CONTROLLING THE WETTABILIT Y OF STEEL SURFACES PROCESSED WITH FEMTOSECOND LASER PULSES

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ABSTRACT: The wettability of a material surface is an essential property that can define the range of applications it can be used for. In the particular case of steel, industrial applications are countless but sometimes limited because of the lack of control over its surface properties. Although different strategies have been proposed to tune the wetting behavior of metal surfaces, most of them require the use of processes such as coatings with different materials or plasma/chemical etching. In this work, we present two different laser-based direct-write strategies that allow tuning the wetting properties of 1.7131 steel over a wide range of contact angles using a high repetition rate femtosecond laser. The strategy consists in the writing of parallel and crossed lines with variable spacing. A detailed morphological analysis confirmed the formation of microstructures superimposed with nanostructures, forming a hierarchical surface topography that influences the wetting properties of the material surface. Contact angle measurements with water confirm that this behavior is mostly dependent on the line-to-line spacing and the polarization-dependent orientation of the structures. Moreover, we demonstrate that the structures can be easily replicated in a polymer using a laser-fabricated steel master, which enables low-cost mass production. These findings provide a practical route for developing user-defined wetting control for new applications of steel and other materials functionalized by rapid laser structuring.

KEYWORDS: wettability, steel, laser-induced periodic surface structures, LIPSS, femtosecond laser, laser direct writing, polarization, polymer replica

INTRODUCTION

The increasing development of surface functionalization techniques has enabled their use in novel applications that were unthinkable decades ago. In the particular case of steel, its surface properties such as color, chemical stability, roughness, and wettability have received special attention in optics, biomedicine, and surface chemistry, just to name a few.1–4 However, in spite of the ubiquity of steel in industry, some applications are limited because of the lack of control over its wetting behavior. The wetting properties of a material mainly depend on its surface properties, such as chemical composition, morphology, and surface complexity. Therefore, the control of the wettability of a surface under given conditions remains as an elusive task.3–7 Different strategies have been applied to achieve wetting changes on steel surfaces either to produce an entirely different wetting behavior over the whole surface or to produce areas with combined wetting behaviors (known as high-contrast wetting surfaces8) on the same substrate. Usually, this requires the use of processes such as the modification of the chemical properties of the surface via plasma or chemical etching,9,10 the over-coating with an extra hydrophobic/hydrophilic top layer,11,12 or the use of chemically assisted laser processing.13 The identification of robust strategies to confer the surface of a given steel with a user-defined wettability to extend its intended use to different applications remains as a challenge.

Laser direct writing with ultrashort pulses has been extensively used to modify the wetting properties of different materials including metals, semiconductors, and dielectrics14–16 following a rather simple and well-known laser-based approach: the fabrication of parallel and crossed grids by ablation of lines.17–19 These modifications induce changes in the morphology, which modify the contact angle (CA) with different liquids. In particular, this strategy has also been used in steel samples, as reported recently by Martínez-Calderon and co-workers,20 using a low repetition rate fs laser. Their
study includes the fabrication of parallel and crossed lines using interline spacing of 20, 50, or 90 μm combined with self-organized nanostructures, the so-called laser-induced periodic surface structures (LIPSS). As a result, the authors fabricated hydrophilic and hydrophobic surfaces with CAs between 80° and 156°, respectively.

In the present work, we exploit the full potential of this irradiation strategy, achieving fine control over the wettability by combining line and grid structures with self-organized nanostructures. In particular, we have evaluated the wetting behavior over a wider range of interline distances, (from 10 to 1000 μm) achieving a continuously tunable wettability of the surface of steel. Besides, because our study has been performed with a high repetition rate laser, it is also possible to evaluate the efficiency and the scalability of the presented approach for the fabrication of large area surfaces with specifically tuned wettability.

