Swen Grossmann*, Lucas Tetzlaff, Niels Grabow, Klaus-Peter Schmitz, and Stefan Siewert

LIPSS on polymeric implant surfaces - a fabrication study

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Abstract: Laser-induced periodic surface structures (LIPSS) offer the potential to engineer cell adhesion, cell orientation, and cell density on implant surfaces through periodic structures on the nanometer and micrometer scale. Due to their straightforward fabrication on metal surfaces, they provide an essential tool for optimizing implants according to their intended use. However, these types of structures can only be produced on a limited amount of polymers. Within this study, methods of implementing LIPSS on polymer films are investigated using manufacturing processes established in biomedical engineering. For this purpose, a polymer possessing USP class VI certification and ISO 10993 proven biocompatibility is used. The presented processes are easy to implement and can contribute significantly to the implementation of surface active structures like LIPSS on medical devices and commercial implants.

Keywords: Femtosecond laser ablation, Laser-induced periodic surface structures, LIPSS, polymer, implants

1 Introduction

Laser-induced periodic surface structures (LIPSS) are periodic structures on the nanometer or micrometer scale generated on a surface due to laser irradiation [1]. Depending on the process parameters, LIPSS can occur as orientated or random structures, as grooves, spikes, and further shapes [2]. Especially periodic nano-sized surface structures like grooves have proved to be suitable for adjusting cell orientation, cell elongation, and cell density, especially for smooth muscle cells and endothelial cells [3–5].

However, the application of LIPSS in biomedical devices is highly limited by their fabrication technique. It is relatively straightforward to produce the structures on metal surfaces such as titanium or stainless steel. However, for most polymers used in biomedical engineering, there are currently no established processes for the direct generation of LIPSS. With regard to the advantages offered by polymers in the field of implant passivation, the fabrication of flexible implantable sensors, and the possibility of drug delivery, an established process for the fabrication of LIPSS on implantable polymers is highly desired.

Within this study, methods for the generation of LIPSS on a polymer with USP class VI certification and ISO 10993 proven biocompatibility are investigated. For this purpose, typical LIPSS are produced on a stainless steel plate by means of femtosecond laser machining. Subsequently, two methods, which are well-established in biomedical engineering, spray coating and spin coating, are used to implement the structures on a polymer film. It is shown that both processes allow the structures to be transferred without any complications. The processes described here can be adapted to established manufacturing processes of cardiovascular implants, flexible electronic implants, and polymer-passivated implants in general [6].

2 Methods

2.1 Femtosecond laser machining

A nickel-based stainless steel substrate (30 mm x 40 mm x 1 mm) was mirror-polished and subsequently structured by a femtosecond laser (Monaco 1035-80-60, Coherent Inc., USA), operating at a pulse duration of 300 fs, which is embedded into a commercial 4-axis CNC system (StarCut Tube Monaco, Coherent Munich GmbH & Co. KG, Germany). In the focal plane the beam diameter is about 22 µm, according to the knife edge method [7]. In order to fabricate groove-like LIPSS, the laser beam was linearly polarized along the y-direction (cf. Figure 1). The pulse energy and repetition rate were set to 4.3 µJ and 1 kHz, respectively. The traverse speed of the substrate was chosen to be 5 mm·s^{-1}. The highest homogeneity of the pattern over the entire substrate was achieved at a line separation Δ in y-direction of 5 µm. No process gas was used for LIPSS fabrication.

***Corresponding author: Swen Grossmann,** Institute for ImplantTechnology and Biomaterials e.V., Friedrich-Barnewitz-Str.4, 18119 Rostock-Warnemünde, Germany, e-mail: swen.grossmann@iib-ev.de
Lucas Tetzlaff, Klaus-Peter Schmitz, Stefan Siewert, Institute for ImplantTechnology and Biomaterials e.V., 18119 Rostock-Warnemünde, Germany
Niels Grabow, Institute for Biomedical Engineering, Rostock University Medical Center, 18119 Rostock-Warnemünde, Germany

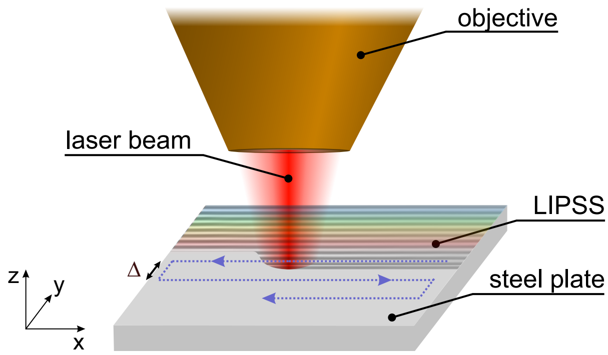

Fig. 1: Illustration of the setup used for fabrication of the laser-induced periodic surface structure (LIPSS). The substrate is scanned line by line using an interline separation Δ of 5 µm. The laser beam is linear polarized in y-direction.

