

Laser Fabrication of Polymer Ferroelectric Nanostructures for Nonvolatile Organic Memory Devices

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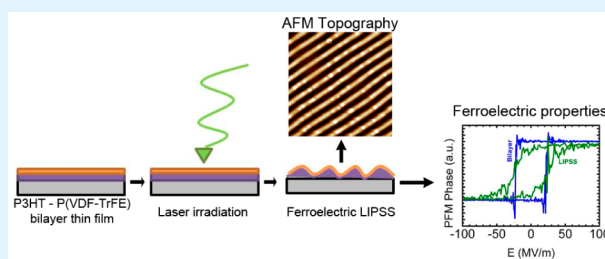
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S Supporting Information

ABSTRACT: Polymer ferroelectric laser-induced periodic surface structures (LIPSS) have been prepared on ferroelectric thin films of a poly(vinylidene fluoride–trifluoroethylene) copolymer. Although this copolymer does not absorb light at the laser wavelength, LIPSS on the copolymer can be obtained by forming a bilayer with other light-absorbing polymers. The ferroelectric nature of the structured bilayer was proven by piezoresponse force microscopy measurements. Ferroelectric hysteresis was found on both the bilayer and the laser-structured bilayer. We show that it is possible to write ferroelectric information at the nanoscale. The laser-structured ferroelectric bilayer showed an increase in the information storage density of an order of magnitude, in comparison to the original bilayer.

KEYWORDS: laser-induced periodic surface structures, nonvolatile ferroelectric memories, piezoresponse force microscopy, polymer bilayers, nanogratings



with periodicities closely related to the wavelength of the irradiating laser.^{24–26} Contrary to other techniques, LIPSS are prepared without the requirement of direct physical contact and clean environments. Also, it avoids problems such as tearing during demolding and mold imperfections found in NIL structures.⁴

1. INTRODUCTION

In recent years, research on ferroelectric polymers has been focused toward the development of functional prototypes for all-organic electronics. Functional devices, such as diodes^{1,2} and transistors,^{3–5} have been fabricated in a *layer-by-layer* approach by combining thin films of ferroelectric polymers with other materials, such as semiconducting polymers⁴ and inorganic alloys.⁶ Moreover, the use of nanopatterned surfaces in these devices has shown to improve the ferroelectric response of the polymers,^{7,8} enhance the storage information density by controlling molecular architecture,^{9–12} and also allow the possibility of preparing three-dimensional nanostructures, such as multiple-gate transistors.^{13–15}

Surface nanostructuring of polymers can be accomplished with a great variety of procedures, such as nanoimprint lithography (NIL),^{16,17} photolithography,¹⁸ laser interference,¹⁹ and optical near-fields.^{20,21} Also, laser-induced periodic surface structures (LIPSS) can be prepared on polymer thin films.^{22,23} LIPSS can appear after irradiation of solid surfaces by intense laser pulses, as a result of the interference between the incoming and the surface-scattered waves of the laser. This causes a heterogeneous energy intensity distribution, which, together with a feedback mechanism, results in a periodic enhancement of the irradiation intensity.²⁴ The final outcome is the appearance of spontaneous periodic surface nanostructures,

with periodicities closely related to the wavelength of the irradiating laser.^{24–26} Contrary to other techniques, LIPSS are prepared without the requirement of direct physical contact and clean environments. Also, it avoids problems such as tearing during demolding and mold imperfections found in NIL structures.⁴

The development of LIPSS on a polymer surface is related to both irradiation conditions and surface properties. The laser wavelength, fluence, pulse duration, polarization, angle of incidence, and repetition rate, dictate the morphology of the resulting structures^{22,23,27,28} and allow the possibility of fabricating different geometrical arrays such as nanogratings and nanodots.²⁹ Typically in polymers, using nanosecond laser pulses, LIPSS are formed parallel to the polarization of the laser with a period L described by

$$L = \frac{\lambda}{n - \sin \theta}$$

where λ is the laser wavelength, n the effective refractive index, and θ the incidence angle.³⁰ On the other hand, the polymer surface must fulfill certain conditions, such as light absorption

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at the specified wavelength and surface roughness on the order of a few nanometers. Previously, we have reported the formation of LIPSS on thin films of poly(ethylene terephthalate), poly(trimethylene terephthalate), and poly(bisphenol A carbonate), using nanosecond (ns) pulses in the ultraviolet (UV) region.²² However, in the case of the poly(vinylidene fluoride) (PVDF), no structuring could be achieved, because of the poor absorption of this polymer, under the same irradiation conditions, and its semicrystalline spherulitic morphology, which introduced further hindrances into the reorganization of the material, as well as higher roughness.²² The limitation of the LIPSS method for nanostructuring nonabsorbing polymers has been also reported by other authors.³¹ For this reason, LIPSS formation was ruled out as a procedure to prepare ferroelectric nanostructures on PVDF and its copolymers.

