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Feature Article

Laser induced periodic surface structures on polymer films: From fundamentals to applications

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ABSTRACT

The generation of nanostructured polymer films has been a challenge during the last decades. Surface nanostructuring based on the imprinting of nanoscale patterns on a homogeneous surface or on the deposition of nanostructures on the surface serves advantageously for nanofabrication of functional polymer materials. Advanced nanolithography typically requires multiple-steps procedures involving clean-room facilities, high vacuum or complex mask fabrication. Alternatively, laser-based methods enable high spatial resolution patterning of soft polymeric matter and afford the sought versatility and reliability without the need of stringent ambient conditions. In particular, the technique of laser induced periodic surface structures (LIPSS) has been successfully applied to nanostructuring of polymer films using a polarized laser source at several laser wavelengths and pulse durations. In this paper the formation of LIPSS on polymer films will be described. In particular, the possibilities of tuning the period and shape of the structures will be discussed since the control of the characteristics of the superficial structures can be crucial in order to match the requirements of a particular application. Additionally, an overview about the main and potential applications of LIPSS in polymer films is provided. In particular, the use of rippled polymer films as substrates for cell culture/alignment, surface enhanced Raman scattering sensors, or applications in photovoltaics will be reviewed.

Contents

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1. Introduction

The surface properties of polymers are of crucial importance in order to provide certain chosen functionalities. In general, nanofabrication allows the manipulation of nanoscale building blocks for a desired purpose by furnishing macroscopic materials with nanometer-scale structural motifs that confer modified physical and chemical properties. Among the most popular examples, the hierarchical structure of the gecko foot or of the lotus leave are paradigmatic cases of an almost universal natural adherence [1] and of a natural superhydrophobic [2] behavior respectively. It therefore appears to be a rewarding project to structure the surface of a polymeric material periodically by varying both pattern and length scales. The periodic surface structures thus obtained can then be used as substrates in many fields stranding from organic photonics and microelectronics to biomedicine [3–7]. These substrates are generally provided as either spin-coated or free-standing polymer films.

Common techniques for generating polymer structures at the nanoscale are mainly based in soft lithography methods, like micro-contact printing or nanoimprint lithography (NIL) among others [4,8–11]. These methods aim at reproducibility and low-cost, and generally provide versatile processing strategies. Lithographic procedures suffer from limitations on spatial resolution. An additional drawback is the need of multiple-steps procedures involving clean-room facilities, high vacuum or complex mask fabrication. Advanced lithographic methods are attracting a lot of interest as a complement to standard lithography aiming to avoid the necessity of the mentioned demanding experimental conditions [12–15]. In this respect electrical [16], chemical [17,18] and mechanical methods [19], block copolymer self-assembly [20], use of templates [21,22] and laser induced [23] patterning of polymer surfaces are some versatile strategies in order to obtain functional polymer materials.

In particular, the last few years have witnessed the emergence of a new family of nanofabrication techniques with specific capabilities based in the use of lasers. They constitute attractive alternatives for high-resolution patterning of soft materials affording the sought versatility and reliability. Examples are laser induced periodic surface structuring (LIPSS) [24], laser foaming [25], and other techniques based on laser ablation, as laser interference lithography (LIL) [26], laser induced forward transfer (LIFT) [27], pulsed laser deposition (PLD) [28] and matrix-assisted pulsed laser evaporation (MAPLE) [29]. All these methods can be used to fabricate substrates with a variety of high-precision patterns at different length scales. More recently, specific laser processing techniques, taking advantage of optical trapping or of plasmonic enhancement effects [30,31], have been developed and applied to the nanopatterning of soft polymer materials. In general, laser-based techniques can be applied to many different materials in non-contact and flexible set-ups under a great variety of environments. Moreover, the processing can be tuned both to the materials properties and to the desired surface pattern by controlling the laser parameters like intensity, fluence, wavelength, pulse duration, total photon dose and several other irradiation conditions [32]. When using laser with pulses in the nanosecond (ns) range the material thermal properties determine the outcome of the laser fabrication process. However, for lasers with femtosecond (fs) pulses the laser-material interaction is the key factor governing the surface modification mechanism [33–35]. In this case, the possibility of temporally shaping femtosecond pulses offers new avenues for controlling and tailoring the features of the created structures [36,37].

LIPSS formation was first observed by Birnbaum [38] after ruby-laser irradiation of several semiconductor materials and since then, this type of structures has been generated on a wide variety of materials. LIPSS originate from the interference of the incident and reflected/refracted laser light with the scattered light near the interface. The interference between the different waves leads to an inhomogeneous energy input which, together with positive feedback mechanisms, can cause surface instabilities [39–41]. LIPSS have been reported on the surface of metals, semiconductors and dielectrics with lasers of different pulse duration from nanosecond to femtosecond, and different wavelengths from the ultraviolet (UV) to the infrared (IR) [42–46]. 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 [39,44,45,47,48]. As an example Fig. 1 illustrates a typical ripple structure on poly(3-hexyl thiophene), P3HT, as observed by atomic force microscopy (AFM) [49].

The period of the ripples L depends on the laser wavelength and on the angle of incidence of the radiation and their direction is related to the direction of the laser beam polarization [50]. The spacing of the structures can be described by the expression [50]:

$$L = \frac{\lambda}{n - \sin(\theta)} \tag{1}$$

where λ is the laser wavelength, n the effective refractive index of the material and θ the angle of incidence of the laser beam.