ESRF	**Experiment title:** Inner structure of Ferroelectric polymer/Conducting polymer bilayers prepared by Laser Induced Periodic Surface Structures (LIPSS) method	**Experiment number**: SC-4204
Beamline:	**Date of experiment**: from: 30/11/2015 to: 04/12/2015	**Date of report**: 11/03/2016
Shifts:	**Local contact(s)**: Daniel Hermida	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Esther Rebollar*, Instituto de Química Física Rocasolano(IQFR-CSIC)[1]

Mari-Cruz García-Gutiérrez*, Instituto de Estructura de la Materia (IEM-CSIC)[2]

Aurora Nogales*, Instituto de Estructura de la Materia (IEM-CSIC)[2]

Margarita Hernández*, Instituto de Estructura de la Materia (IEM-CSIC)[2]

Jing Cui*, Instituto de Estructura de la Materia (IEM-CSIC)[2]

Tiberio A. Ezquerra*, Instituto de Estructura de la Materia (IEM-CSIC)[2]

1Serrano 119, Madrid 28006, Spain

2Serrano 121, Madrid 28006, Spain.

Report:

Summary:

The aim of this proposal was to investigate by Grazing incidence X-ray Scattering at Wide (GIWAXS) and Small (GISAXS) angles the inner structure of a series of bilayers of laser induced periodic surface structures (LIPSS) prepared on ferroelectric thin films of poly(vinylidene fluoride-trifluoro ethylene) (P(VDF-TrFE)) copolymers deposited over a poly3(hexyl thiophene) (P3HT) thin film.

Scientific background:

Organic memory devices have focused attention on ferroelectric polymers based on poly(vinylidene fluoride)(PVDF) and its copolymer with trifluoro-ethylene P(VDF-TrFE) [1]. In these semicrystalline systems nanopatterning can play an important role in order to enhance information density by controlling molecular architecture [1]. Surface nanostructuring of polymers can be accomplished by Laser Induced Periodic Surface Structures (LIPSS) over polymer thin films [2]. LIPSS appear by appropriate irradiation of solid surfaces by intense laser pulses. However, the polymer surface must fulfil certain conditions, such as light absorption at the specific wavelength. For ferroelectric copolymers like P(VDF-TrFE) no structuring could be achieved due to its poor absorption at the irradiation conditions . Recently, we have demonstrated the possibility of LIPSS formation on non-absorbing polymer thin films by the preparation of polymer bilayers in which the bottom layer absorbs light at the specific wavelength and therefore LIPSS can be formed

while the top layer is made of the non-absorbing polymer of interest. In this case we selected semicrystalline P3HT as bottom absorbing layer and P(VDF-TrFE) as non-absorbing top layer. We proved that laser nanopatterning of the P(VDF-TrFE) is achievable without compromising its ferroelectric response creating nanostructures of P(VDF-TrFE). However, since the performance of the bilayer, as defined by its capacity to storage information, can be strongly dependent on both the level of crystallinity and the orientation of the ferroelectric crystals along the thickness of the LIPSS bilayer, morphology studies based exclusively on AFM are not enough. Therefore the microstructure of the patterned bilayer requires GIWAXS and GISAXS investigation in order to elucidate the fine structures across the direction perpendicular to the free surface.

Experimental:

We carried out X-ray scattering experiments on thin polymer films in grazing incidence geometry at the beamline BM26B at ESRF. For GISAXS and GIWAXS experiments, incidence angles $0.14° < \alpha_i < 0.4°$ were chosen depending on the nature of the formed nanostructure. GISAXS and GIWAXS detection was accomplished using an X-ray wavelength of $\lambda = 0.103$ nm (12 KeV), with a beam size (HxV) of (0.7x0.3 mm^2). Scattered intensity was recorded by a PILATUS detector at a sample-to-detector distance of 7.2 m for GISAXS and 0.079 m for GIWAXS. Acquisition times were optimized in order to get maximum number of counts avoiding saturation of the detector. In the present case, typical acquisition times of 10 s were used.

Results and Discussion:

We have investigated several samples including:

(1) Poly-3-hexylthiophene (P3HT) with different thicknesses (40, 80, 150, 190, 270, 360 and 390 nm) spin-coated on silicon wafers from chloroform solutions.