In this work, we demonstrate two main effects. First, the possibility of LIPSS formation on nonabsorbing polymer thin films using nanosecond laser pulses. In order to overcome the absorption limitations, we have prepared bilayer polymer thin films in which the bottom layer absorbs light at the specified wavelength, while the top layer is formed by the nonabsorbing polymer of interest. We have selected two functional polymer materials: P3HT as the bottom absorbing layer, and poly(vinylidene fluoride–trifluoroethylene) (P(VDF-TrFE)) as the nonabsorbing top layer. Second, we proved that laser nanopatterning of the P(VDF-TrFE) is achievable without compromising its ferroelectric response. We created nanostructures of P(VDF-TrFE) whose storage information density increases in ~ 1 order of magnitude, in comparison to the nonstructured bilayer. This validates the potential of our procedure in order to develop nonvolatile organic memory devices.

2. EXPERIMENTAL SECTION

2.1. Materials. Poly(vinylidene fluoride–trifluoroethylene) P(VDF-TrFE) was purchased from Piezotech S.A.S. The molar concentration of the random copolymer is 76:24 (VDF:TrFE content), its molecular weight is $M_w = 367\,000$ g/mol, $M_w/M_n = 1.72$, and the melting temperature (T_m) is 148 ± 1 °C. Poly(3-hexylthiophene) (P3HT) was purchased from Ossila (Batch M106, tradename Lisicon, molecular weight of $M_w = 34\,100$ g/mol, $M_w/M_n = 1.7$, $T_m = 235 \pm 5$ °C).

2.2. Polymer Thin Films. Polymers were used as received. Single-layer (SL) and bilayer (BL) thin films were prepared by spin coating. For SL films, 0.2 mL of polymer solution was deposited on top of a 2 cm \times 2 cm square conductive silicon wafer (resistivity = 0.001–0.005 Ω cm) and rotated at 2400 rpm for 2 min. Specifically, P(VDF-TrFE) was dissolved in 2-butanone (C₄H₈O) (5 mg/mL), at 72 °C, under continuous stirring for 3 h. P3HT was dissolved in chloroform (CHCl₃) (24 mg/mL) at room temperature. Dissolution was achieved immediately within a few minutes.

The protocol for preparation of BL thin films is described next and is similar to previous reports.^{32,33} Solution concentrations were kept equal to those presented for SL films. First, a thin film of P3HT was spin-coated on a 2 cm \times 2 cm conductive silicon wafer. Afterward, the P(VDF-TrFE) solution was coated on top of the P3HT film. In both cases, a fixed rotation speed of 2400 rpm for 2 min was used. In order to determine whether the 2-butanone had any effect on the P3HT, we performed a solubility test. The P3HT solution showed no coloration of the colorless 2-butanone after stirring, as previously reported in the literature.³² This indicates the nonsoluble character of the semi-conducting polymer in the solvent.

2.3. Laser Irradiation. Laser irradiation was carried out in ambient air, at normal incidence, with the linearly polarized laser beam of a Q-switched Nd:YAG laser (Lotis TII LS-2131M, pulse duration of $\tau = 8$ ns, full width at half-maximum) at a repetition rate of 10 Hz. The

second harmonic, at a wavelength (λ) of 532 nm, was used for the experiments. At this wavelength, P3HT has an absorption coefficient^{34,35} of 2×10^5 cm⁻¹, while the PVDF-based copolymer²² has one on the order of 10^2 cm⁻¹. This great difference among the absorption coefficients, at $\lambda = 532$ nm, indicates that, in the bilayer geometry, light will pass through the top P(VDF-TrFE) layer without a significant loss of energy, and reach the bottom P3HT film, where it will be absorbed. The fluences of irradiation were determined by measuring the laser energy in front of the sample with a joule meter (Gentec-E, QE2SSP-H-MB-DO) and calculating the area of the irradiated spots.