2.2 Spray coating

The spray coating was performed using a self-constructed coating system, which contains a motorized linear translation stage for moving the target in one direction. The LIPSS-structured metal plate was used as the target for the spray coating process. A commercially available silicone polycarbonate elastomer, having a USP class VI certification and ISO 10993 proved biocompatibility, was dissolved in trichloromethane (2.7 wt.%) and vaporized using ambient air at a pressure of 0.3 bar. After 2 h spray coating, the thickness of the polymer layer varies between 150 µm and 30 µm across the substrate, which is caused by the jet profile induced by the nozzle perpendicular to the translation axis. After 24 h drying at ambient conditions, the polymer film was turned upside-down within a water bath and subsequently transferred to a flat non-structured substrate, a mirror-polished stainless steel plate.

2.3 Spin coating

The same polymer solution was used for spin coating as for spray coating. Within a commercial coater (Spin Coater SCE, KLM) the structured substrate was coated at 1200 rpm for 2 min, followed by heating for 3 min on a 60 °C hot plate. The process was repeated twice in order to increase the film thickness. Finally, a thickness of 750 nm to 1 µm was achieved. The film was turned upside-down during removing it from the substrate in water and placed on a second steel plate for electron microscopy analysis or on a microscope glass slide for confocal microscopy.

2.4 Surface analysis

In order to analyze the LIPSS, the metal substrate as well as the polymer surfaces were imaged by means of scanning electron microscopy (Quattro S, Thermo Fisher Scientific Inc., USA). The electron micrographs were obtained using a secondary electron detector. The polymer films were imaged in low vacuum mode without any further preparation. Confocal laser-scanning microscopy (CLSM) (LEXT OLS5000, Olympus, Japan) was used for 3D imaging of the structured surfaces.

3 Results and discussion

First, the stainless steel substrate was structured by the femtosecond laser system. Two arrays with horizontal and vertical oriented ripple-like LIPSS, respectively, are shown by the optical photograph in Figure 2a. The colored bottom array represents the diffractive character of the surface structure. A very homogeneous structure has formed on the surface during laser processing, as shown by the electron micrograph in Figure 2b. To obtain a 3-dimensional representation, the surface was analyzed using CLSM.

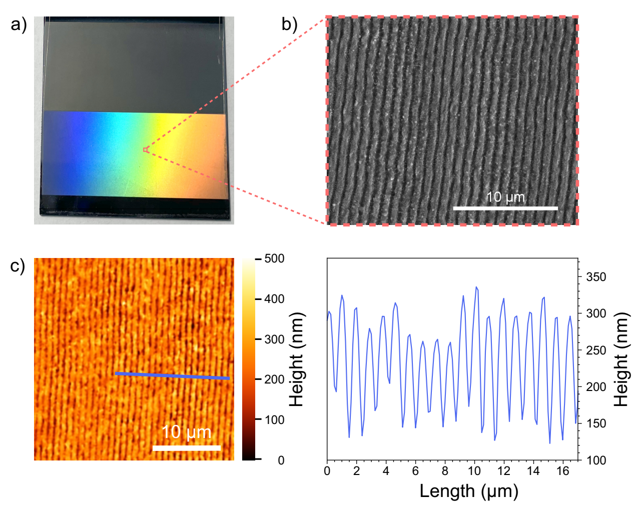

Fig. 2: LIPSS fabricated on stainless steel. (a) An optical image of the metal plate showing diffracting properties of the LIPSS. (b) Electron micrograph of the LIPSS (c) 3D image of the surface and height profile taken along the blue line.

Figure 2c shows a CLSM map and one extracted height profile. The height profile was used to calculate the mean value of the peak-to-valley height difference of 147 nm ± 30 nm. Using Fast Fourier Transformation, the periodicity of the structure was found to be 915 nm.

