Functional Nanostructured Surfaces Induced by Laser on Fullerene Thin Films

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ABSTRACT

We report a method to produce nanosecond pulsed laser induced periodic nanostructured surfaces (LIPSS) on spin-coated [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM) films exhibiting a photoinduced resist-free imprinting (PRI) property. LIPSS in PC₇₁BM are resist free and can be solvent developed, under certain conditions, leaving the laser illuminated zone as an undissolved residue. LIPSS prepared with a wavelength of 532 nm selectively preserve the electrical conductivity on the LIPSS valleys. The heterogeneous conducting pattern consisting in conducting valleys and less conducting hills observed in the LIPSS has been interpreted as due to a reduction in the crystallinity of the hills provoked by the fast heating/cooling process induced by every laser pulse. On the basis of the experiments we propose that irradiated PC₇₁BM films: i) suffer a fast heating/cooling process tending to reduce the overall crystallinity of the LIPSS and therefore decreasing the electrical conductivity of the hills while leaving a

remnant conducting film underneath the hills, ii) during laser irradiation the sample suffers a heat treatment leading to the development of a buried phase with enhanced crystallinity, close to the silicon substrate, formed by larger crystals with enhanced electrical conductivity and iii) further solvent treatment reveals the buried phase which remains in the form of partially electrically conducting nanowires. These results point towards the potential use of the described technology for nanofabrication of organic electronic devices.

KEYWORDS: Laser induced periodic surface structures, fullerene, PCBM, GIWAXS, C-AFM

1. Introduction

The continuous emerging of applications for organic nanostructured materials makes the controlled generation of micro and nanostructured functional surfaces to be a demanding challenge. Mostly driven by the field of organic electronics, alternative lithographic processes are being investigated in order to produce surface nanostructures [1-5]. Avoiding the necessity of stringent environmental conditions like those implied in using clean rooms, high vacuum or complex mask fabrication is one of the driving forces to seek for simpler alternative lithographic procedures as a complement, or even as a substitution, for standard patterning [6-8]. In particular, laser induced patterning of organic surfaces is a versatile strategy in order to produce functional materials [9]. The formation of Laser Induced Periodic Surface Structures (LIPSS) is a phenomenon which may occur by illumination of solid surfaces by intense either nanosecond [10, 11] or femtosecond [12] laser pulses. In these cases, spontaneous formation of periodic structures on the surface takes place. The structures typically consist of ripples [11] although also more complex structures have been described [13] whose periodicities are closely related to the wavelength of the irradiating laser. LIPSS formation has been proposed to be the result of the interference between the incoming and the surface scattered wave, resulting in an intensity modulation on the material surface [14] in conjunction with a feedback mechanism [14, 15]. Among organic materials both semiconducting polymers and fullerenes have attracted much attention due to their potential applications in optics, electronics and photovoltaics among others [16, 17]. In particular, [6,6]-phenyl C₆₁-butyric acid methyl ester (PC₆₁BM) and [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM) have been used as acceptor systems in organic photovoltaics [18] PC₇₁BM possesses stronger absorption in the visible range than its PC₆₁BM [19] and hence it has attracted much interest in the last few years [20].

Nanostructuring by laser of semiconducting polymers has been recently accomplished rendering to functional surfaces of selective electrical conductivity [21] and with photovoltaic properties [22]. Micron size patterning by light of fullerene materials including C₆₀ and PC₆₁BM has been previously described by several authors [23-25]. At nanometer scale, ordering of fullerenes typically implies bottom-up strategies involving either a template surface [26, 27] or a template nanoadditive [28]. Here, we introduce a novel one-step top-down laser-induced method based on LIPSS capable of nanostructuring fullerene materials. We demonstrate the possibility of producing nanostructured functional surfaces on spin-coated PC₇₁BM films. Important enough, we show that fullerene LIPSS exhibit peculiar electric conducting properties which make them of potential interest in organic electronics.

2. Experimental Methods

PC₇₁BM (phenyl C₇₁-butyric acid methyl ester, Ossila (UK)) was dissolved in chlorobenzene (40 mg/mL) and stirred at room temperature for 60 minutes. Thin films were prepared by spin-coating using a spin processor (Laurell WS-650 Series). A fixed amount of 0.2 mL of fullerene solution was dropped by a syringe on a square n-silicon (100, Arsenic dopant, ACM (France)) substrate. A rotation rate of 2400 rpm was kept during 120 s. By this procedure PC₇₁BM thin films of $\approx$ 80-100 nm thickness are obtained in a reproducible manner.