2.4. Atomic Force Microscopy (AFM). Morphology of the polymer SL and BL thin films was characterized by atomic force microscopy (AFM). A Multimode 8 AFM with a Nanoscope V controller (Bruker) was used under tapping mode with NSG-30 probes (NT-MDT). Square images with a resolution of 512 \times 512 pixels were taken. Analysis of the size and shape of the nanometric features was performed with the NanoScope Analysis 1.50 software (Bruker).

2.5. Piezoresponse Force Microscopy (PFM). PFM measurements were carried out by means of a Nanoscope V AFM (Bruker), in the piezoresponse mode. The topography and the ferroelectric signals were acquired simultaneously. The microscope was used in contact mode, with a low deflection setpoint (0.3 V), in order to avoid damaging the samples. Conductive PtIr-covered probes (Model SCM-PIC, Bruker, $k = 0.2$ N/m) were used. Through the PFM technique, hysteresis cycles were recorded applying a tip bias ramp from -12 V to 12 V at a frequency of 0.1 Hz and collection of 1024 samples. Local poling was carried out using the tip as the top electrode. In every case, a DC bias (± 12 V) was applied for 5 min. The control of points and lines drawn in the ferroelectric phase was made by means of the Point and Shoot protocol, available in the Nanoscope 8.15 software. The PFM out-of-plane signal was taken applying an AC voltage of 2 V at a frequency of 60 kHz between sample and tip. Measured amplitudes are related to the local electromechanical response of the sample surface during application of an AC voltage.

2.6. Electrostatic Force Microscopy (EFM). Electrical measurements on the sample surface were also performed using the Nanoscope V AFM (Bruker). EFM images were taken using a double pass approach.^{36–38} In this work, EFM experiments were carried out using PtIr-covered Si probes (SCM-PIT, Bruker, $k = 4$ N/m). Lift height was kept constant at 80 nm above each point on the surface, and the applied tip voltage was +5 V. Lift height was chosen in order to avoid any effect from the topography.

2.7. Conductive Atomic Force Microscopy (C-AFM). Electrical measurements were performed with conductive probes (PtIr-covered Si cantilevers with a low spring constant, $k = 0.2$ N m⁻¹, Model SCM-PIC, Bruker) in contact mode by measuring both topography and electrical current images simultaneously. In these measurements, the conducting probe makes contact with the sample, acting like a nanoelectrode, and maps a current image at a fixed bias of -5 V. The current was measured by a preamplifier.

2.8. Cross-Sectional Scanning Electron Microscopy. For the characterization of the bilayer thickness, cross-sectional scanning electron microscopy (SEM) images were performed with a focused ion beam (FIB, CrossBeam 1560 XB, Zeiss). To fabricate the cross sections, the FIB was operated at 30 keV for accelerating the gallium ion beam. In order to avoid damage to the polymer layers, small apertures were selected to provide a beam current of 50 pA. The sample was not covered with any metal layer during the FIB milling. The same equipment was used to obtain the high-resolution SEM images. The conditions for the imaging were 5 keV, 30 μ m of aperture, a working distance of 5.1 mm. The images were obtained using the InLens detector to enhance material contrast and resolution.

3. RESULTS AND DISCUSSION

3.1. Polymer Bilayers. AFM topography images of the polymer thin films are shown in Figure 1, before and after laser irradiation. Figures 1a and 1b show 5 μ m \times 5 μ m AFM