## EXPERIMENTAL METHODS

### Samples Preparation.

The samples used in this work were square substrates of 45 × 45 mm² and 0.5 mm thickness made of 1.7131 steel (16MoCr5 alloy steel). The mirror-like polished substrates had an average surface roughness of root mean square <2 nm as measured with an atomic force microscope (AFM, Agilent S100 AFM/SPM in tapping mode). Before and after irradiation, the samples were cleaned in an ultrasound bath with isopropanol and stored in a desiccator at a relative humidity of 30%. Before wetting measurements, the samples were stored at least 15 days to allow chemical reactions to take place, rendering the irradiated area stable in terms of wettability. Surface chemistry is a crucial factor in the wetting properties of many materials. For the particular case of steel, it is known that the laser-processed material evolves from an initial superhydrophilic state to a (super-)hydrophobic state within ≈10 days because of the progressive attachment of carbon and its compounds to the surface. After this time, the surface has stabilized chemically and also in terms of its wetting behavior.

### Laser System.

A scheme of the experimental setup is shown in Figure 1A. The laser system used was a Satsuma Yb fiber laser from Amplitude Systemes. It delivers 350 fs pulses at a repetition rate up to 2 MHz with a maximum pulse energy of 20 μJ at a central wavelength of 1030 nm. The pulse energy was controlled by rotating a half-wave plate placed before a fixed double thin-film polarizer. A rotatable quarter-wave plate was used to allow changing continuously the polarization of the laser pulses from linear, through elliptical to circular for the results shown in Figures 5–7. The focusing system was composed of two computer-controlled galvanometer-driven mirrors that scan the beam over the sample surface over a working area of 7 × 7 cm² at speeds ranging from 0.001 to 7 m/s. The scanner was coupled to an F-Theta lens (f = 100 mm) focusing the beam down to a spot diameter indicated in each experiment following the 1/e² criterion, which is controlled by the input beam diameter. The sample was fixed on a 3D stage with tilt adjustment to align its surface perpendicular to the laser beam axis. All of the irradiations were made in air.

### Irradiation Strategy.

The aim of the irradiation experiments was producing laser-processed areas with controlled water wettability. For that purpose, structures formed by parallel and crossed lines with different interline spacing were produced. The formation of a single line was achieved by overlapping consecutive laser pulses of sufficiently high energy, as it is shown in Figure 1B. The spatial separation between two pulses (measured from center to center) and the actual overlap among them, taking into account (Δω0), can be set by choosing properly the beam scan speed (V) and the laser repetition rate (c). Equation 1 allows determining the effective number of pulses (Neff) that impinge on the sample per spot diameter.

\[
N_{\text{eff, 1D}} = \frac{2N\omega_0V}{\Delta}
\]

It is possible to fabricate grids of parallel lines using different interline spacing (Δ) as sketched in Figure 1C. The interline spacing used in the present study ranged from 10 to 1000 μm, resulting in structures as the ones similarly sketched in Figure 1E,F for parallel and crossed lines, respectively. When Δ < 2Nω0, the laser intensity of the wings of the Gaussian beam incident onto the interline spacing region Δ is sufficiently high to induce material transformation within Δ. From a practical point of view, this allows the formation of continuously modified areas that are approximately homogenous. In that case, the effective number of pulses per spot can be calculated following eq 2.

\[
N_{\text{eff, 2D}} = \frac{N\omega_0^2V}{\Delta^2}
\]

The effective number of pulses in eqs 1 and 2 are valid when the structures are produced by a single scan. In what follows, the specific irradiations conditions including the used laser beam waist and the total number of overscans are indicated in each experiment.

### Surface Characterization.

The optical characterization of the samples was performed with an optical microscope (Nikon Eclipse Ti) in reflection mode using objectives with nominal magnifications of 2.5X, 10X and 50X and numerical apertures of 0.06, 0.3, and 0.8, respectively. The nominal magnifications were increased by a factor 1.5 by means of a Barlow lens. The illumination source was a blue light-emitting diode (LED; 460 nm wavelength) enabling a maximum lateral resolution R xy ≈ 300 nm. Micrographs of the surface morphology were recorded with a monochrome charge-coupled device (CCD) camera (Hamamatsu Orca ER, 1.3 MP). Three-dimensional topography images were acquired with an optical surface profiler (Sensofar Plu-2200) using a 50X objective lens (NA = 0.55) to quantify the depth of the structures. The lateral (xy) and vertical (z) nominal resolutions of the system are R xy = 600 nm and R z < 1 nm, respectively. Moreover, scanning electron microscopy (SEM) micrographs of the laser-processed regions were obtained with a field emission electron microscope (Hitachi S-4800).

