# Assessment of Laser Induced Periodic Surface Structures (LIPSS) on Spin-coated Polymer Films with Micrometer Resolution

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## 1. Introduction

Illumination of solid surfaces by intense laser pulses may induce the appearance of spontaneous periodic surface structures with periodicities closely related to the wavelength of the irradiating laser [1]. Formation of Laser Induced Periodic Surface Structures (LIPSS) has been observed on the surface of metals, semiconductors and dielectrics with lasers of different pulse duration from nanosecond (ns) to femtosecond (fs), and different wavelengths from UV to IR [2-4]. In the case of polymers, several studies have shown that irradiation by a polarized laser beam induces self-organized ripple structure formation within a narrow fluence range well below the ablation threshold [3,4]. The period of the ripples L depends on the laser wavelength and on the angle of incidence of the radiation. In order to control the development of these structures for a particular application, it is necessary to understand how they are generated and to study the homogeneity of the nanostructures over the irradiated area. On LIPSS, structure properties, i.e. period and height, change depending on the laser fluence and number of pulses, and also structural order is modified for different irradiation parameters. To assess order in LIPSS we have proposed the use of GISAXS. One drawback of LIPSS is that in the case of laser beams with gaussian energy distribution, LIPSS with different periods and heights can be formed along the diameter of the irradiated spot. In order to seek for applications of LIPSS a complete assessment of this effect is compulsory.

## 2. Experimental

Different polymers including poly (ethylene terephthalate) (PET), poly (trimethylene terephthalate) (PTT), and polycarbonate bisphenol A (PC) have been investigated. Polymer thin films were prepared by spin coating on silicon wafers (100). 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 II, LS-2147, pulse duration $\tau$ = 15 ns full width half maximum) at a repetition rate of 10 Hz. Fourth harmonic at 266 nm, was used for the experiments. Irradiated areas with a diameter of ca. 9 mm with LIPSS having periods in the range 200- 260 nm and depths of about 20-80 nm, were analysed by GISAXS using the facilities of the P03 beamline at PETRA III (DESY, Hamburg). A X-ray wavelength of $\lambda$= 0.1033 nm, with a beam size of 20 x 13 $\mu m^2$ was used in our experiments. Scattered intensity was recorded by a PILATUS 487 x 619 pixels detector (readout time < 3 ms and pixel size 172 $\mu$m), and a distance sample-to-detector of 4.175 m The samples were positioned in such a way that the X ray beam was parallel to the direction of the LIPSS. An incidence angle $\alpha_i$ = 0.4° and acquisition times between 1 and 20 s were chosen. The treatment of the GISAXS images was performed using the software Fit2D. The structures have been studied over small areas to assess their homogeneity over the whole irradiated region.

## 3. Results and Discussion

Figure 1 shows characteristic GISAXS patterns for PTT irradiated with 1200 pulses at a fluence of 7 mJ/cm$^2$, conditions at which LIPSS are formed. In the figure we have presented the corresponding GISAXS patterns at different positions along the modified area (dashed circle). Scattering maxima out of the meridian ($\omega \neq 0$) are clearly visible in the area with LIPSS. The period L of the nanostructures can be determined from these patterns, and a good qualitative correlation between AFM and GISAXS results is obtained.

LIPSS with periods similar to the laser wavelength, and parallel to the laser polarization direction, are observed in the three polymers studied. GISAXS has been introduced for the study of LIPSS to mainly assess morphology order over the irradiated area. LIPSS formation starts after irradiation with some tens of pulses using a repetition rate of 10 Hz, which implies that only a few seconds are needed to induce the formation, and optimal LIPSS are obtained for around 600 pulses, i.e. 60 seconds. In fact, as reported previously [3], for a few nanoseconds the polymer is heated above its corresponding $T_g$, which is expected to induce an increase in surface roughness caused by capillary waves, enhancing surface inhomogeneities and facilitating the feedback mechanism needed for LIPSS formation. Repetitive cycles of irradiation for a few seconds, followed by GISAXS measurements on the same spot would be expected to illustrate the development of this kind of structures. The reported results validate GISAXS as an appropriate technique for the analysis of this kind of nanostructures and herald the way for further studies involving the on-line monitoring of LIPSS by X-ray synchrotron techniques.

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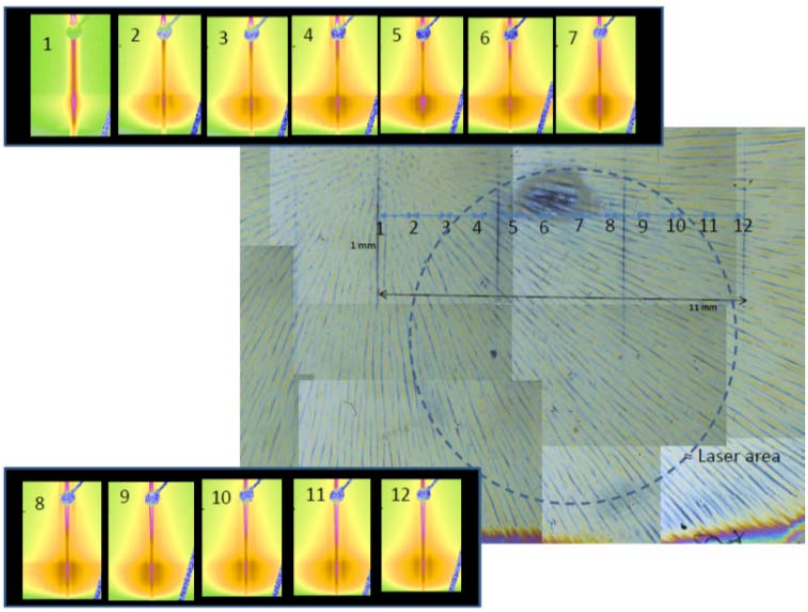


Figure 1: GISAXS patterns along the modified area of PTT irradiated at 7 mJ/cm$^2$ and 1200 pulses.

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