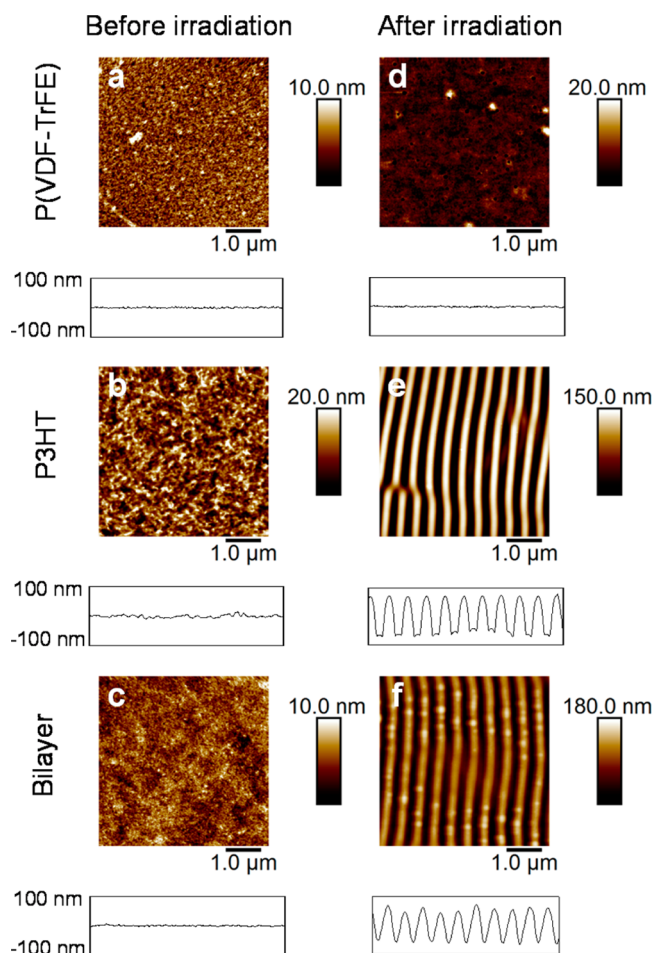


Figure 1. AFM topography images, before (left column) and after (right column) laser irradiation of single-layer thin films of (a,d) P(VDF-TrFE) and (b,e) P3HT and of (c,f) a P(VDF-TrFE)/P3HT thin bilayer film. LIPSS are formed on the P3HT thin film and on the bilayer. The height profile along a $5 \mu\text{m}$ line is shown below every image.

topography images of the as-prepared P(VDF-TrFE) and P3HT SL films, respectively. In both cases, the AFM image shows a continuous surface without dewetting and/or agglomerates. The P(VDF-TrFE) SL film exhibits a roughness of $1.0 \pm 0.5 \text{ nm}$, while the P3HT SL film shows a roughness of $4 \pm 1 \text{ nm}$. These two polymers are semicrystalline; thus, the roughness can be related to the presence of crystallites on the surface. Thickness of the films was measured by AFM. A scratch was made on the surface of the films and the step between the silicon surface and the polymer layer was quantified in different locations of several samples. The P(VDF-TrFE) SL thin film showed a thickness of $h_{\text{P(VDF-TrFE)}} = 35 \pm 5 \text{ nm}$. The thickness of the P3HT SL thin film was found to be $h_{\text{P3HT}} = 140 \pm 10 \text{ nm}$.

Figure 1c shows a $5 \mu\text{m} \times 5 \mu\text{m}$ AFM topography image of the bilayer film. The resulting surface does not exhibit either signs of dewetting or mechanical instabilities, as reported in other cases.^{39–42} Also, it is worth noticing that our bilayers were prepared without requiring any external elements to improve its mechanical stability, in contrast to previous reports in the literature.⁴³ Roughness of the BL surface was quantified to be $1.2 \pm 0.5 \text{ nm}$, comparable to the original P(VDF-TrFE) thin film. Step measurements of the bilayer film showed that

the total thickness was $h_{\text{bilayer}} = 200 \pm 50 \text{ nm}$. In principle, this value is compatible with the addition of the individual thicknesses of every layer. However, in order to reach a more precise characterization of thickness and continuity of the upper polymer layer, we have performed cross-sectional SEM measurements, which are shown in Figure 2. The two polymers

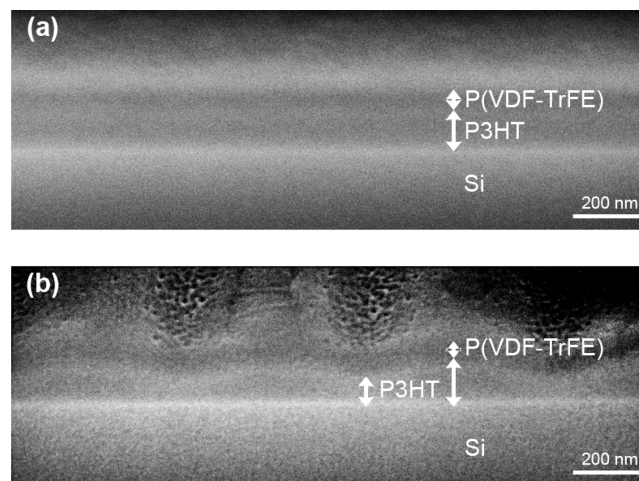


Figure 2. Cross-section SEM images of a P(VDF-TrFE)/P3HT thin bilayer film (a) before irradiation and (b) after irradiation.

appear as continuous layers of different electronic density in Figure 2a. The thickness of the bilayer polymer film estimated by SEM gives values of $150 \pm 30 \text{ nm}$, while the upper and bottom layers exhibit thicknesses of $38 \pm 5 \text{ nm}$ and $120 \pm 10 \text{ nm}$, respectively. This result, and the fact that the AFM topography image does not show signs of phase separation, allows us to conclude that the bilayer consists of two separate and continuous polymer layers, one on top of the other, in agreement with previous reports.^{32,33}