Laser irradiation was carried out in ambient air conditions at normal incidence with a linearly polarized laser beam of a Q-switched Nd:YAG laser (Lotis TII LS-2131M, pulse duration of 8 ns). A wavelength of $\lambda_{\text{laser}} = 532$ nm was used by selecting the second laser harmonic at a repetition rate of 10 Hz. This wavelength was selected for the experiments since PC₇₁BM absorbs efficiently with an absorption coefficient $\sim 1.10^5$

cm^{-1} . The spot of the laser in the sample was defined by using an iris of 1.2 mm in diameter. The irradiation fluences were determined by measuring the laser energy in front of the sample. Spin-coated PC₇₁BM films were laser irradiated at different fluences from $F=13.6 \text{ mJ/cm}^2$ to $F=24.4 \text{ mJ/cm}^2$. These irradiation conditions were chosen on the basis of previous experiments about LIPSS formation in poly(3-hexylthiophene)/PC₇₁BM blends [21, 22].

Atomic force microscopy (AFM) measurements were carried out under ambient conditions using a scanning probe microscope (MultiMode 8 equipped with a C-AFM module and with the Nanoscope V controller, Bruker). The AFM topography images were collected in tapping mode using silicon probes (NSG30 probes by NT-MDT). Electrical measurements were performed by C-AFM with conductive tips (Pt-Ir covered Si probes with a low spring constant, $k = 0.2 \text{ Nm}^{-1}$, SCM-PIC by Bruker) in contact mode by measuring simultaneously both topography and electrical images. The sample was attached with conductive silver epoxy (CW2400, Chemtronics) onto an iron support. In C-AFM measurements the conducting tip makes contact with the sample, acting as a nanoelectrode, and maps a current image at a fixed bias. The bias was applied between the cantilever and the conducting substrate.

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) experiments were performed at the DUBBLE beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) as previously described [15, 29]. An X-ray wavelength of $\lambda_{\text{X-ray}} = 0.103 \text{ nm}$ and a beam size (HxV) of $(0.8 \times 0.1) \text{ mm}^2$ was employed. The GIWAXS patterns were recorded by a Frelon detector located at 0.121 m from the sample position. Patterns, acquired with an acquisition time of 10 s, were corrected from background scattering and analyzed by the Fit2D software [30].

Raman spectroscopy was performed by using a Renishaw Raman InVia Reflex Spectrophotometer, equipped with a Leica Microscope, and an electrically refrigerated CCD camera, using the excitation line at $\lambda_{\text{Raman}}=532$ nm (Nd:YAG laser). The spectra were acquired with a spectral resolution of 2 cm^{-1} using a $50\times$ magnification objective to a spot with a diameter $< 1 \text{ }\mu\text{m}$ on the samples.

3. Results and Discussion.

3.1. LIPSS Formation on PC₇₁BM spin-coated films.

Rather smooth spin-coated PC₇₁BM films can be obtained with mean surface roughness $R_a \leq 0.3 \text{ nm}$ as revealed by AFM. Figure 1a shows an optical micrograph of the laser fingerprint after irradiation with $\lambda_{\text{laser}} = 532 \text{ nm}$ for 3600 pulses at a fluence of $F=17.2 \text{ mJ/cm}^2$ on a spin-coated film PC₇₁BM. A bright outer ring is clearly observed surrounding the spot due to a near field diffraction effect caused by the iris enhancing irradiation in the border of the spot [31]. Figure 1b and 1c show AFM topographic images in the indicated positions of the spot showing the characteristic grating like morphology obtained by LIPSS with lines roughly parallel to the laser polarization as indicated by the double arrow and periodicity close to the value of λ_{laser} . A characteristic grating like morphology is obtained by LIPSS.

Figure 1. (a) Optical micrograph of the laser fingerprint on a spin-coated PC₇₁BM film after irradiation at $\lambda_{\text{laser}}=532$ nm with 3600 pulses at a fluence of $F=17.2$ mJ/cm². (b and c) AFM topographic images in the indicated positions. The yellow double arrow indicates the laser polarization. (d) Optical micrograph of the residue remaining after solvent washing. (e and f) AFM topographic images in the indicated positions.