### Contact Angle Measurements.

The equipment employed for the CA measurements was an OCA 15EC system equipped with a CCD camera to capture lateral snapshots of a droplet deposited on top of the area of interest. A 3 μL deionized water droplet was deposited by an automated syringe dosing system. The camera, the droplet, and the LED illumination source are aligned so that the shadow of the droplet is projected and acquired on the CCD as...
sketched in Figure 1G. CA values as well as measured errors were obtained via software analysis. Because it has been shown that the CA with water of laser-irradiated steel surfaces evolves during approximately 10 days after the irradiation and then stabilizes, all of the measurements presented in this work were performed at least 15 days after laser exposure.

To determine the wetting regime of the surfaces, the theoretical CAs were calculated using the Wenzel (\(\Theta^W\)) and Cassie–Baxter (\(\Theta^CB\)) eqs 3 and 4

\[
\cos \Theta^W = R_f \cos \Theta^{\text{ flat}}
\]

\[
\cos \Theta^\text{CB} = R_{f-1} \cos \theta^{\text{ flat}} + f_{s-1} - 1
\]

taking into account the equilibrium CA on the pristine steel surface (\(\Theta^{\text{ flat}}\)), the roughness factor (\(R_f\)), defined as the ratio between the effective solid–liquid area to its normal projection on the surface plane, and the fraction of the solid surface area wetted by the liquid (\(f_{s-1}\)). The specific expressions for \(R_f\) and \(f_{s-1}\) for the case of trench structures can be derived geometrically and read as

\[
R_f = \frac{1 + \text{trench depth}}{\text{line separation}} \times 2
\]

\[
f_{s-1} = \pi (\text{radius at the base of the droplet})^2
\]
\[
\times \frac{1 - (\text{trench width})}{\text{line separation}}
\]

The underlying theory is based on the minimization of the Gibbs energy of the system, taking into account interfacial tensions between substrate, liquid, and vapor. While the above equations focus onto the influence of the surface geometry and can be calculated to a good approximation for our particular case of trenches, the role of surface chemistry has been studied so far only experimentally through processing or storing in different environments, which is why we limit our study to the situation when the material has achieved chemical stability.

CA hysteresis (CAH) measurements were performed using the sessile drop goniometry (needle-in droplet technique) at different stages of advancing CA (ACA) and receding CA (RCA), as described in ref 23. Initially the surface of interest was force wetted with a ~2 \(\mu\)L droplet, and the needle was placed exactly at the middle of the droplet. The measurements were performed after advancing and receding ~2.8 \(\mu\)L of additional distilled water volume. The surface hysteresis was calculated by averaging the ACA values and subtracting them from the average of the CA receding values.

Robustness measurements of the wetting state of the two surfaces have been performed measured via measuring the direct transition number of pulses for a single scan in all experiments was \(N_{\text{eff,1D}} = 9.5\) (\(\omega_0 = 9.5 \mu\)m, \(v = 500 \text{ kHz}, V = 1 \text{ m/s}, \Delta = 30 \mu\)m). The micrograph shows the steel surface after the irradiation, displaying three features: brighter areas that correspond to the unexposed steel surface, gray out-of-focus areas where the laser ablated the sample (indicated by an arrow in Figure 2A), and two dark areas that surround each ablated line (borders). The geometry and morphology of the written lines should define the resulting CA changes; therefore, here we performed several series of experiments with varying parameters to identify a suitable irradiation strategy for the fabrication of surfaces with customizable wettability.

\[\text{Figure 2. A) Optical micrograph of two ablated parallel lines with an interline spacing of 30 \(\mu\)m. The laser scanned the surface following the direction indicated by the arrow. (B) (Left axis) CAs for parallel line structures produced with } \Delta = 30 \mu\text{m, as a function of the number of overscans. Continuous lines in green and violet correspond to the CAs modeled for CB and Wenzel (W) regimes (see text) considering the plotted depths and widths of 15 \(\mu\)m of the produced lines. (Right axis) Plot of the line depth vs. scan number.}\]

