

# LIPSS FORMATION ON POLYMER THIN FILMS: INFLUENCE OF THICKNESS, ROUGHNESS AND SUBSTRATE

J. PRADA-RODRIGO<sup>1,2</sup>, R.I. RODRÍGUEZ-BELTRÁN<sup>1,3</sup>, J. CUI<sup>4,5</sup>, A. NOGALES<sup>4</sup>, T.A. EZQUERRA<sup>4</sup>, P. MORENO<sup>1</sup>, AND E. REBOLLAR<sup>2\*</sup>

<sup>1</sup>Grupo de Aplicaciones del Láser y Fotónica (ALF-USAL), Universidad de Salamanca, Pl. de la Merced s/n, 37008, Salamanca, Spain

<sup>2</sup>Instituto de Química Física Rocasolano, IQFR-CSIC, Serrano 119, 28006, Madrid, Spain

<sup>3</sup>CONACYT- Centro de Investigación Científica y de Educación Superior de Ensenada, Unidad Foránea Monterrey, Alianza Centro 504, PIIT, Apodaca, Nuevo León CP 66629, México

<sup>4</sup>Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Científicas (IEM-CSIC), Serrano 121, 28006 Madrid, Spain

<sup>5</sup>Key Laboratory of Surface & Interface Science of Henan Province, School of Material and Chemical Engineering, Zhengzhou University of Light Industry, N°136, Science Avenue, Zhengzhou, Henan, 450002, China

\*e.rebollar@csic.es

## ABSTRACT

Laser induced periodic surface structures (LIPSS) have been formed on polymers using lasers with different wavelengths and pulse durations. Here, we focus on the influence of substrate nature and roughness, and film thickness on the formation of LIPSS using nanosecond and femtosecond laser pulses. In the case of nanosecond laser pulses at wavelengths efficiently absorbed by the polymer, we found that well-ordered LIPSS are formed for a range of thicknesses of polymer films supported on silicon substrates as well as on thicker free standing films. The results are explained considering the thermal properties of the materials. LIPSS can also be formed on polymer thin films despite the absence of light absorption at the wavelength of the irradiating laser by using a bilayer approach, employing as bottom layer another polymer which absorbs efficiently at the laser wavelength. In this case, for a thickness larger than a threshold value, no periodic structures are formed. This can be explained considering a mechanical restriction that prevents rearrangement of the bottom polymer film.

In the case of femtosecond pulses, for wavelengths in the UV region LIPSS are formed in both free standing and thin films deposited on different substrates while irradiation with near infrared femtosecond pulses lead to the generation of LIPSS only in the case of deposited thin films. Additionally, when the substrate is gold the influence of the gold substrate roughness and the polymer film thickness on LIPSS formation has been studied in terms of the features of the electric field distribution obtained by computer simulations. We obtain LIPSS as long as the aforementioned substrate and film parameters remain below certain threshold values. These experimental findings are explained by the formation and behavior of SPP in the thin film-substrate interface.

## 1. INTRODUCTION

It is widely accepted that LIPSS on the polymer surfaces originates from the interference between the incident and the surface scattered waves, which induced a heterogeneous intensity distribution, and together with a feedback mechanism results in the enhancement of the modulation intensity [1-2]. The features of LIPSS might be affected by the polymer properties, which are dependent not only on the chemical composition, but also on the polymer state, amorphous or semicrystalline, and on the hierarchical structure of the crystalline phase. It has been reported that when a polymer film is irradiated with a laser beam at a wavelength efficiently absorbed, the surface temperature increases. Thus, in order to obtain LIPSS, the temperature should be high enough to grant significant polymer chain mobility. In particular, temperature should be either above the glass transition temperature ( $T_g$ ) for the case of amorphous polymer, allowing polymer chains to rearrange [3], or above its melting temperature ( $T_m$ ) in the case of a semicrystalline polymer so that melting of the surface crystallites occurs providing enough polymer dynamics [4] and the redistribution of the material. In general, LIPSS can be prepared

in both spin-coated and in free standing polymer films, which makes LIPSS a potential method to obtain large processed surface area and good quality samples.

Film thickness may play also an important role on LIPSS formation. Csete et al. observed [5] that linear LIPSS are formed in films with thickness above a minimum thickness value. Also, substrate nature may affect LIPSS properties as reported by Kalachyova et al. [6] for doped poly(methyl methacrylate). P. Nürberger et al. [7] observed a change in orientation of LIPSS on a SiO<sub>2</sub>/Si layered system by varying the thickness of the dielectric SiO<sub>2</sub> on the semiconducting Si substrate.

