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Superhydrophilic Properties Driven by Highly-regular Laser-induced Periodic Structures on Si Surface

Iaroslav Gnilitskyi[1,2], Alberto Rota[3] and Leonardo Orazi[2]

[1]NoviNano Inc., Lviv, Ukraine
[2]Department of Sciences and Methods for Engineering, University of Modena and Reggio Emilia (UNIMORE), Reggio Emilia, Italy
[3]Department of Physics, Computer Science and Mathematics, University of Modena and Reggio Emilia (UNIMORE), Modena, Italy

leonardo.orazi@unimore.it

Abstract
In this work an investigation about the effects of high-speed, highly-regular laser induced periodic surface structures (HR-LIPSS) on wetting properties of silicon surface are presented and discussed. In order to investigate the influence of chemistry on wetting properties of textured surfaces, treatments were performed both under air and N_2 shielding gas. The morphology was investigated by Scanning Electron Microscope (SEM), the chemistry by energy dispersive X-ray (EDX) and X-ray photoelectron spectroscopy and the wetting properties by camera recording. The results demonstrate substantial effects of HR-LIPSS on wetting properties of silicon surface. The hydrophilic Si surface becomes superhydrophilic after femtosecond nanopatterning and the addition of N_2 in laser treated zone essentially influences the chemistry of the surface, this permits to control the water flowing and makes HR-LIPSS more flexible, bringing up to a new level of control of wettability properties for several applications.

Laser beam machining (LBM), Silicon, Surface

1. Introduction

Material processing by femtosecond lasers has recently drawn a lot of attention due their peculiar characteristics. In particular femtosecond pulses have been exploited to induce periodic surface structures in various materials [1-3].

The so called Laser Induced Periodic Surface Structures (LIPSS) was observerd just five years after the invention of laser [4]. LIPSS can be described as a single step, maskless optical patterning technique. It has been applied on metals, semiconductors, dielectric surfaces and polymers and has been used in various applications including solar cells [5], plasmonics [6], metals colorization [7], wettability [8,9], adhesion [10] and tribology applications [11,12]. Highly-regular LIPSS is an advanced technique to produce LIPSS which can circumvent the periodicity and quality problems of LIPPS by using coherently scanning and laser parameters [13].

Nature gives tips how to produce superhydrophobic [14] as well as superhydrophilic surfaces [15] that can be useful for many applications, such as self-cleaning surfaces, enhancement of biological interactions, preferred fluid flow paths in machinery, gas seal conditions, directional syringes, microprocessor cooling, high-efficiency hydropower turbines, reduction of friction and stiction in data storage devices, nanoscale digital fluidics and a lot of others. The effect of LIPSS on wetting properties have been mostly investigated on metals [9,16] while few works can be found about effects on semiconductors.

Here, we present the investigation about HR-LIPSS effects on wetting properties of silicon surface. It is also introduced the possibility to control the movements of water drops by pre-drawing any form or track pattern. Also, the effects of adding additional N_2 gas in laser treated zone and effect on wetting properties of LIPSS patterned Si were investigated.

2. Experimental

A commercial femtosecond Light Conversion Pharos laser system was used, it can generate up to 20 W of average power with ~200-400 fs of pulse duration. The galvanometer scanner system (ProSeries Cambridge Technology) was equipped with an f-theta lens with 56 mm focal length. The laser beam was focused on the Si samples and raster scanned with bidirectional strategy to obtain rectangular area of 10 x 5 mm^2. Optical curved path was generated by translating the sample with translation XYZ stage under galvoscanner. The sample was single crystalline p-doped Si wafer, with 4 Ω•cm resistivity and thickness – 300 µm.

2. Results and discussion

The HR-LIPSS were created in a very specific and non-common way, by accumulating only 2-3 pulses for each point on the surface, with intensity and fluence well above the ablation threshold. Such conditions lead to strong ablation mechanism where the removal and modification processes are confined to the material surfaces and does not interest the bulk. This approach for LIPSS generation significantly differs from whose can be found in literature to produce traditional LIPSS [17-18], where the intensity and the fluence of each laser pulse is just slightly above the ablation threshold compensated by a higher quantity of laser pulses (up to 10^3). In order to check the possibility to modify the chemical properties and as consequence the wetting surface properties, during laser processing nitrogen was supplied on the surface. The morphological and chemical changes were explored in details.

2.1. Morphological analysis

The macroimage of HR-LIPSS treated sample is shown in Fig. 1(left). The effects of LIPSS on surface optical properties are clear from the picture as structured area represents spectral colors due to diffraction of white light. The SEM images (Figures 1(right)) permit to appreciate the presence of highly regular and homogeneous linear ripples with no bifurcations over the entire treated surface. The ripples direction result perpendicular to the laser polarization plane. The periodicity of the structures is roughly 900 nm.