Influence of the Number of Scans and Line Depth. The first parameter to analyze is the influence of the number of total scans on the depth of the structures and its impact on the wetting behavior of the surface. For this purpose, experiments with parallel line structures were performed with different number of overscans, ranging from 10 to 35. These structures were produced at a relatively large laser fluence compared with the used in subsequent experiments of \(F = 6.8 \text{ J/cm}^2\) to increase material removal (and therefore the line depth) with few overscans, keeping an \(N_{\text{eff,1D}} = 8.5\) (\(\omega_0 = 8.5 \mu\)m, \(v = 500 \text{ kHz}, V = 1 \text{ m/s}, \Delta = 30 \mu\)m). The results of the measured CAs and W are shown in the plot of Figure 2B. It can be seen that the depth of the ablated lines increases with the number of laser overscans. Yet, despite this depth increment, the CA remains essentially constant, with values around 135 ± 4°. Theoretical values for the CAs are plotted in Figure 2B using 3 for both wetting regimes, taking into consideration the line geometry with a constant line width of 15 \(\mu\)m and the different depth for each structure. These modeling results, when compared with the experimental ones indicate that the observed wetting behavior is consistent with the CB wetting
regime. At the same time, it can be concluded that structures with different depths present the same wetting behavior at least for the number of overscans studied.

**Tuning the Wettability of Steel: Influence of the Interline Spacing.** To achieve CA tunability, we also analyzed the influence of the interline spacing for both parallel and crossed-line structures. The experiment consisted in the fabrication of areas with different interline spacing using $P = 0.46 \text{ J/cm}^2$, $N_{eff \, 1D} = 18.85$ ($\omega = 18.9 \mu m$, $\nu = 500 \text{ kHz}$, $V = 1 \text{ m/s}$) and variable $N_{eff \, 2D}$ in the cases where continuous areas ($\Delta < 2\omega$) are fabricated. The interline spacing of the fabricated structures ranged from 10 to 1000 $\mu m$, forming continuous irradiated areas only for interline spacing lower than 20 $\mu m$. Because for in-plane asymmetric structures (like line structures) the CA might show anisotropy, the CA was measured along two viewing directions, $X$ and $Y$.

For crossed-line structures, the CA versus the interline spacing is plotted in Figure 3A. In this case, the CAs measured from both directions present, as expected, essentially the same behavior, regardless the viewing direction. The line drawn at 100° corresponds to the CA of the steel surface without irradiation ($\theta_{wu}$, Figure 3C). At the right axis, three colored bars indicate the wetting behavior of the surface, including hydrophilic, hydrophobic, and superhydrophobic surfaces. For parallel lines, the data are plotted in Figure 3B. The general behavior is similar when viewing from the $X$ direction, as sketched in Figure 3D,E. In contrast, the CAs measured from the $Y$ viewing direction in the case of the parallel lines (Figure 3F) are lower than the ones measured in $X$. This difference in the CA can be attributed to the anisotropic nature of the structure itself. Once the droplet is deposited, it will elongate following the line direction because no crossed laser-fabricated structures impede its flow along the lines path, whereas perpendicularly the parallel lines hinder the flow, producing an increase in the CA compared with the $Y$ viewing direction.

The CAs of the fabricated structures, parallel and crossed, present some common features: both types of structures show the highest CAs close to the corresponding value of a superhydrophobic surface for small $\Delta$. As the interline spacing increases, the CA gradually decreases, reaching the value of the nonirradiated surface ($\theta_{wu} = 100^\circ$). When analyzing the CA plots in detail, for interline spacing higher than 650 $\mu m$, the CA trend displays a sudden increase. A simple calculation shows that this change depends on the droplet geometry and the exact position where the droplet is placed, producing an undesired pinning effect that increases suddenly the CA for both parallel and crossed grids. Note that the droplet diameter at the base for $\Delta = 650 \mu m$ is similar to the one without structuring, $a_{eff}$, because also here CA = 100°. Taking into account its volume, it is possible to calculate the base diameter $d_b$ of the droplet according to the following equation

$$d_b = 2 \times \sin \theta \times \sqrt[3]{\frac{3 \times \text{drop volume}}{\pi(2 - 3 \times \sin(0.5\pi - \theta) + \sin(0.5\pi - \theta))}}$$