3.2. Laser-Induced Periodic Surface Structures (LIPSS)

Irradiation parameters (fluence and number of pulses) were chosen according to previously reported systematic experiments related to LIPSS formation on P3HT.⁴⁴ The right-hand column of Figure 1 shows $5 \mu\text{m} \times 5 \mu\text{m}$ AFM topography images of SL and BL films after laser irradiation, at a fluence of 27 mJ cm^{-2} and for 3600 pulses in every case. Figure 1d shows the result of laser irradiation on the P(VDF-TrFE) SL film. No development of nanostructures or any other surface features is observed, while its roughness was found to remain at $\sim 1 \text{ nm}$. The absence of surface structures on this copolymer can be related to its weak optical absorption.²² Increasing the laser beam fluence did not allow the formation of any structuring until high fluence values, close to 700 mJ cm^{-2} , led to swelling of the film. Similar results have been previously reported for nonabsorbing polymers⁴⁵ such as PVDF.⁴⁶

Comparison between Figures 1b and 1e evidence the morphology changes in the P3HT SL film. After laser irradiation, the formation of LIPSS is observed on its surface. The nanostructures consist of elongated ridges along a specific direction, giving rise to the development of nanogratings. The height of the nanostructures was found to be $100 \pm 20 \text{ nm}$, while their period was $460 \pm 10 \text{ nm}$. As in our case, the laser fluence is well below the ablation threshold, and the structuring of the surface takes place without material removal.²³

Figure 1f shows a $5 \mu\text{m} \times 5 \mu\text{m}$ AFM topography image of the BL film, after laser irradiation. It can be seen that surface

structuring took place and continuous linear nanostructures, with quantitative geometrical features similar to those of the P3HT, are observed. The continuity of the nanostructured upper polymer layer is corroborated by the cross-section SEM image shown in Figure 2b. However, in order to rule out the possibility of discontinuity of the ferroelectric upper layer, we have also performed both EFM and C-AFM measurements. The results are shown in Figures S1 and S2 in the Supporting Information. The EFM images reveal a fairly constant value of the electrostatic signal on either ridges or trench regions, with some contrast among them. The SEM images (see Figure 2b, and Figure S3 in the Supporting Information) reveal that the trench regions of the nanostructure present some holes. Therefore, in a first approach, the contrast of the electrostatic field observed in the EFM images can be associated with this effect. Moreover, C-AFM images show that samples are nonconducting, confirming that the upper layer must be the P(VDF-TrFE) film, homogeneously covering the P3HT.

Considering that the P(VDF-TrFE) thin film did not show LIPSS under similar irradiation conditions (Figure 1d), the development of the LIPSS on the bilayer must be associated with the P3HT bottom layer. Since the P(VDF-TrFE) does not absorb light at the irradiating laser wavelength, the laser beam passes through the upper polymer layer, without significantly altering its energy or polarization before reaching the P3HT bottom layer. Here, structuring of the bottom layer takes place, just as in the SL P3HT film, heating this polymer above its melting temperature in such a way that the polymer segments acquire enough mobility to rearrange following the modulation imposed by the laser. Afterward, heat dissipation from the P3HT allows cooling and fixing the nanostructure of the bottom layer while heating the P(VDF-TrFE) on top. This heat transfer is expected to melt the ferroelectric polymer, gaining mobility and accommodating on the pattern of the bottom layer. The possibility of forming a nanostructured bilayer on which the top nonabsorbing layer follows the bottom one is new and differs from previous reports in the literature. For example, Zhao and collaborators⁴⁷ prepared surface patterns by laser irradiation on thin layers of poly(methyl methacrylate) (PMMA) on azobenzene liquid crystalline polymer (LCP) films. These authors found that the LCP single-layer film reorganized, following a grating-like structure after laser irradiation, using nanosecond pulses. However, when dealing with the PMMA/LCP bilayer structure, the upper, non-absorbing layer of PMMA did not follow the LCP pattern but rather developed wavelike surface structures, whose periods did not relate to the wavelength of the laser pulse. Thus, by using this simple approach, it is possible to form LIPSS on nonabsorbing polymers.