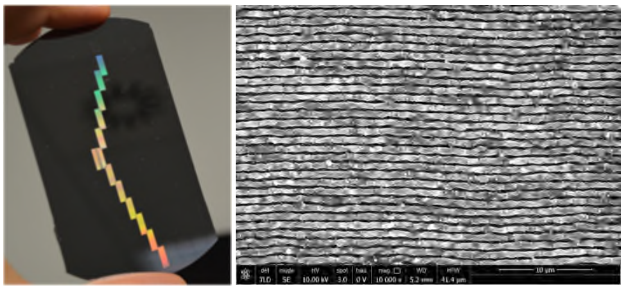

Figure 1. HR-LIPSS: (left) photo of generated path for testing water drops flow control; (right) SEM image on one pattern with magnification X 10000.

2.2 Chemical analysis

The energy dispersive X-ray (EDX) spectrum analysis indicates that LIPSS treated sample in air slightly increased (approximately by 2%) the content of oxygen compared to untreated one, the presence of carbon can be attributed to polishing-induced contamination. When nitrogen was supplied on the surface the content of oxygen essentially decreases while nitrogen appears.

Table 1 Roughness parameters for untreated and laser irradiated in air and nitrogen Si samples

Roughness parameters [nm]	Polished Si Wafers	LIPSS Air treatment	LIPSS N_2 treatment
Ra	3.5 ± 1.1	39 ± 3.8	36 ± 2.2
Rq	4.9 ± 1.4	42 ± 4.9	42 ± 2.4
Rsk	1.34 ± 0.80	-0.25 ± 0.16	-0.32 ± 0.16
λa		1056 ± 59	928 ± 13

2.3 Wetting investigation

We observe the HR-LIPSS treated silicon surface wetting properties by investigating the kinematic of rolling water drops by means of camera with a framerate of 30 frames per second. The tested 5 samples were obtained from Si wafer on which an angulated path 5 mm width was obtained and the surface was tilted at an angle of 60 degrees. Tests were conducted by using deionized water by dripping down single drops on both treated and untreated part of the surfaces and measuring the time requested to rolling down the oblique plan. Tests shows that silicon surface treated by HR-LIPSS presents superwetting properties, the water exactly flows following the angulated path. Meanwhile, the speed of water drop on treated surface is 3 times higher compared to untreated one. Thus, we demonstrate possible use of HR-LIPSS as a tool to control and accelerate water flow. Transforming silicon to be super wetting can be ensured either by changing morphology or chemistry, it is clear that after laser treatment in air oxidation occurs. In fig. 2 it is shown how the chemical changes of the surface during the laser process alter wetting properties. The average speed of rolling drops on N_2 treated area is sensibly lower respect that measured in air treated samples but higher in comparison with untreated surface.

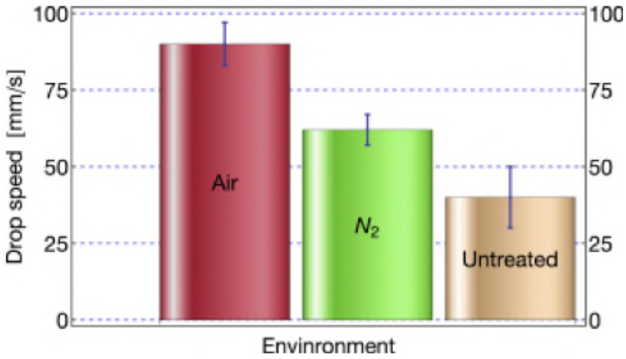

Figure 2. The average rolling water drops speed in different conditions.

Taking in account that surface roughness of HR-LIPSS treated in air and nitrogen are almost the same there is a clear influence of the nanometric oxided layer on the surface energy and this play a key role in wetting surface properties. Thereby, shielding gas in laser process allows to control wetting properties.

5. Conclusions

In summary, the capability of HR-LIPSS method to selectively generate superhydrophilic tracks on Si surface was demonstrated. Moreover, it was shown possibility to control dynamic movement of water drops by drawn with HR-LIPSS complex optical path. The speed of rolling water drops on patterned area is 3 times higher compared to untreated one. Both the effects of nanomorphology and chemistry changes on the surface was outlined. The effect of supplied gas nitrogen clearly shows essential chemical alteration but without influence on morphology. This chemical changing outlines new possibility to control of wetting properties. Due to relatively low cost and the possibility of formation of high-periodic structures at high speed, the proposed technique can be successfully applicable for nanoscale digital fluidics and many other applications.

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