Figure 2a shows the profiles of the LIPSS perpendicular to the ripple axis for the PC₇₁BM sample shown in Fig. 1a after removing part of the film with a razor blade. The left part of the data showing a flat background corresponds to the surface of the silicon substrate after removal of the material by the blade. The corresponding image for the initial spin-coated PC₇₁BM film is also presented for comparison (Figure 2b). In this case, the difference in height between the flat background on the left and the upper plateau on the right corresponds to the thickness of the spin-coated PC₇₁BM film which is about 100 nm. The superposition of the height profiles of both the initial spin-coated and that of the irradiated one suggests that LIPSS formation with a pitch of $L \approx 400$ nm

proceeds on the PC₇₁BM surface by a redistribution of the material into hills and valleys.

Figure 2. Height profiles after removing part of the film with a razor blade for: (red line) LIPSS perpendicular to the ripple axis for the PC₇₁BM irradiated at $\lambda_{\text{laser}}=532$ nm with 3600 pulses, $F=17.2$ mJ/cm² and (black line) initial spin-coated PC₇₁BM film. The insets (a) and (b) show the AFM height images where the profiles were calculated corresponding to the LIPSS and unstructured samples respectively. The darker zone on the left corresponds to the part which has been removed by the razor blade.

3.2. Resist-free characteristics of LIPSS on PC₇₁BM spin-coated films

One attractive property of the LIPSS formed by laser irradiation of PC₇₁BM films is that they present the characteristics of a photoinduced and resist-free imprinting (PRI). In fact, the non-irradiated areas can be removed by a solution development procedure

while irradiated ones partially remain on the silicon substrate. We have accomplished a quick solution development process by putting the irradiated sample in the spin-coater and depositing a drop of chlorobenzene on top. Subsequently a rotation of 2400 rpm is applied for 120 s. The result of this process is illustrated in Figure 1d where the result of the development process for the samples from Fig.1a is shown. The optical microscopy image (Fig.1d) suggests that apparently after development only the central part of the irradiated area remains. Additional information about the developed irradiated area can be obtained by further AFM inspection. Fig. 1e and 1f show AFM topographic images in the indicated positions of the spot for solvent washed PC₇₁BM sample. Interestingly enough LIPSS appears in all zones even in the outer part where no optical contrast is detected. However, a different morphology is observed especially in the outer region. Here the LIPSS are characterized by thinner hills of ≈ 5 -10 nm forming nanowires with a granular texture. This effect is illustrated in Fig. 3a where the tapping-mode AFM topographic image taken across the border of the irradiated and the non-irradiated zone of PC₇₁BM sample after development is shown.

Figure 3. Height profile across the border of the irradiated and the non-irradiated zone of the PC₇₁BM sample irradiated with $\lambda_{\text{laser}}=532$ nm (3600 pulses, $F=17.2$ mJ/cm²) after development. The inset (a) shows the AFM tapping mode topographic image used to measure the profile.

The situation in the central area of the original spot is qualitatively similar as shown in Figure S1 although the nanowires tend to be one order of magnitude thicker in the central part. The profile of the washed LIPSS suggests that after developing the residue consists of nanowires over the silicon substrate. As one sees in the one-dimensional height profile, the original LIPSS sample (Fig. 2), consists of both hills and valleys roughly centered on the surface of the initial spin-coated PC₇₁BM film. On the contrary in the washed LIPSS residue the hills seem to protrude from the silicon substrate level indicating that the solvent was capable of removing a significant superficial layer of the

film though leaving a remnant LIPSS profile. In addition, these results also reveal that the non-irradiated material can be effectively removed by a solvent in the present conditions.

