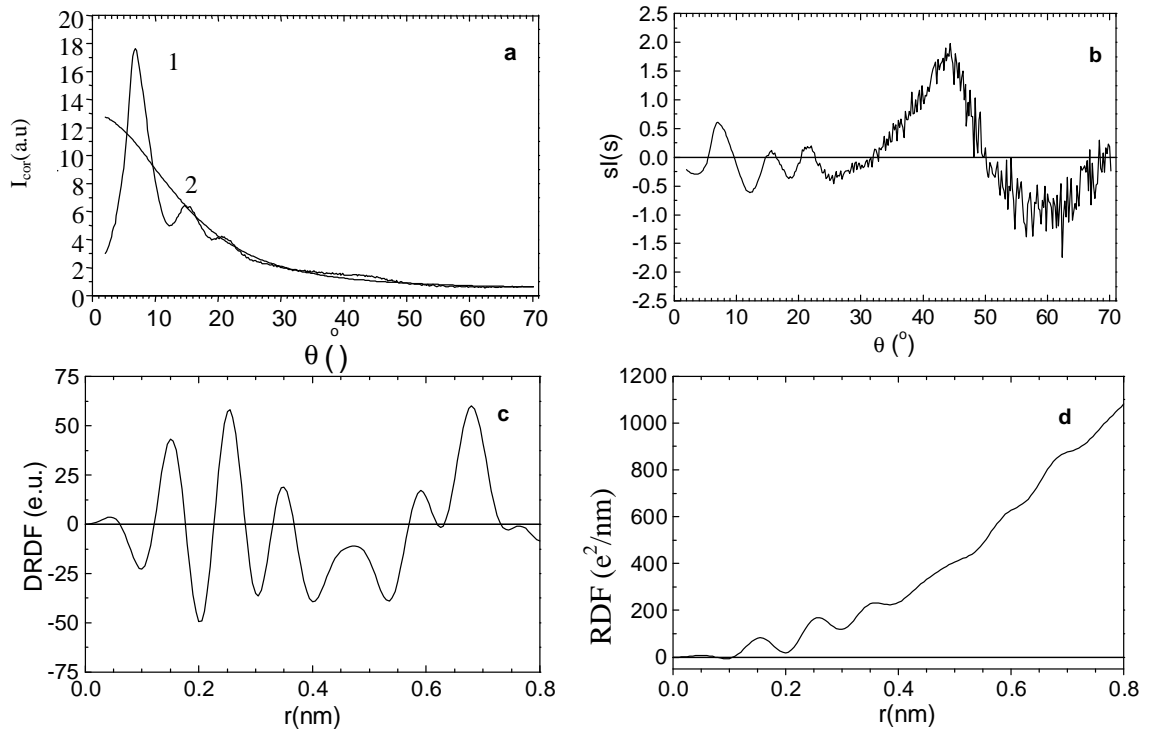


Fig. 2. Structural results for PMMA material; a. Structure factor of PMMA (1) compared to the curve of independent scattering (2); b. Reduced interference function,  $sI(s)$ ; c. Differential RDF (DRDF); d. RDF.

The radial distribution function was calculated, also, for the film deposited at room temperature (Fig. 3 a-d). In this case the first neighbour distance (bonding distance) deduced from DRDF is 1.447 Å, and this value corresponds to that calculated when polymeric bonds in PMMA are broken (1.442 Å). This result speaks in favour of the destruction of the polymeric backbone structure during PLD process. In all calculations we have used the bonding distances  $d_{c=O} = 1.35$  Å and  $d_{c-o} = 1.46$  Å from butadiene. The other bonding distances used for PMMA were  $d_{c-c} = 1.54$  Å and  $d_{c-c} = 1.32$  Å. The smooth part before the noisy region in the curve from Fig. 3b is due to the interpolation procedure used. The background under the silicon peak (400) given by the well-oriented wafer substrate, in the region  $\theta = 26^\circ - 54.5^\circ$  was approximated by a polynomial interpolation.

