Applied Surface Science 371 (2016) 583–589

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Laser textured surface gradients

Van Duong Ta[a,*], Andrew Dunn[a], Thomas J. Wasley[b], Ji Li[b], Robert W. Kay[b], Jonathan Stringer[c], Patrick J. Smith[c], Emre Esenturk[d], Colm Connaughton[d,e], Jonathan D. Shephard[a]

[a] *Institute of Photonics and Quantum Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK*
[b] *Additive Manufacturing Research Group, Loughborough University, Leicestershire LE11 3TU, UK*
[c] *Laboratory of Applied Inkjet Printing, Department of Mechanical Engineering, University of Sheffield, Sheffield S1 4BJ, UK*
[d] *Warwick Mathematics Institute, Zeeman Building, University of Warwick, Coventry CV4 7AL, UK*
[e] *Centre for Complexity Science, Zeeman Building, University of Warwick, Coventry CV4 7AL, UK*

ARTICLE INFO

Article history:
Received 11 January 2016
Received in revised form 3 March 2016
Accepted 5 March 2016
Available online 9 March 2016

Keywords:
Roughness gradients
Wettability gradients
Laser surface texturing
Nanosecond laser
Chemical sensors

ABSTRACT

This work demonstrates a novel technique for fabricating surfaces with roughness and wettability gradients and their subsequent applications for chemical sensors. Surface roughness gradients on brass sheets are obtained directly by nanosecond laser texturing. When these structured surfaces are exposed to air, their wettability decreases with time (up to 20 days) achieving both spatial and temporal wettability gradients. The surfaces are responsive to organic solvents. Contact angles of a series of dilute isopropanol solutions decay exponentially with concentration. In particular, a fall of 132° in contact angle is observed on a surface gradient, one order of magnitude higher than the 14° observed for the unprocessed surface, when the isopropanol concentration increased from 0 to 15.6 wt%. As the wettability changes gradually over the surface, contact angle also changes correspondingly. This effect offers multi-sensitivity at different zones on the surface and is useful for accurate measurement of chemical concentration.

1. Introduction

Surfaces with special properties including superhydrophobicity, superhydrophilicity and gradient are important for numerous applications in biomedical, microfluidics, sensors and suppression of the coffee-stain effect [1–6]. While super-hydrophobic/-hydrophilic surfaces exhibit either incomplete or complete wetting, surfaces with wettability gradients are more interesting because their wettability changes gradually over their length in space and may even develop in time [5]. Surface gradients are common in nature which demonstrate unique abilities such as directional water collection (from humid air or fog) [7,8]. Artificial gradients have also been fabricated with potential in controlling liquid movement, solving heat transfer problems and, pH sensitive devices [9–12].

Gradients can be simply classified into two categories where surfaces possess either a gradual variation of chemical or physical properties [5]. Physical gradients have gradual patterns or roughness processed on the surface [13–17]. Chemical gradients are more common, which are primarily formed by coating or depositing thin chemical layers on original material [9–12,18–24].

Recently, laser texturing has been demonstrated as an excellent tool for modifying surface roughness on nearly all types of materials [25–29]. Compared with chemical methods, direct laser texturing is a low waste, single-step procedure with potentially high processing rate and importantly, the ability to control surface roughness or wettability directly on the original materials without coating [30–32]. However, directly laser texturing these surface gradients have been rarely studied with a few reports that involve laser textured groove structures with a regular change in groove spacing [33,34]. As a result, investigation of direct laser patterning structure gradients (both spatially and temporally) using novel approaches is necessary and significant for taking advantage of laser technology for the creation of smart surfaces.

This work demonstrates surface gradients obtained by direct nanosecond laser texturing and their applications as multi-sensitivity chemical sensors.

---

* Corresponding author.
E-mail address: d.ta@hw.ac.uk (V.D. Ta).