Equation 7

For CA = 100° ($\Delta = 650 \mu m$), $d_b = 1.9 \text{ mm}$, which corresponds to a droplet covering approximately four lines, two of them in the proximities of the droplet perimeter causing this sudden variation. Although the base diameter decreases for higher CAs, we have verified that for our experimental case and measured CAs, the line-covering versus line separation is an approximately reciprocal function, strongly increasing as the line separation gets smaller.
Overall, the information displayed in Figure 3 confirms that it is feasible to control the CA selectively using the proposed irradiation strategy without additional surface treatments. Importantly, for the parallel line strategy there is a range of interline spacing from 10 to 200 μm and a wider range in the case of crossed lines from 10 to 650 μm to tune the CA from 146° to 100°.

CAH and Transition from CB to Wenzel Regime. Measuring the CAH is an excellent qualitative method to distinguish between a high-hysteresis surface, where droplets tend to stick, and a low hysteresis surface, where they tend to slide down easily. We have performed such measurements on two representative surfaces with different line spacing (Δ = 20 and 100 μm) using the method described in the Experimental Methods section. Figure 4 displays the result for surfaces with 20 μm line spacing. It can be seen that the ACA curve is only little above that of the RCA. The CAH can be calculated according by a point-to-point average subtraction of CA<sub>receding</sub> from CA<sub>advancing</sub> yielding CAH<sub>100μm</sub> = 7.5° and CAH<sub>20μm</sub> = 2.7°. This suggests that surface with the smaller hysteresis (Δ = 100 μm) allows water droplets to slide more easily in comparison with the surface with a narrower line spacing. This outcome might be related to a higher robustness of the CB state.

To investigate this possibility, we have performed robustness measurements of the wetting state of the two surfaces upon pressure increase, using the method described in more detail the Experimental Methods section. Briefly, pressure increase is obtained by placing droplets of different sizes, and the resulting change of the CA is monitored. At low pressures P (large droplets), CAs were found to remain constantly high for both cases of crossed lines from 10 to 650 μm and a wider range in the two viewing directions X (solid red circles ●) and Y (empty blue circles ○) using both polarizations, linear and circular, respectively. For interline spacing smaller than 20 μm, the shaded area indicates the line separations for which continuous irradiated areas are formed (Δ ≤ 2ω<sub>th</sub>).}

![Figure 4](image-url)

**Figure 4.** CAH of a parallel line structure with an interline spacing of Δ = 100 μm. The ACAs and RCAs are plotted using the needle-in-droplet technique (CA[Monitored]), measured as the droplet volume is increased or decreased by adding water volume. Please note that these CAs should not be compared with the other CA values reported in this paper, as they are influenced by the presence of the needle (additional interface).

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**Influence of the Beam Polarization on Line Fabrication.** An additional parameter influencing the wetting behavior of the irradiated areas is the polarization of the laser beam. Figure 5 summarizes the main findings for different line structures using interline spacing from 10 to 50 μm with linear and circular beam polarizations, respectively, at F = 0.5 J/cm², keeping N<sub>eff</sub> = 9.5 (ω<sub>th</sub> = 9.5 μm, η = 500 kHz, V = 1 m/s), and N<sub>eff</sub> = 14 (for interline spacing Δ = 10 μm). The nanostructures formed inside the lines using linear polarization are shown in Figure 5A. The morphology corresponds to linear protuberances oriented parallel or perpendicular to the line. These nanostructures are so-called LIPSS<sup>14</sup> which are formed by interference of the incident laser light with a scattered surface wave leading to periodic features with dimensions related to the laser wavelength. Similarly, Figure 5B shows a structured line with the same irradiation conditions but using circular polarization. The resulting nanostructures show a different wavy morphology with tilted orientation. The CAs of the grid structures fabricated with linear and circular polarization are plotted in Figure 5C,D, respectively. From the plotted data, two conclusions can be straightforwardly drawn: first, regardless the polarization used during laser irradiation, the CA for interline spacing larger than 20 μm is practically the same, implying that the CA behavior is dominated by the microstructure formed by the lines. This is in agreement with the CB regime found in Figure 2 for similar interline spacing. The second conclusion is that the wetting behavior changes significantly when a homogeneously irradiated area is formed (for large N<sub>eff</sub> = 14), corresponding to interline spacing between 10 and 20 μm (shaded area of Figure 5A).
5 plots). In this small range, the CAs of the areas processed with linear polarization are higher than the ones produced by circular one. This difference can be attributed to the effect produced by the nanostructures, in contrast to the microscale topography associated with separated lines, in agreement with the results reported in ref 20 where periodic structures with periodicities around the used laser wavelength were fabricated.