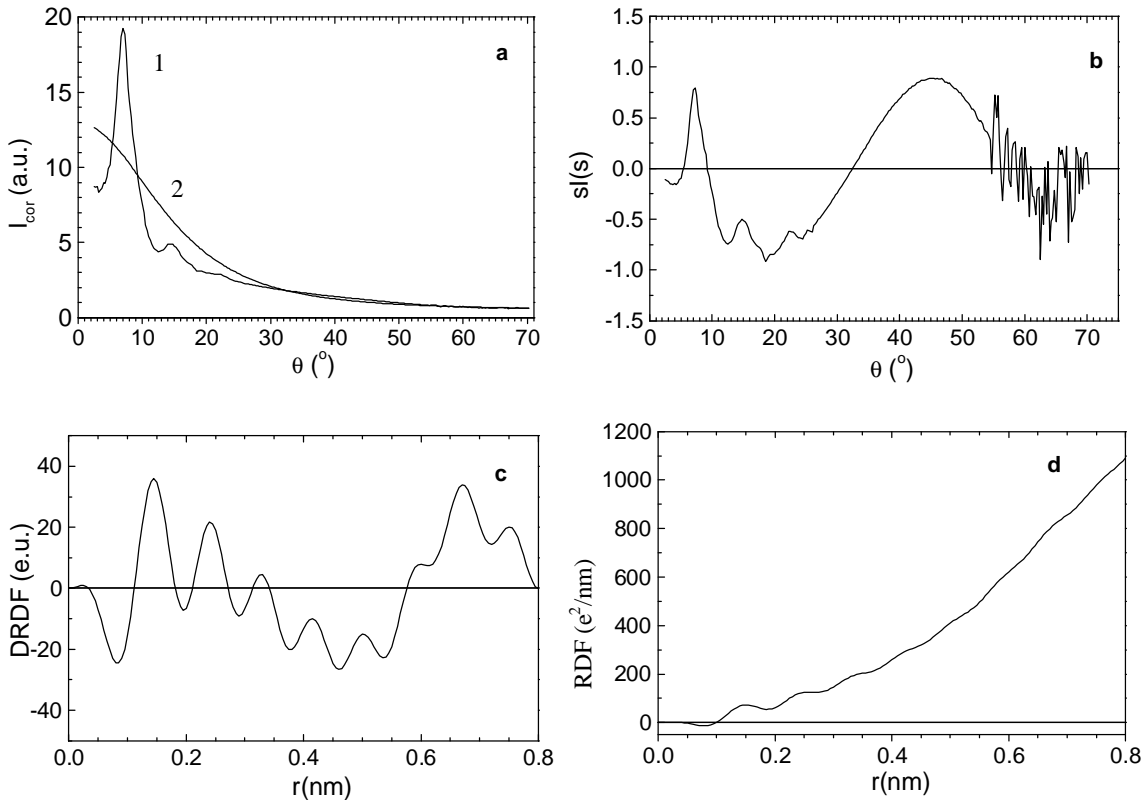


Fig. 3. Structural results for PLD thin film of PMMA. a. Structure factor of PMMA (1) compared to the curve of independent scattering (2); b. Reduced interference function,  $sI(s)$ ; c. Differential RDF (DRDF); d. RDF.

#### 4. Discussion

From the width of the first maximum we have calculated, by applying the Scherrer formula [6], the thickness of the ordered domains in the material, related to the packing of polymer chains. Fig. 4 shows the correlation between the mean size of the ordered domains,  $D$ , and the fluence of the laser radiation on the target,  $\Phi$ . The general trend is the increase of  $D$  with  $\Phi$ . The room temperature deposition leads to low  $D$  values. An exception is the film  $F_1$ , that exhibits low order for highest fluence of the laser radiation.

The experimental data obtained on the films deposited by PLD from a PMMA bulk target, show interesting features. One of the most important one is the different structure of the films as compared to the bulk material. The film deposited at room temperature ( $F_1$ ) exhibits an unusual ordering reflected in the larger intensity and narrowness of the second diffraction maximum. The film  $F_3$ , deposited at  $200^\circ\text{C}$ , exhibits a different structure: both the first and second diffraction maxima

become narrower, and this indicates a better ordering in the material. The unusual behaviour of the  $F_1$  film could be due to the formation of the DLC configuration.

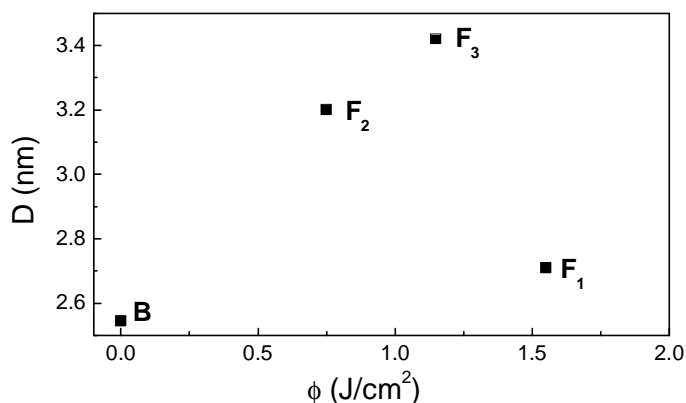
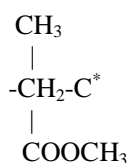


Fig. 4. The correlation between the mean size of the ordered domains,  $D$ , and the laser fluence on the target,  $\phi$ .

The correlation between the size of the domains and the fluence of the laser pulse energy on the PMMA target during PLD process speaks in favour of the importance of the laser energy in the ablation process. More energy concentrated on the surface of the PMMA determines an advanced destruction of the polymer. The deposited particles on the substrate are more dispersed in composition and structure. As a consequence, the molecular ordering in the film is rapidly triggered after deposition, by small movements of the molecular fragments impinging on the substrate.

As well-known, during the irradiation by gamma,  $\beta$ -particles or UV light the bulk PMMA exhibits a specific ESR spectrum with 9 lines [7]. This spectrum was interpreted as given by the following macro-radical



in two stable configurations: the first one with the bond C-H from  $\text{CH}_3$  situated in the plane of the unpaired electron orbital and the second one with both protons from  $\text{CH}_3$  are situated in the plane of the orbital  $\pi$ . The existence of such radicals in the laser deposited films is very probable. Obviously, a proof by ESR measurement is necessary. Anyway, more experimental investigations are needed for a better understanding of the structure and chemical binding in thin films deposited from PMMA polymer.

## 5. Conclusions

Thin homogeneous PMMA films were successfully deposited by PLD method. The structure of the thin films is at variance with that of bulk PMMA. The polymeric structure is destroyed, in the PMMA thin films while the medium-range order related to the packing of the monomeric or other molecular fragments is preserved.

The obtaining of thin transparent coatings with higher microhardness than that of the bulk PMMA, (due to a possible DLC component), opens new opportunities for applications, as e.g. in the protection of the art objects against the corrosive agents or bacteria and fungal attack [8] without the modification of the artistic qualities.

**References**

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