http://dx.doi.org/10.1016/j.apsusc.2016.03.054

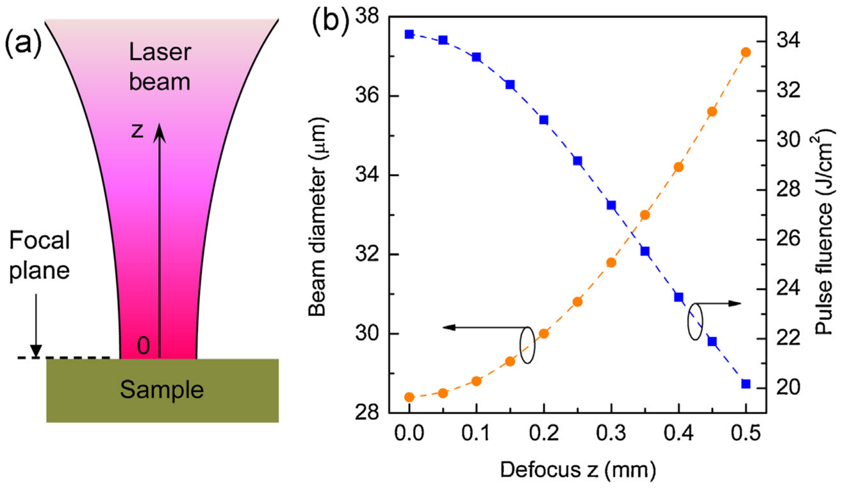

Fig. 1. Characteristics of focused laser beam used for surface texturing. (a) Schematic of the beam shape during fabrication process. (b) Calculated beam diameter determined as $1/e^2$ of maximum intensity profile and the corresponding pulse fluence as function of the defocus distance z.

2. Materials and methods

2.1. Materials

All laser processing was performed on 0.6 mm thick brass sheets (CZ121M, RS Components). The samples were cleaned with isopropanol before irradiating with laser.

2.2. Laser surface texturing

The surface morphology of the samples was modified by a nanosecond pulsed fibre laser (SPI, 20W EP-S) with a wavelength of 1064 nm, pulse duration of ~220 ns and repetition rate of 25 kHz. The fibre laser output is collimated before delivery to a galvanometer scanner and F-Theta focusing lens. The laser beam is scanned across the sample surface with a nominal focal spot size of 28.4 μm. Parallel micro-groove structures with a fixed hatch (scan line separation *h*) distance between them were textured. The scanning speed of 75 mm/s and the laser pulse energy of 0.252 mJ was fixed for all fabrication processes.

2.3. Surface characterization

The surface morphology of the laser textured samples was studied by means of scanning electron microscope (SEM) and optical microscope (Leica DM6000M). The arithmetic average of surface roughness (R_s) was obtained from *z* data measured with the Leica microscope on an area of ~1 mm^2.

Surface wettability was characterized by contact angle (θ) of ~5 μL deionized water droplets deposited on top of the samples. The contact angle was determined by analyzing droplet images (captured by a Unibrain 1394 camera) using the software FTA32 (version 2.0).

2.4. Preparation of isopropanol solution and sensing demonstration

Several isopropanol solutions with percent compositions (mass of solute/total mass of solution) up to 15.6 wt% were made by mixing various amounts of isopropanol (99.5% purity) in deionized water. Isopropanol solution droplets (~5 μL) on gradient surfaces were captured and their contact angles were determined as described in Section 2.3.

3. Results and discussion

3.1. Characteristics of focused laser beam

For laser processing, the laser beam is generally focused on the sample surface during fabrication to optimize light-matter interaction (Fig. 1a). The beam spot can be characterized by a defocus distance (*z*) where a positive value indicates that the beam focus is above the surface. Fig. 1b plots calculated pulse fluences versus *z*. It can be seen that at the focal plane ($z = 0$ mm), the fluence is the highest, about 34 mJ/cm^2, corresponding to the smallest beam diameter of 28.4 μm. The fluence reduces with increasing *z* and when $z = 0.5$ mm (a beam size of 37.1 μm), it drops to 20 mJ/cm^2, about 59% of the original value. As the morphology of laser textured surface strongly relates to laser power, the gradual change of laser fluence with *z* opens up the possibility of creating surface gradients by direct laser writing. It is demonstrated that by tilting the sample (discussed later) laser texturing surface gradients can be fabricated.

3.2. Effect of laser radiation on surface morphology

Fig. 2a shows schematic of direct laser writing parallel microgrooves on the brass surface using the scan head. The effect of laser radiation on surface morphology depends on the value of *h* and sample's position relative to focal point. For fixed *h*, the effect is the greatest when the processing surface is at the focal plane ($z = 0$ mm). As shown in Fig. 2b, the textured sample exhibits a dark colour due to a combination of oxide formation and non-reflecting properties caused by increased roughness. In contrast, for $z = 0.45$ mm (Fig. 2c), the fabricated surface shows a much lighter colour which indicates that the surface has less oxide and a lower roughness. Surface roughness measurements were performed on these samples and the average R_s was found to be ~2.6 μm for $z = 0$ mm, which is two times higher than that of 1.3 μm for $z = 0.45$ mm. The result confirms that laser induced roughness can be controlled by adjusting sample position vertically to laser beam direction. To get better understanding of surface morphology, SEM analysis was carried out and is shown in Fig. 3. The result indicates clear differences between the two cases. For $z = 0$ mm, corresponding to a fluence of 34.3 mJ/cm^2, a large amount of material was evaporated which created significant debris and formed obvious microgrooves. In contrast, for $z = 0.45$ mm the line structures were not completely formed as the laser fluence of 21.9 mJ/cm^2 is close to the ablation threshold.