To separate the influence of the superimposed nanostructure on the wetting behavior, a supplementary experiment of a crossed-line structure with an interline spacing of 50 μm was performed with an additional preirradiation step on top of the squares (as shown in Figure 6), producing a continuous area of LIPSS using linear and circular polarizations. In both cases, ripples were produced by five overscans with the same irradiations conditions as in Figure 5. Figure 6A shows the surface of the unirradiated area in between two irradiated lines. The surface presents some nanometric debris deposited after the previous line irradiation. The morphology of these areas after irradiation with linear and circular polarization is shown in Figure 6B,C. The morphology on top of the squares in the case of linear polarization corresponds to the formation of ripples perpendicular to the laser polarization, as typically observed for metals.26 Similar results are obtained for the experiment with circular polarization, shown in Figure 6C; however, the morphology in the plateaus consists in a variety of features with lower degree of alignment.

The CAs found for this structure using linear polarization is CA_X = 138° and CA_Y = 137°, and for circular polarization CA_X = 137° and CA_Y = 136°. Both types of nanostructured plateaus produce an increase of the CA compared with the same structure produced with flat plateaus (nonirradiated areas, CA = 135°) shown in Figure 5. Therefore, the nanostructures formed on top of the structures induce subtle wettability changes that agree with the results obtained for interline spacing smaller than 20 μm (i.e., continuous irradiated areas). In those cases, the new surface morphology induced by the formation of the nanostructures could also regulate the wetting behavior of the final structure. Thus, an additional parameter that modifies the wettability on the irradiated sample comes into play: the orientation and type of nanostructures generated on homogeneous areas.

**Generation of LIPSS and Their Influence on the CA.** To study the effect of the LIPSS orientation on wetting behavior, a new irradiation strategy was tested, consisting in the fabrication of continuous areas with an elliptically polarized beam and variable ellipticity. The polarization state was set by changing the orientation of the quarter-wave plate inserted before the scanner, as shown in Figure 1A. In this case, the areas were produced with 50 scans at $F = 0.3$ J/cm², keeping $N_{eff 1D} = 10$ ($ω_0 = 10.2$ μm, $ν = 500$ kHz, $V = 1$ m/s) and $N_{eff 2D} = 16$ ($Δ = 10$ μm). For this experiment, the polarization used for processing the different areas was gradually changed from linear through elliptical and circular polarizations and back to linear, in steps of 10°. SEM images of the fabricated areas with its corresponding polarization angle are shown in Figure 7A. It is possible to appreciate subtle changes in the orientation of the produced LIPSS that are initially oriented perpendicular to the polarization. When the polarization changes to elliptical, the nanostructures initially keep their morphology and orientation, but new small protuberances with spiky shapes emerge. When the polarizer position is between

Figure 6. (A) Pristine surface of a nonirradiated steel area in between two ablated lines, as indicated by the sketch. (B,C) SEM image of the LIPSS structures with interline spacing of 50 μm and an additional surface preirradiation, using linearly and circularly polarized light, as indicated by the yellow arrow. This produces a notable change in the surface morphology compared with the nonirradiated one.