3.3. Chemical characterization of resist-free LIPSS on PC₇₁BM spin-coated films.

For PC₆₁BM a PRI procedure was previously reported [23, 25] capable of producing micron size patterns by using a non-pulsed diverging laser beam. Here we have used a pulsed laser to produce resist-free PC₇₁BM regions decorated with nanoscale patterns. It has been proven for both low-solubility fullerene C₆₀ and PC₆₁BM that during exposure to light, chemically connected fullerene structures appear [25]. Actually, it is proposed that the intramolecular sp² bonds are affected by laser light enabling the formation either of C₆₀ polymers [32] or of PC₆₁BM dimers [25]. In these cases, Raman spectroscopy has been shown to be a powerful method in order to investigate intramolecular bond formation. In particular, significant changes in the A_g(2) mode ($\approx 1468 \text{ cm}^{-1}$) for C₆₀ is observed indicating the formation of polymers [25]. For PC₆₁BM Raman modifications in the same spectral region are observed indicating the coexistence of a fraction of both free molecules and dimers [25]. It has been proposed that the side group PC₆₁BM affects the chemical reaction hindering the formation of higher molecular weight oligomers [25]. Figure 4a and 4b show the Raman spectra of PC₇₁BM spin-coated films before and after irradiation with $\lambda_{\text{laser}}=532 \text{ nm}$ respectively. The spectrum of the reference non-irradiated PC₇₁BM spin-coated film (Fig.4a) presents the characteristic bands associated to C₇₀ [33, 34] and PC₇₁BM [35]. In particular the ones at $\approx 1565 \text{ cm}^{-1}$ and 1467 cm^{-1} which are assigned to the anti-symmetry and symmetry C=C stretch mode, respectively[35]. For the PC₇₁BM film after irradiation with $\lambda_{\text{laser}}=532 \text{ nm}$ (3600 pulses, $F=17.2 \text{ mJ/cm}^2$) the Raman spectrum presents two

additional broad bands, indicated by arrows in Fig. 4b, centered around $\approx 1400\text{ cm}^{-1}$ and $\approx 1600\text{ cm}^{-1}$. The appearance of the two mentioned broad bands suggests the onset of a graphitization process upon laser irradiation since the observed bands can be associated to the characteristic D (1350 cm^{-1}) and G (1584 cm^{-1}) bands of graphene oxide [36-38]. It is known that fullerenes are not stable at high temperatures. As a matter of fact, the synthesis of graphene films obtained by thermal treatment of fullerenes in the presence of a metal substrate has been reported in the literature [37, 39]. Dimers of C_{70} , i.e. C_{140} , have been obtained [33] by high pressure and high temperature treatment of C_{70} . In this case the characteristic Raman bands associated to the coupled translational and rotational motions of the two C_{70} molecules appear at low frequency, namely at 89, 118, and 129 cm^{-1} . In our case the presence of such bands is not detectable. Similarly to C_{60} , for C_{70} cycloaddition across parallel double bonds is also possible [40]. However it has been reported that for C_{70} , although insoluble films upon irradiation are obtained, no significant changes in the vibrational spectra are detected [40]. This was explained considering that vibronic properties of C_{70} and its dimer, i.e C_{140} , are very similar [33]. The Raman spectrum of the washed sample, Fig. 4c, essentially shows the bands associated to the silicon substrate corroborating that a substantial amount of material was removed during development.

Figure 4. Raman spectra at $\lambda_{\text{Raman}}=532$ nm (3600 pulses, $F=17.2$ mJ/cm²) of: (a) PC₇₁BM spin-coated film, (b) PC₇₁BM after irradiation with $\lambda_{\text{laser}}=532$ nm and (c) subsequently washed with chlorobenzene. Spectra have been base-line corrected and shifted vertically for comparison reasons. The arrows indicate the two new broad bands that appear after irradiation.

On the basis of the Raman spectroscopy data are in agreement with previous reports [33, 40] in which dimers is the most likely structure to be formed. Similarly as for PC₆₀BM [25] it is expected that the side group hinders the formation of higher molecular weight oligomers. Accordingly, it seems plausible that the PRI effect is caused by a chemical modification of the PC₇₁BM upon laser irradiation rendering to a fraction of dimers and graphene oxide. In order to gain further information, Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) experiments were performed in

