Polymer nanograting perfection and chain alignment investigated by GISAXS and GIWAXS


Instituto de Estructura de la Materia, IEM-CSIC, Serrano 121, 28006 Madrid, Spain
1 Instituto de Microelectrónica de Barcelona IMB-CNM (CSIC), Campus UAB 08193, Cerdanyola del Vallès (Bellaterra) Barcelona, Spain

1. Introduction

The development of non-volatile organic memories, defined as devices where the information is stored permanently without the requirement of a continuous electrical feed, is currently subject of strong debate in the scientific and technological society. Several approaches and prototypes have already been proposed, for example, metalpolymer-metal capacitors [1], field-effect transistors [2] and tunnel-junctions, all of them based on thin polymer films, generally with thickness smaller than 100 nm, and with the possibility of a readily integration with flexible complementary metal oxide semiconductor devices or other organic electronic devices. Among ferroelectric polymers, poly(vinylidene fluoride) (PVDF) and its copolymers with trifluorethylene, P(VDF-TrFE), are mostly proposed as candidates for the development of organic memories since they exhibit excellent ferro-, piezo- and pyroelectric properties which allows a direct application in organic electronics. Instead of the classical approach of using simple thin films as the main memory component, it has been recently proposed that the geometrical structuring of the films could serve as a strong technological improvement. Here, we report how the development of nanogratings on thin films of P(VDF-TrFE), prepared by Nanoimprint Lithography can be a straightforward approach to improve the management of writing and reading high density of information [3].

2. Experimental

Poly(vinylidene fluoride–trifluoroethylene)(P(VDF-TrFE)) copolymers have been investigated. Polymer thin films were prepared by spin coating on silicon wafers (100). For NIL, mesa-type silicon stamps have been fabricated. The mesas have been obtained by optical lithography and wet etching, whereas the nanostructures were defined in the substrate by means of e-beam lithography, lift-off and reactive ion etching. Periodic superficial nanogratings have been produced by pressing the stamps over polymer films at temperatures above its glass transition. Structured areas were analysed by GISAXS using the facilities of the BW4 beamline at HASYLAB (DESY, Hamburg). An X-ray wavelength of $\lambda = 0.13808$ nm, with a beam size of 40x20 $\mu$m$^2$ was used in our experiments. Scattered intensity was recorded by a Mar CCD detector of 2048x2048 pixels with a resolution of 79.1 $\mu$m per pixel, using a distance sample-to-detector of 2.325 m for GISAXS experiments and of 0.106 m for GIWAXS experiments. An incidence angle $\alpha_i = 0.4^\circ$ was chosen, which is larger than the critical angle of polymer materials and then full penetration in the sample is ensured. Samples were positioned in such a way that the beam was parallel to the nanograting lines. Acquisition times between 1 and 100 s were used. GISAXS images were treated with the Fit2D software.

3. Results and Discussion

Fig.1a shows an AFM topographic image of a thin film of P(VDF-TrFE) of thickness $\approx 100 \pm 2$nm. This type of spin-coated films typically exhibit roughness values of r.m.s. $\approx \pm 20$ nm. In Fig.1a left one sees the characteristic morphology of P(VDF-TrFE) copolymers characterized by random large needlelike crystals, which has been associated to edge-on lamellae, which coexist with flat-on crystals appearing as irregular flakes on the image. This morphology is corroborated by Scanning Electron Microscopy micrographs (Inset Fig.1a left). This morphology is also supported by GIWAXS experiments which delivers the type of patterns included in Fig.1a right. The GIWAXS pattern for the thin film (Fig. 1a right) shows the strongest reflections (200) and (110), of similar lattice spacing, corresponding to the orthorhombic crystal lattice of P(VDF-TrFE) copolymers [4].
These two reflections are separated 60° from one another in a hk0 diffraction pattern, indicating that the c-axis, which coincides with the polymer chain direction, is parallel to the X-ray beam [4]. The intensity distribution on the observed semi-ring can be used to characterize both polymer chain and lamellae orientation on these thin films. On one hand, the existence of significant intensity on the equatorial region can be attributed to the presence of flat-on lamellae with polymer chains oriented perpendicular to the surface [4]. On the other hand, a high intensity on the meridian indicates the existence of edge-on lamellae with polymer chains lying on the substrate [2]. According to Figs. 1a and 1b right, GIWAXS patterns of the gratings are qualitatively similar to those of the films. However, azimuth intensity profiles of the semi-ring reveal subtle differences between films and gratings as shown in Fig. 1c right. In the case of the grating, clear maxima at 30° and 90° are resolved. This feature is characteristic for an edge-on morphology with the polymer chain parallel to the beam. Considering that the X-rays beam impinges the grating along the lines this indicates that for the gratings edge-on lamellae are more abundant than in the film.

![Image of AFM topographic images and GIWAXS patterns](image)

**Figure 1:** Left panel: AFM topographic images of P(VDF-TrFE) thin film of thickness \(\approx 100 \pm 2\) nm (a) (Inset in 1a shows a SEM micrograph of a similar sample) and of P(VDF-TrFE) grating prepared by NIL (b). Inset in 2b shows a GISAXS pattern as a function of the q-vectors. Right panel: GIWAXS patterns of P(VDF-TrFE) thin film of thickness \(\approx 100 \pm 2\) nm (a) and a P(VDF-TrFE) grating prepared by NIL (b). (c) Azimuth intensity profiles of the multiple reflection (200)/(110) for both film and grating.

**Acknowledgements**

Funding from MINECO, Spain, (Project MAT2011-23455) is gratefully acknowledged. The experiments performed at BW4 in HASYLAB were supported by the European Community (Contract II-20100103 EC). We thank J. Perlich for his support during measurements at BW4.

**References**