Here, we focus on the influence of the thickness of the polymer film in the form of thin films deposited over different substrates or as free-standing films, and of the substrates properties, on LIPSS formation. We use for that both nanosecond laser pulses and femtosecond laser pulses.

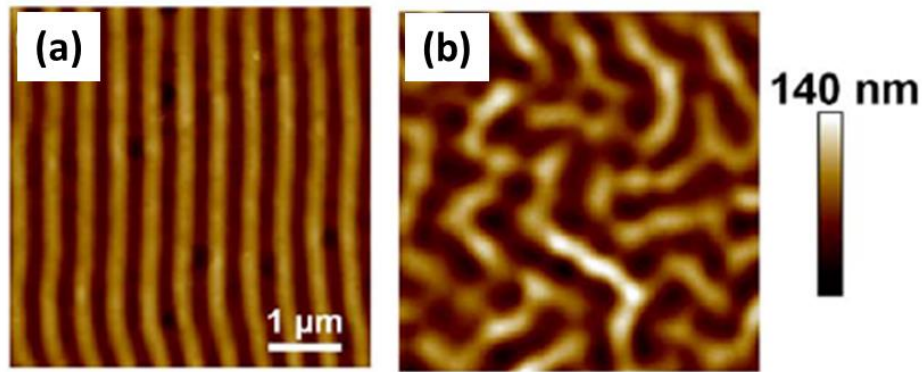
## 2. LIPSS FORMATION USING NANOSECOND LASER PULSES

For inducing the formation of LIPSS on the surface of polymer films using nanosecond laser pulses it is important that the polymer absorbs at the laser irradiation wavelength. We have studied the influence of film thickness in the LIPSS formation using polystyrene (PS) films with thickness values ranging from 70 to  $150 \times 10^3$  nm upon irradiation at 266 nm [8]. Films from 70 to 400 nm were casted on silicon and the thicker one is a free-standing film. The samples were irradiated at fixed values of fluence and number of pulses.

For the thinnest film, disordered LIPSS are formed. In contrast for thicker films, parallel ripples are observed. In the case of films with intermediate thicknesses, distorted LIPSS decorated with droplet-like entities can be observed. From the above results it is possible to conclude that, for silicon supported thin films, a critical range of film thicknesses exists at which the formation of well-ordered LIPSS is hindered. The laser irradiation of the PS films of different thicknesses provokes the substrate temperature to increase very fast. However, the heat is effectively dissipated on the basis of the high thermal diffusivity of silicon. Thus, the high thermal conductivity and thermal diffusivity of silicon makes the cooling of the polymer material heated by the laser pulse to be more efficient for thinner films. Accordingly, the silicon substrate acts as a thermal heat sink making that thinner films need more irradiation energy, either in terms of pulses or in terms of fluence, in order to reach similar temperature values than those reached by thicker films.

In order to explain the singular behavior of the PS films with intermediate thicknesses values in the range 200–400 nm, for which droplet-like entities are observed, we can consider different facts. On the one hand, the heat dissipation by the substrate of the heat generated by surface irradiation is less efficient than for the thinnest film, but still it plays a role. On the other hand, we can consider the optical properties of the silicon, in particular the refractive index at 266 nm, which for silicon is higher than for PS. When the laser light reaches the silicon substrate the reflection from the substrate may introduce additional thermal effects and thus, less ordered LIPSS are expected.

In the case of polymers which do not absorb at the laser wavelength as is the case of the ferroelectric copolymer P(VDF-TrFE), which is transparent in all the UV-VIS-NIR range, LIPSS may be formed by using a bilayer approach. Nanostructuring of a bottom polymer layer, in this case P3HT, by laser irradiation, covered by a thin layer of P(VDF-TrFE), allows the development of a grating-like structure on the surface (Fig.1.a). The range of thicknesses of the upper layer which leads to the formation of LIPSS has been determined. In this case, for a thickness larger than 40 nm, no periodic structures are formed (Fig.1.b), neither in the upper layer nor in the bottom P3HT one. This can be explained considering a mechanical restriction which prevents P3HT rearrangement. P3HT cannot rearrange freely during the time it is melted and the formation of grating-like structure is not possible.