In Figure 1f, the LIPSS generated on the BL film also show the development of droplet-like structures on the ridges. These are evidenced by the bright spots in the image and could be related to agglomeration of P(VDF-TrFE) appearing during the melting and recrystallization process. These features, which are also visualized in the SEM images (see Figure S2), exhibit a round top with mean diameters in the range of 100–200 nm and heights in the range of 20–50 nm.

3.3. Ferroelectric Response of Nanostructured Bilayer Films. Figure 3 shows the PFM phase shifts, as a function of an applied tip bias, for the prepared samples. Since obtaining accurate electric field on films with complicated morphology can be misleading, we have represented the phase shift as a function of the nominal applied voltage bias. In PFM,

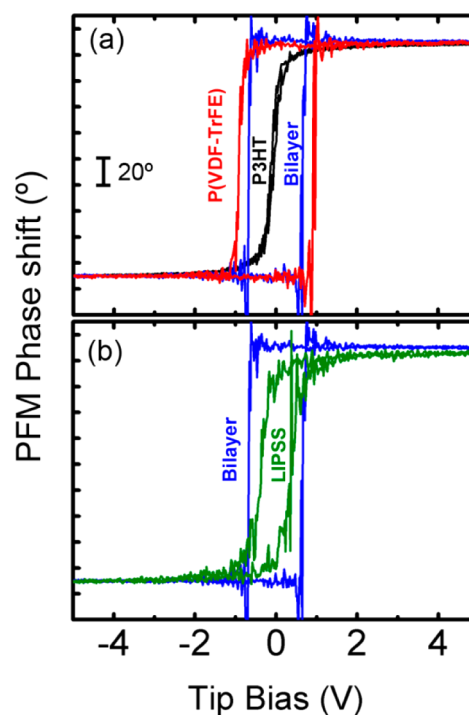


Figure 3. (a) PFM phase shift as a function of applied electric field for P3HT SL film (black), P(VDF-TrFE) SL film (red), and polymer bilayer (blue). Both P(VDF-TrFE) and bilayer film show ferroelectric hysteresis. (b) PFM phase shift as a function of applied bias for the LIPSS on the bilayer film (green) and continuous bilayer (blue) for comparison.

ferroelectric materials are characterized by hysteresis cycles with a 180° shift of the PFM phase.⁴⁸ These changes are related to the flipping of polymer dipoles in the vertical direction, with respect to the sample surface (out-of-plane polarization), as in the charge displacement versus applied electric field measurements on thin-film capacitors.⁴⁹ The value of the electric field where the shift of the PFM phase occurs is known as the coercive field (E_c). As expected from its chemical composition, the P3HT sample (black line, Figure 3a) shows no ferroelectric hysteresis, but simply a sudden transition from one state to other, as a consequence of the polarization of the tip and charge injection. Results for the P(VDF-TrFE) SL film are depicted by the red lines in Figure 3a. In this case, the ferroelectricity of the copolymer is evidenced by the 180° PFM phase-shift transition observed at nonzero field values. The coercive field can be estimated to be $E_c = 25 \pm 6$ MV/m, considering $h_{P(\text{VDF-TrFE})}$ has a value of 35 ± 5 nm. This value is similar to those found in previous works for continuous films of this ferroelectric copolymer,^{10,48} although smaller than previously reported values for thicker films.⁵⁰ In a first approach, we can attribute this fact to differences in crystallinity, depending on the thickness. Finally, the nonirradiated bilayer film exhibits also a ferroelectric response, as evidenced from the hysteresis cycle shown by the blue curve in Figure 3a. In this case, the coercive field was found to be $E_c = 19 \pm 4$ MV/m.

The ferroelectric response of the LIPSS BL film is shown as the green line in Figure 3b. Data of the nonirradiated BL film are included for comparison. The presence of hysteresis indicates that the LIPSS have a ferroelectric response, with a coercive field close to $E_c = 10 \pm 4$ MV/m. Hysteresis cycles were taken on several areas of the LIPSS BL and found to be

equivalent. Evidence of ferroelectricity in the nanostructured layer further supports that the top layer follows the topography of the P3HT one. In addition, since the ferroelectricity of P(VDF-TrFE) is strongly dependent on its crystalline structure,⁴⁹ Figure 3 suggests that laser irradiation did not inhibit the recrystallization of the P(VDF-TrFE) copolymer.