these samples. Figure 5 shows a series of two dimensional (2D) GIWAXS patterns for the PC₇₁BM spin-coated sample and for the irradiated ones at $\lambda_{\text{laser}}=532$ nm for different fluences as labelled. The one dimensional intensity profile extracted from the integration of the GIWAXS pattern for the reference non-irradiated PC₇₁BM spin-coated film is shown in Figure 6a. The X-ray diffraction pattern exhibits three main broad maxima appearing at q-values of 7.27 nm⁻¹, 14.23 nm⁻¹ and 21.19 nm⁻¹ which agree with previously reported data [41] for PC₇₁BM and correspond to the reflections associated to the 311,222,422 and 333 planes [39], of the fcc crystalline structure [42] of C₇₀. The broadness of the diffraction maxima suggests that PC₇₁BM spin-coated films exhibit low crystallinity in agreement with previous reports [43, 44]. Figure 6b shows the diffraction pattern of the PC₇₁BM spin-coated film after irradiation with $\lambda_{\text{laser}}=532$ nm. The pattern presents essentially the same features of the non-irradiated samples although a sharp peak appears in the q-region of the 422, 333 reflection. This fact has been visualized by arrows in Fig.5 where one detects the appearance of a sharp peak for fluences in the range between 17.2 mJ/cm² and 22.6 mJ/cm². In a first approach we can assign this peak with the formation of a genuine crystalline phase upon irradiation starting around fluences of 17.2 mJ/cm², reaching a maximum around 22.6 mJ/cm² and disappearing at high fluence values (24.4 mJ/cm²). The appearance of sharper maxima decorated with discrete spots is characteristic of the formation of larger crystals as previously described for thermal treated PC₆₁BM and PC₇₁BM spin-coated films [43, 44].

Figure 5. 2D GIWAXS patterns, taken at a grazing angle of 0.2° , for the PC₇₁BM spin-coated sample and for the irradiated ones at $\lambda_{\text{laser}}=532$ nm for different fluences, in mJ/cm^2 , as labelled. The arrows indicate the appearance of a sharp peak for fluences in the range between $17.2 \text{ mJ}/\text{cm}^2$ and $22.6 \text{ mJ}/\text{cm}^2$.

Figure 6. Normalized one dimensional intensity profiles extracted from the integration of the GIWAXS 2D patterns for: (a) PC₇₁BM spin-coated film, (b) PC₇₁BM irradiated at $\lambda_{\text{laser}}=532$ nm,

$F=17.2 \text{ mJ/cm}^2$, 3600 pulses (c) subsequently washed and (d) Silicon substrate that has been vertically displaced for the sake of clarity.

Upon irradiation with nanosecond laser pulses the sample is heated. The temperature increment can be estimated as a function of time at different depths from the film surface by solving the one-dimensional heat conduction equation as previously reported [45]. The values of the magnitudes used for the calculation of the temperature profiles have been taken from the literature and are the following ones: density [46] 1630 Kg/m^3 , specific heat [47] $820 \text{ J/Kg}\cdot\text{K}$, and thermal conductivity [47] $0.07 \text{ W/m}\cdot\text{K}$.

For simplification, the temperature dependence of the polymer physical parameters and the possible changes in the thermal properties were not taken into account in the calculation. Figure S2 shows the temperature reached at the surface of PC₇₁BM after irradiation with a single pulse at a laser fluence of 17 mJ/cm^2 . Temperature reaches a value of around 123°C which is close to the glass transition temperature, T_g , reported for PCBM [43, 48]. It is known that increasing the temperature of a glass above its T_g but below its melting temperature induces a metastable supercooled state that may give rise to the formation of a crystalline state by a process frequently referred to as cold crystallization [49, 50]. It is also important to mention that the optical penetration depth ($1/\alpha$) is around 100 nm and thus, all the material is affected and heated by the laser irradiation. Then heat is subsequently dissipated mostly through the silicon substrate [45]. Thus, it is plausible that during laser irradiation the sample suffers a heat treatment leading to the development of a crystalline phase. Previous GIWAXS experiments performed in thermal annealed PC₆₁BM spin-coated films have shown that the silicon substrate acts as a heterogeneous nucleation surface for crystallization [43]. This finding suggests that in our case the crystalline phase may appear close to the fullerene silicon

interface. In order to corroborate this hypothesis, chlorobenzene washed samples were subjected to GIWAXS experiments. Figure 7 compares the GIWAXS patterns of the irradiated PC₇₁BM spin-coated films with those of the chlorobenzene washed samples. Although the overall scattered intensity decreases significantly after washing, the presence of the sharp ring although weak is still detected both in the GIWAXS patterns and on the one dimensional intensity profiles (Fig. 6c). This finding indicates that in our case the crystalline phase appears as a buried phase close to the fullerene-substrate silicon interface.

Figure 7. 2D GIWAXS patterns, taken at a grazing angle of 0.2°, for the PC₇₁BM spin-coated sample irradiated with $\lambda_{\text{laser}}=532$ nm for fluences (a) $F=17.2$ mJ/cm² and (c) $F=19.0$ mJ/cm² and those of their corresponding washed counterparts (b) and (d) respectively.