**Fig.1.** AFM topography images ( $5\ \mu\text{m}\times 5\ \mu\text{m}$ ) of P3HT/P(VDF-TrFE) bilayer films irradiated with a fluence of  $26\ \text{mJ}/\text{cm}^2$  and 3600 pulses: (a): P(VDF-TrFE) thickness: 20 nm (b) P(VDF-TrFE) thickness: 90 nm.

### 3.LIPSS FORMATION USING FEMTOSECOND LASER PULSES

We have experimentally observed that it was possible to induce the formation of LIPSS in polymer thin films by using both UV and NIR fs laser pulses. Irradiation of polymer thin films deposited on silicon, glass and gold and of thicker free-standing films with fs-UV pulses leads to the formation of LIPSS as a result of mechanisms analogous to those described for ns-UV pulses, because the materials studied have a high linear absorption coefficient in this region. It was also possible to nanostructure these polymers by irradiating them with fs-NIR pulses, where linear absorption is negligible. In this case LIPSS have been observed only on thin films deposited on the different substrates but they are not formed on the surface of free-standing films.

In a further step, polymer films of different thicknesses were deposited over gold substrates of different roughness and samples were irradiated with NIR fs pulses. We found LIPSS perpendicular to the laser polarization only for film thicknesses smaller than 150 nm deposited over the low roughness substrate. In order to evaluate how the substrate roughness and the thin film thickness affect the formation of surface plasmon polaritons (SPPs) and whether it can be related to the formation of LIPSS, we simulated the electromagnetic field resulting from the propagation and dispersion of the laser incident wave inside our samples and we compared the results to the experimental measurements. The results lead us to the hypothesis that the formation mechanism could be related to the SPP excited in the boundary between substrate and thin film. From our study of the penetration length we know that it must be similar to or smaller than the thickness of the thin film for SPP to intervene in LIPSS formation. In our experiments, we observe LIPSS for samples from 90 to 150 nm thick, which are in the range of SPP penetration distance. Consistently, we do not find LIPSS for thicker samples, as far as SPP cannot have any influence.

In our simulations, the intensity of the SPP increases with roughness ( $R_q$ ) reaching a plateau above 20 nm. To sum up, the larger the  $R_q$ , the higher the coupling between the incident beam and the SPP, resulting in higher intensity. However, for  $R_q$  values higher than a certain threshold, periodicity is destroyed. Although there is a formation of hot spots on the surface, due to excessive scattering induced by oversized roughness, they cannot propagate to generate a periodic field. The final effect is a local field enhancement dependent on the specific roughness profile of the substrate but without periodicity. This explains why we do not observe LIPSS formation for the sample with the higher  $R_q$  substrate, but we do see an increase in its roughness after irradiation.

### 3.CONCLUSIONS

LIPSS can be obtained on the surface of polymer films deposited on silicon with different degrees of order by changing the polymer film thickness. The thinner and thicker films develop well ordered LIPSS, because in the first case the substrate acts as a thermal heat sink and in the second one surface heating effects are more relevant.

LIPSS 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. But in this case, for a thickness of the upper layer larger than a certain threshold, no periodic structures are formed, neither in the upper layer nor in the bottom one. This can be explained by considering a mechanical restriction which prevents the rearrangement of the bottom layer.

LIPSS are formed on polymer films upon irradiation with fs pulses. UV fs pulses lead to the formation of LIPSS both on deposited films and free-standing film, while NIR fs pulses induce the formation of LIPSS only on deposited thin films. This indicates that different mechanisms take place at the different wavelengths. There is also an influence of the substrate. In particular, we have performed an experimental study and simulations of the influence of the substrate roughness and film thickness on the formation of LIPSS on polymer films deposited over gold with a near-infrared ultrashort pulsed laser. Experimentally we found LIPSS below threshold values of  $R_q$  and thin film thickness. However, above that threshold, we could not generate LIPSS. According to the simulations, for the gold substrate with high  $R_q$ , there is a large dispersion in the simulated period of SPP so that we cannot consider periodic structures, and for the thickest films, the penetration distance of the SPP is much smaller than the film thickness, so the coupling with the electric field at the film surface is negligible. We observe the same tendencies in the experimental period of LIPSS and the period of the SPP measured in the simulations. Both the experiments and simulations agree with the hypothesis that for LIPSS in thin films of a non-absorbing polymer deposited over a metal, the inhomogeneous electric field that starts the mechanism of LIPSS formation is the SPP generated in the thin film-substrate interface.

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