3.4. Ferroelectric Information Storage on Polymer Bilayers. Recently, PFM has also been used to store nanoscale information on ferroelectric organic films,^{10,48,51–56} using the tip as a stylus to write the information by applying a bias above the coercive field. Readings are attained using the piezoelectric response of the sample, which gives different contrast between written and unwritten zones,⁵³ or via the difference in the electrical current that flows through the material.^{2,4} Figure 4

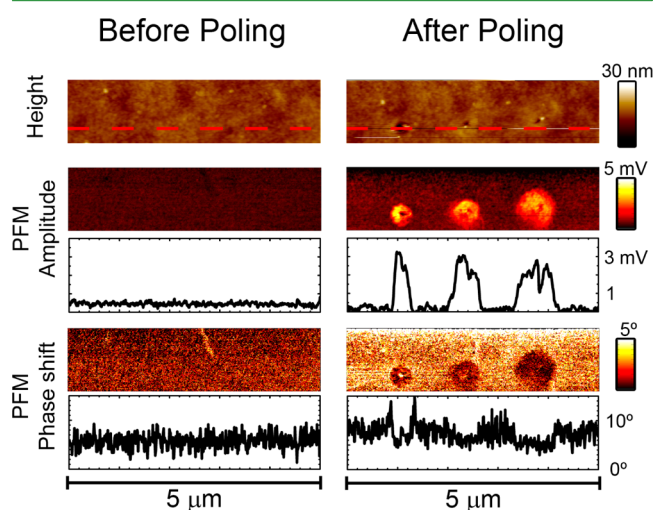


Figure 4. (Left column) Topography, PFM amplitude, and PFM phase shift of the bilayer film before poling. (Right column) Topography, PFM amplitude, and PFM phase shift of the bilayer film after poling at three points, for 5 min, at +12 V. Panels third and fifth from the top represent the amplitude and phase shift across a single line indicated in the height image.

shows $5 \mu\text{m} \times 1 \mu\text{m}$ PFM images, where the ferroelectric state of the nonirradiated bilayer film, before and after poling for 5 min at a bias of +12 V, is observed. For the electric poling, the tip was fixed at a certain position on the bilayer surface, while the bias was applied. The magnitude of the physical contact between the tip and the surface was controlled by setting a low cantilever setpoint.

The left-hand column of Figure 4 shows the topographic and ferroelectric state of the bilayer before poling. Neither the PFM amplitude nor the phase shift show any contrast along the entire area. This indicates a nonpreferential orientation of the polymer dipoles in the as-casted film. The right-hand column of Figure 4 shows the topography and ferroelectric response of the polymer bilayer after poling in three selected positions. The topography image shows that, in every case, the tip–surface interaction leads to indentation of the surface. Nonetheless, PFM amplitude and phase-shift images show the development of ferroelectric contrast in the poled areas. The phase shift after poling is significantly smaller than that observed in the hysteresis experiments (Figure 3). This effect has been previously reported^{10,11,48} and has been related to the fact that the average vertical orientation of the dipole moments does not change significantly by the application of the electric field. It is known that P(VDF-TrFE) crystals in thin films and in

gratings are embedded in an amorphous phase and they exhibit a needlelike morphology, which adopts a variety of orientations, from flat-on to edge-on.¹⁰ Therefore, the value of the phase change can be attributed to the fact that the electric field is not applied over a single crystal but over a polycrystalline sample where crystals adopt different orientations. This fact makes phase change be less than that expected for a single crystal.

In all three cases, the magnitude of the ferroelectric contrast seems to be comparable. However, the surface extension of the ferroelectric response varies from point to point. One might argue that this difference can be related to the indentation of the probe into the surface and the possible damage it may have caused to the ferroelectric top layer. The profile along the written spots, in the ferroelectric channels, show that the dipole orientation caused by the applied tip bias extends over a range of 400–800 nm. This result is in agreement with previous PFM studies in P(VDF-TrFE) SL thin films.⁵¹ Considering the spreading of the ferroelectric information in the bilayer film, information storage density can be estimated to be $\sim 2 \pm 1 \text{ Gb/in}^2$.