There is another aspect in relation to the GIWAXS patterns that needs to be discussed. By comparing the data of the PC₇₁BM spin-coated film, Fig. 6a, with those of the irradiated one, Fig. 6b, one sees that the irradiated sample exhibits a clear broadening of

the Bragg maxima. As mentioned, upon irradiation with nanosecond pulsed lasers heating in nanosecond range of the sample is produced followed by cooling down in a microsecond or millisecond range [11]. LIPSS formation in organic materials typically requires the sample surface to be heated either above the glass transition temperature, for amorphous systems, or above the melting point if the material is crystalline [9, 11]. As a matter of fact, on the basis of both Raman spectroscopy and GIWAXS experiments, irradiation of poly(3-hexylthiophene) at $\lambda_{\text{laser}} = 532$ nm to form LIPSS irradiated was shown to reduce the crystallinity of the LIPSS sample in comparison to the original one [21]. Accordingly, our results suggest that irradiated PC₇₁BM films suffer a fast heating/cooling process that reduces the overall crystallinity of the LIPSS while provoking the presence of a phase of larger crystals close to the fullerene-substrate silicon interface.

3.4. Functionality of resist-free LIPSS on PC₇₁BM spin-coated films.

In order to verify the functionality of the prepared fullerene LIPSS in terms of electrical conduction we have accomplished C-AFM measurements in PC₇₁BM spin-coated films, and in the irradiated and washed samples. The I/V characteristic for these samples, shown in Figure S3 for the PC₇₁BM spin-coated film and for the irradiated ($\lambda_{\text{laser}}=532$ nm) one, presents the typical features of a Schottky diode [51] formed by the metallic C-AFM tip and the semiconducting PC₇₁BM. The I/V characteristic is qualitatively similar to those previously reported for macroscopic Schottky diodes formed by different metals and both C₆₀ and C₇₀ [51]. For the irradiated PC₇₁BM films the measurements were taken in the LIPSS valleys. Interestingly enough, the PC₇₁BM LIPSS sample exhibits I/V characteristic very similar to the non-irradiated one suggesting that its electronic properties are not endangered by laser illumination.

Figure 8 shows the electrical current image of irradiated PC₇₁BM film (Fig. 8b) in comparison with its topographic image (Fig. 8a). It is worth mentioning that since for C-AFM, working in contact mode is a requirement then the topographic image (Fig. 8a) exhibits lower resolution than the corresponding ones obtained in tapping mode (see Fig.1b and 1c). Additionally, in soft surfaces the cantilever tip provokes a dragging effect responsible for the horizontal lines observed in Fig. 8a. The irradiated PC₇₁BM spin-coated sample (Figure 8b) exhibits a series of conducting stripes alternating with non-conducting ones. A direct comparison with its topographic counterpart can be done by docking both topography and current images as illustrated in Figure 8c. There one sees that the conducting regions of the irradiated sample correspond to the valleys of the LIPSS while the non-conducting regions are associated to the hills. A similar effect has been recently reported for LIPSS in poly(3-hexylthiophene) [21]. For organic materials crystallinity is a key factor as far as electrical conductivity is concerned. A paradigmatic case is the one related to poly(3-hexylthiophene) mixed with PCBM which is one of the most popular photovoltaic blends. As previously mentioned in this case the low conducting hills of the LIPSS were associated to lower crystallinity regions caused by fast quenching after laser pulse heating. As a matter of fact LIPSS of poly(3-hexylthiophene) fabricated by irradiation at $\lambda=532$ nm exhibit C-AFM images very similar to those shown in Figure 7b [21]. On the basis of both Raman spectroscopy and GIWAXS experiments it was proposed that LIPSS hills possess lower crystallinity and therefore lower electrical conductivity than LIPSS valleys. For PC₇₁BM LIPSS irradiated at $\lambda_{\text{laser}}=532$ nm we proposed a similar explanation suggesting that lower conductivity of LIPSS hills is caused by a decrease in crystallinity. This is consistent with the GIWAXS experiments suggesting that irradiated PC₇₁BM films suffer a fast heating/cooling process which reduces the overall crystallinity of the LIPSS. However,