According to current theory, the formation of LIPSS on conductive substrates such as transition metals and their alloys is mediated by surface plasmon polaritons [2]. For moderate structure depths, the LIPSS periodicity can be estimated by the effective wavelength λ_{SPP} of the surface plasmons, which can be obtained from the wave vector k_{SPP} calculated by the dispersion relation of the surface plasmon at the steel-air interface [9]

$$k_{\text{SPP}} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}}.$$

Here ω denotes the laser frequency. The dielectric constant of the metal substrate and the ambient medium (air) are described by ε_1 and ε_2, respectively. Using the dielectric constant of iron $\varepsilon_1 = -6.715+i23.10$ at the laser frequency, an effective wavelength of $\lambda_{\text{SPP}} = 955$ nm is obtained [8]. This value provides a reasonable estimate of the periodicity, despite the small deviation, which might be caused by the multi-pulse structure formation [2].

Next, the substrate was used to fabricate the polymer films first by spray coating and subsequently by spin coating. Figure 3a shows the electron micrographs for the spray-coated and spin-coated polymer layers. A very homogeneous structure on both samples resembles the inverted LIPSS. The 3-dimensional maps in Figure 3b demonstrate that the structures from the spray coating process exhibit a slightly higher quality. This is observed throughout the entire polymer film.

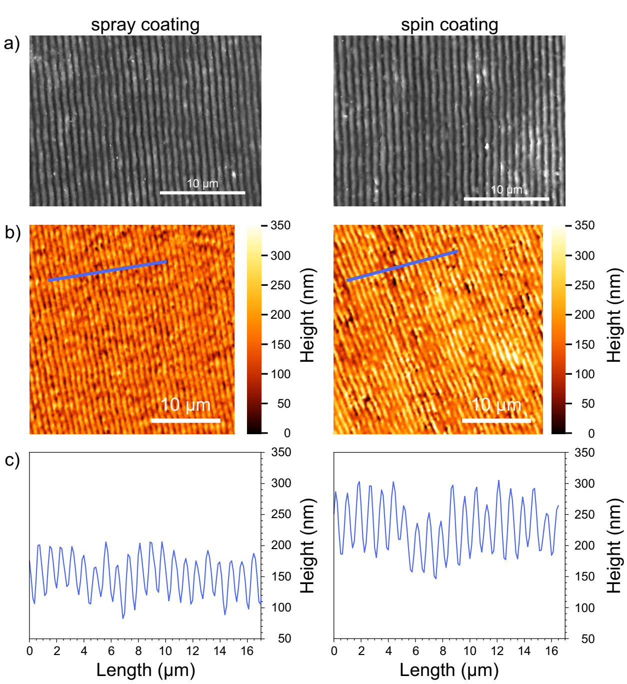

Fig. 3: LIPSS on the spray-coated and spin-coated polymer films. (a) Electron micrographs showing the quality of the LIPSS. (b) 3D maps of the polymer surface. (c) Height profiles taken at the blue line marked in (b).

Analog to the metal substrate, the extracted height profiles (cf. Figure 3c) are used to obtain the peak-to-valley height difference of 76 nm $\pm$ 14 nm and 98 nm $\pm$ 19 nm for the spray-coated and the spin-coated layer, respectively. Both values are considerably smaller than the height difference of the LIPSS on the metal substrate. Furthermore, the periodicities of 832 nm and 866 nm (spray-coated and spin-coated) are also well below the corresponding value of the metal substrate. However, the observed reduction of 9% and 5% is expected due to a polymer shrinking of up to 10% when drying after the water-based transfer process.

4 Conclusion

In conclusion, a sequential process was used to fabricate LIPSS-like structures on polymer films. First, a stainless steel substrate was structured by a commercial femtosecond laser system to realize the LIPSS. In the second step, spray coating and spin coating, two of the most common methods for processing polymer in biomedical engineering, were used to fabricate the polymer films on the metal substrate. It was shown that beside the expected shrinking of the polymer, the LIPSS can perfectly be transferred to the polymer. Note that the LIPSS structure, which is known to influence cell adhesion on surfaces, can be tuned to the desired cell response by changing the laser structuring process. Thus, due to the USP class VI certification and the ISO 10993 proved biocompatibility of the used polymer, the established process can directly be used to apply the field of nanostructured polymer surfaces to polymer-encapsulated or polymer-finished implants, i.e., devices containing flexible electronics, polymer-covered vascular implants, and implantable mechanical and electrical probes.

Author Statement

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