Figure 5 shows the LIPSS BL film, before and after poling at three spots, at +12 V for 5 min. In this case, besides setting a

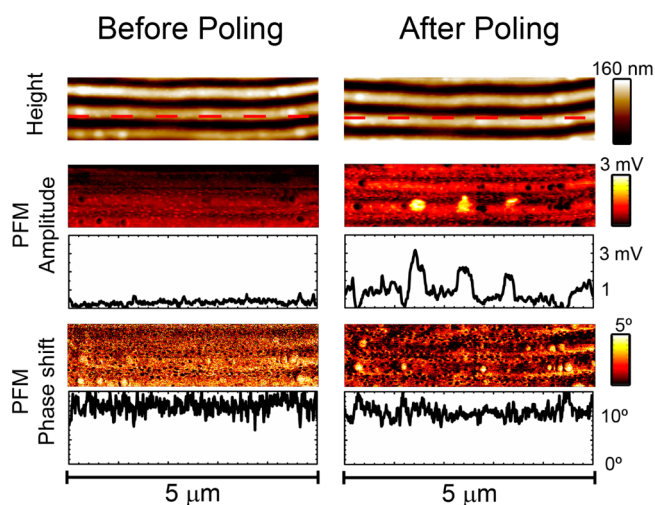


Figure 5. Topography, PFM amplitude, and PFM phase shift of the LIPSS on the bilayer film before poling (left-hand column) and after poling at three points, for 5 min, at +12 V (right-hand column). Panels third and fifth from the top represent the amplitude and phase shift across a single line indicated in the height image.

low deflection cantilever setpoint, the PFM study was carried out by scanning the tip in a direction parallel to the LIPSS (thus, possible damage due to tip–surface interaction was minimized).¹⁰ Before poling, the left column of Figure 5 shows that the irradiated structures have no preferential ferroelectric response. This indicates that the laser-induced ripples do not align the P(VDF-TrFE) dipole moment in any preferential direction. However, it is interesting to note that, in the P(VDF-TrFE) droplets, on top of the LIPSS, the ferroelectric amplitude signal seems to have a lower value. This could serve as an indication of different crystallinity inside the droplets. The ferroelectric response of the LIPSS, after poling, is shown in the right-hand column of Figure 5. First, it is possible to observe that no change in the morphology of the nanostructures was generated by the tip interaction, as evidenced in the topography image. Then, the PFM amplitude image shows the three written points on the LIPSS. The

magnitude of the ferroelectric signal is comparable to that in the continuous BL film. Nonetheless, the surface extension of the ferroelectric domains decreases significantly, in comparison to the nonirradiated film. In the LIPSS, the electrical poling generates circular domains ~ 100 – 200 nm in diameter, which correspond to an information density of 35 ± 5 Gb/in². Note the presence of some dots on the trench region; this is due to the nanometric control limitations of the piezoelectric scanner in the point-and-shoot protocol. Nevertheless, this proves that the material is also ferroelectric on the trench, further supporting the continuity of the upper polymer layer. The hindrance of the ferroelectric interaction in confined polymer structures has been previously reported in nanogratings generated by nanoimprint lithography^{10,11,48} and attributed to the development of a higher proportion of edge-on lamellae, because of the confinement of the polymer crystals. Moreover, we have performed PFM measurements to test the dipole moment retention of the LIPSS bilayer. As presented in Figure S4 in the Supporting Information, four different points were poled at +12 V (left side points) and –12 V (right side points) for 5 min each. We then measured both the PFM amplitude and the phase signals 18 h after poling. First, it is possible to affirm that, at laboratory times, the laser-structured bilayer retains the dipole information, since both PFM signals did not show any quantitative variation with time. Second, we further highlight that poling with positive or negative bias does not strongly affect the absolute magnitude of the PFM amplitude signal (~ 3 – 5 mV), while the direction of both amplitude and phase show the characteristic behavior reported previously in the literature.⁴⁸

4. CONCLUSIONS

Laser-induced periodic surface structures can be prepared on polymer thin films, despite the absence of light absorption at the wavelength of the irradiating laser, by using a bilayer approach. We have shown that the structuring of a P3HT layer, by laser irradiation at $\lambda = 532$ nm, covered by a ferroelectric P(VDF-TrFE) thin layer, allowed the development of surface nanogratings. This approach will be useful not only for the case of P(VDF-TrFE) but for any other nonabsorbing polymer, making the technique more versatile and thus paving the way for a wider range of applications. The LIPSS preserve the ferroelectric properties of the P(VDF-TrFE), as evidenced by the hysteresis cycles recorded by PFM. The laser-fabricated nanogratings showed an increase of the storage information density of ~ 1 order of magnitude, in comparison to the nonstructured bilayer.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b05213.

Atomic force microscopy (AFM), electric field force microscopy (EFM), and scanning electron microscopy (SEM) images of the poly(vinylidene fluoride–trifluoroethylene) (P(VDF-TrFE)) bilayers; plots showing the PFM height, amplitude, and phase shift 18 h after poling (PDF)

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Notes

The authors declare no competing financial interest.

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