there is another aspect in relation to the C-AFM experiments that needs to be discussed. As shown before, laser irradiation provokes the appearance of a sharp maximum in the GIWAXS patterns (Fig. 5) that can be assigned to the formation of a buried crystalline phase close to the silicon substrate that can be assigned by AFM to the observed granular motives (Fig. 1e, S1b and 3a) for the washed PC₇₁BM samples previously irradiated. Figure 7e shows the C-AFM image of one of the nanowires remaining on the silicon substrate after washing the PC₇₁BM samples previously irradiated in comparison with its topographic image (Fig. 8d). A direct comparison with its topographic counterpart can be done by docking both topography and current images as illustrated in Figure 8f. There one sees that the conducting region of the washed irradiated sample corresponds to the thinner part of the nanowire while the non-conducting regions are associated to the thicker part. In addition, some conducting dots appear suggesting that granular texture observed in the irradiated samples after washing (Fig. 1e, S1b and 3a) contains PC₇₁BM crystallites with enhanced conductivity. Moreover, the C-AFM image is consistent with the above formulated hypothesis proposing that irradiated PC₇₁BM films: i) suffer a fast heating/cooling process tending to reduce the overall crystallinity of the LIPSS and therefore decreasing the electrical conductivity of the hills and leaving a remnant conducting film underneath the hills and ii) during laser irradiation the sample suffers a heat treatment leading to the development of a buried phase close to the substrate formed by larger crystals with enhanced electrical conductivity.

Figure 8. (a) AFM contact mode topographic image and (b) C-AFM image (bias voltage=10 V) of a spin-coated PC₇₁BM film irradiated with $\lambda_{\text{laser}}=532$ nm for a fluence $F=17.2$ mJ/cm², 3600 pulses (c) Docking of the topography and current images. (d) Topographic image of typical nanowire remaining after solvent washing and (e) corresponding C-AFM image (bias voltage=10 V). (f) Docking of the topography (d) and current (e) images.

3.5. Laser Photoinduced and Resist-free Imprinting LIPSS on PC₇₁BM spin-coated films over large areas.

Larger irradiated areas can be obtained by eliminating the iris. In this case the spot of the laser illuminates a circular area of about 5 mm in diameter. In this case, as an example, Figure 9 shows AFM contact mode topographic image (9a) and the C-AFM current image (9b). Here, the more conducting regions, that in the C-AFM image appear as darker spots, are now located in the LIPSS hills of the sample as emphasized by Figure 8c where a docking of both topography and current images has been accomplished. PC₇₁BM crystallites can be better observed through the higher resolution AFM tapping mode topography image showed in Figure 9d. Moreover, by depositing the sample over an automatic mobile X-Y displacement table it is possible to continuously illuminate macroscopic areas.

Figure 9. (a) AFM contact mode topographic image (2x2 μm) and (b) C-AFM image of a residue obtained after solvent development of PC₇₁BM spin-coated sample irradiated without iris (i.e. using full laser beam area) with $\lambda_{\text{laser}}=532$ nm for a fluence $F=17.1$ mJ/cm², 3600 pulses. (c) Docking of the topography and current images. (d) AFM tapping mode topographic image of the same sample.

4. Conclusions

To conclude, we have proven that it is possible to prepare laser induced periodic nanostructured surfaces (LIPSS) and Photoinduced Resist-free Imprinting (PRI) on PC₇₁BM laser by illumination of spin-coated films with nanosecond pulsed lasers. LIPSS prepared with a wavelength of 532 nm selectively preserve the electrical conductivity on the LIPSS valleys. The heterogeneous conducting pattern consisting in conducting valleys and less conducting hills observed in the LIPSS prepared under these conditions has been interpreted, on the basis of GIWAXS experiments, as due to a reduction in the crystallinity of the hills provoked by the fast heating/cooling process induced by every laser pulse. PC₇₁BM LIPSS exhibit a resist free character and can be developed by spin coating a solvent leaving the laser illuminated zone as an undissolved residue. On the basis of the experiments it is proposed that irradiated PC₇₁BM films suffer, on one hand, a fast heating/cooling process tending to reduce the overall crystallinity of the LIPSS and therefore decreasing the electrical conductivity of the hills and leaving a remnant conducting film underneath the hills. On a second hand, during laser irradiation the sample suffers a heat treatment induced by the substrate leading to the development of a buried phase close to the substrate formed by larger crystals with enhanced electrical conductivity. Further solvent treatment reveals the buried phase which remains in the form of partially electrically conducting nanowires. With these facts in mind it seems plausible to further exploit the here described technology to fabricate organic electronic devices.

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