(2) Poly(vinylidene fluoride- trifluoro-ethylene) P(VDF-TrFE) copolymers with different thicknesses (10, 20, 40, 60 and 90nm) spin-coated from 2-butanone solutions on silicon wafers.

(3) P(VDF-TrFE)-P3HT bilayers spin-coated on silicon wafers with different P(VDF-TrFE)/P3HT relative thicknesses (twenty nine samples).

(4) LIPSS formed over the spin-coated P(VDF-TrFE)-P3HT bilayers with different P(VDF-TrFE)/P3HTrelative thicknesses (twenty two samples).

As an example of the results we show in Fig. 1a an AFM topography image of a bilayer ca. 200 nm thick formed by a bottom P3HT film prepared from a 20g/L chloroform solution and a top P(VDF-TrFE) film formed by a 5g/L 2-butanone solution. The middle panel shows the GIWAXS experiment where the reflections characteristics of the P3HT bottom layer can be detected. Fig.1c shows the corresponding AFM topography image of the LIPSS sample irradiated by a nanosecond laser (Nd:YAG, Lotis TII LS-2131M, λ=532 nm) with a linearly polarized beam at a fluence of 26 mJ/cm^2 with 3600 pulses (8 ns each) at 10 Hz. The sample presents the characteristic morphology consisting of ripples with a period value close the laser wave length. The corresponding GIWAXS pattern reveals the presence of the P3HT bottom layer and the GISAXS pattern (right panel) exhibit the characteristic rods corresponding to the scattering of a one dimensional paracristal[1,2]. Deep analysis of the collected data is currently in progress in separating the contribution to the GIWAXS patterns of the top P(VDF-TrFE) layer 20 nm thick (Fig.2a) from that of the bottom P3HT one 190 nm thick (Fig. 2b). The role of these features on the piezoelectric effect is being investigated by Piezoelectric Force Microscopy (PFM).