Figure 7. (A) SEM images of the resulting LIPSS structures morphology for the corresponding polarization states, accompanied with the respective water droplet visualized laterally. The polarization state is sketched in each case from linear vertically polarized light to linear horizontally polarized light passing through elliptical and circular polarization. The measured CAs vs the relative polarizer position are plotted in (B).
40° and 50°, the observed morphology still contains ripples oriented at 45° with respect to those produced at 0°, combined with spikes. This residual appearance of ripples for circular polarization, slanted by 45°, has been also observed by other authors but is out of scope of the present study.27 As the position of the polarizer increases to 90°, the LIPSS orientation turns again perpendicular to the polarization. The measurements of the CA’s from the different areas are plotted in Figure 6B. This plot shows that the CAs for both linear polarizations, regardless of the orientation, are comparable, while elliptical and circular polarization show a gradual CA decrease. This data is in agreement with the data plotted on Figures 5 and 6 for grids fabricated with 10 μm interline spacing. The plots demonstrate that the CAs can be finely tuned from 135° to 150°, just by changing the orientation and shape of the produced nanostructures.

**Replication of Laser-Structured Surfaces in Polymers.**

We have investigated the possibility to replicate the laser-fabricated structures in steel into polymer material. To this end, we have developed a four-step procedure, as shown in Figure 8A. First, a few drops of acetone were deposited on the steel master template immediately before placing a single 35 μm thick, commercially available cellulose-based acetate film on top. After evaporation of the acetone, the film was removed, containing the negative imprint of the structures. In the third step, a composite liquid polymer (commercially available NOA60 at Norland Optics) was prepared and deposited onto the negative replica, fixed on a glass slide. The polymer was cured by exposure to UV light during 3 h and could be removed from the negative replica, containing a positive replica of the original steel structure.

The excellent reproducibility of even very small features, such as LIPSS with a period of about 1 μm can be appreciated in Figure 8B–D. The structures are reproduced well, not only in the first replication step but also in the second one (replica from a replica). To illustrate the strong influence of the material on the CA on, besides the influence of the surface morphology, images of a water drop placed on each structured surface are shown in Figure 8E–G. While the CA for ripples on steel is very high (CA = 149 ± 4°), the corresponding values for ripples on the different polymers are much smaller (CA_{polymer} = 97 ± 4° and CA_{polymer} = 67 ± 4°). Considering that both polymers used are moderately hydrophilic before structuring (CA ≈ 60°), it can be concluded that ripple fabrication leads to a moderate increase of the CA.

Figure 9 displays a photograph of a polymer negative replica obtained with the method described above. Seven different fields can be observed that are composed of crossed lines with different line spacings. The one displaying a different (cyan) color corresponds to the smallest spacing (20 μm), which is a result of light diffraction. Figure 9B shows a bar diagram with a representation of the different CAs that can be achieved for different laser-fabricated structures and a flat surface (bottom axis) in steel, polymer negative replicas and polymer positive replicas. The shaded areas plotted for line structures indicate that a range of different CAs can be achieved, depending on the line separation. While the CA can be tuned continuously in the case of line structures in steel (indicated by a double arrow), as shown in Figure 3, no clear relation between CA and line spacing was observed for corresponding structures in polymer.

**CONCLUSIONS**

The results obtained with the implemented laser structuring strategies show that by inducing controlled changes in the surface morphology of steel it is possible to tune the wetting behavior over a wide range of CAs, obtaining superhydrophobic and hydrophobic surfaces with CAs between 100° and 150°. The results on the wetting behavior of the structured surfaces show that the wetting regime corresponds to the CB scenario, which transforms into a Wenzel regime at increased pressure. The superimposition of nanostructured
LIPSS on the microstructured grids showed that it is feasible to finely tune the CAs. The orientation of these nanostructures is strongly influenced by the polarization of the laser beam, which also plays an important role in the final wetting behavior of the laser-processed surface. The laser structuring process is very fast and the structures can be easily replicated in different polymers without the need of lasers, which enables inexpensive mass production. The CAs of water on these replicated structures differ from those in steel, considerably widening the accessible range of CAs.

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**Author Contributions**
C.F. and D.P. conducted the irradiation experiments and the sample characterization. E.S. and A.M. performed the wetting characterization; C.F. wrote the manuscript. All authors contributed to the analysis of the results, scientific discussion, and revision of the article. J.S. directed the project.

**Notes**
The authors declare no competing financial interest.

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**ABBREVIATION**
LIPSS, laser-induced periodic surface structures

**REFERENCES**
(21) Marmur, A. Wetting on Hydrophobic Rough Surfaces: To Be Heterogeneous or Not To Be? Langmuir 2003, 19, 8343–8348.