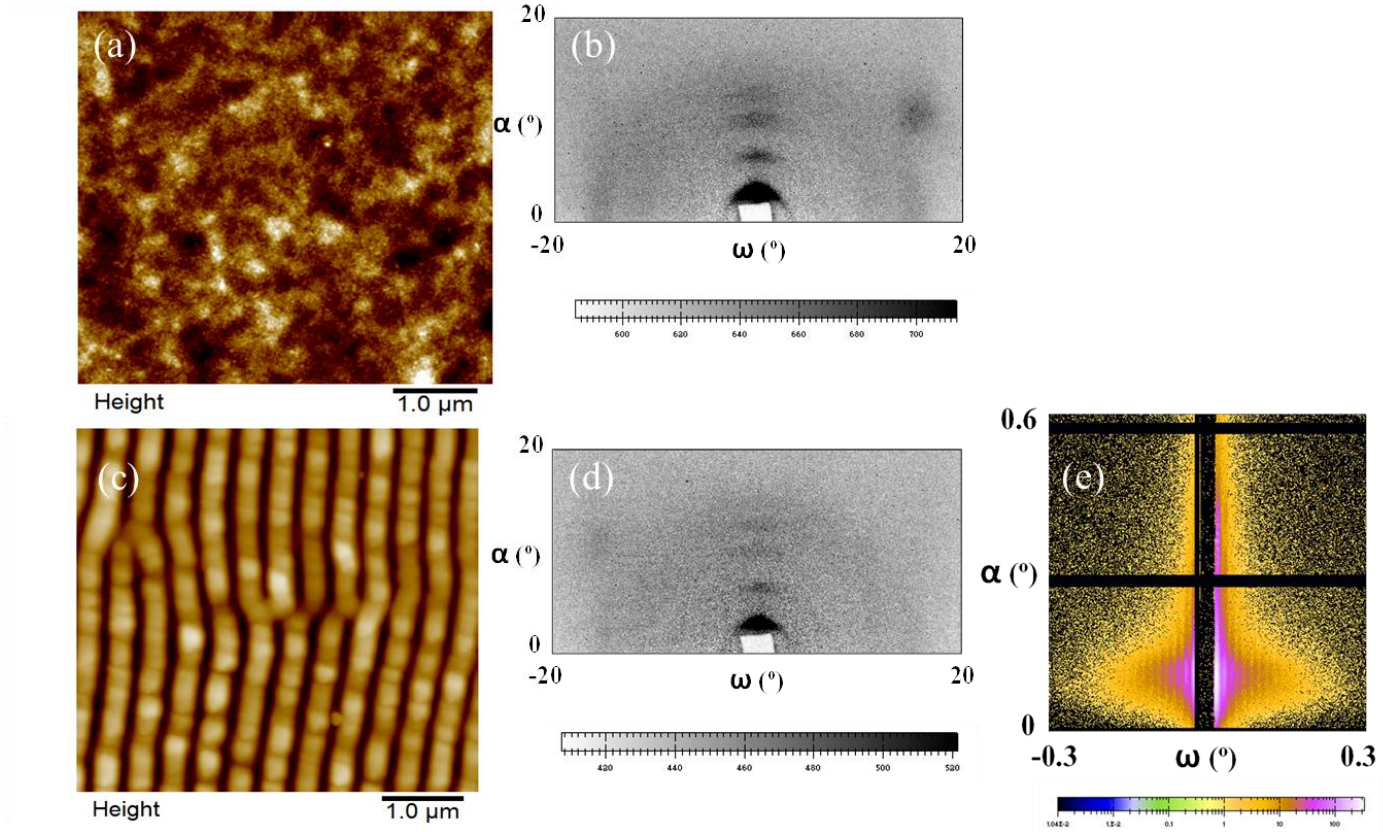

Fig.1. (a) AFM topography image and (b) GIWAXS pattern of a bilayer 200 nm thick formed by a bottom P3HT film prepared from a 20g/L chloroform solution and a top P(VDF-TrFE) film formed by a 5g/L 2-butanone solution. (c) AFM topography image of the LIPSS sample and its corresponding (d) GIWAXS and (e) GISAXS pattern.

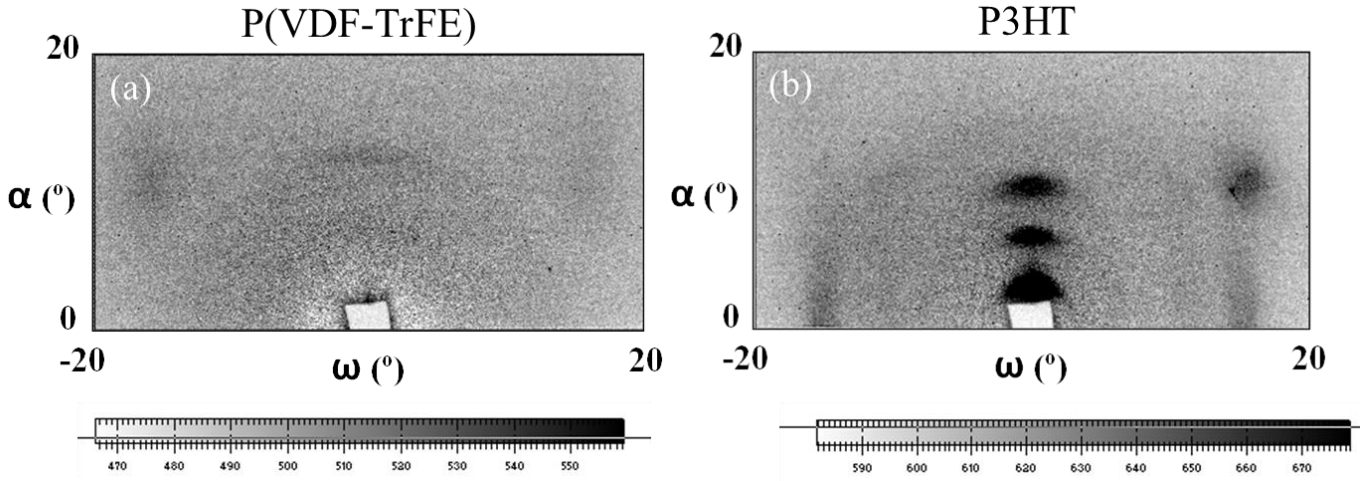

Fig.2. GIWAXS patterns of (a) a single P(VDF-TrFE) film formed by a 5g/L 2-butanone solution and (b) a single P3HT film prepared from a 20g/L chloroform solution.

References

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