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Fabrication of hydrophobic structures on stent by direct three-beam laser interference lithography

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ABSTRACT

Coronary heart disease has become one of the important causes of human death, and the current clinical treatment has a high long-term restenosis rate and is easy to form late stent thrombosis. In order to solve these problems, coronary artery stent surface was directly modified by laser interference lithography and the highly ordered concave structures were fabricated. The morphology and contact angle (CA) of the microstructure were measured with scanning electron microscopy and CA system. The water repellent property of the stent was also evaluated by the method of contacting the water drop with the stent and then separating. The results show that the close-packed concave structure with the period of about 12 μ m can be fabricated on the stent surface under special parameters (laser energy density of 3 J cm⁻², incident angles of 2.8°, exposure time of 60 s) by the three-beam laser interference of 1064 nm and the form structure has good water repellency with contact angle of 120°.

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20 1. Introduction

Coronary heart disease (CHD) is one of the most common causes 21 of human death [1]. The coronary artery stent implantation has cur-22 rently become the first choice for treatment of CHD in the world. 23 Despite the equipment and medication in contrast progress and 24 improvement, in-stent restenosis (ISR) is still a major defect of stent 25 implantation [2]. ISR is an important postoperative complication of 26 coronary stent implantation, the rate of ISR is 20% to 50% after 3-6 27 months [3]. The restenosis rate of bare-metal stents is 20% to 30% 28 within one year, which can be reduced to 7% or less by adopting the 29 drug-eluting stent [4]. However, the long-term restenosis rate of 30 drug-eluting stents is indifference with general bare-metal stents 31 [5]. Due to the occurrence of restenosis, there are still more than 15% 32 of patients with coronary stent implantation accept interventional 33 therapy in a year, which includes excimer laser coronary angio-34 plasty, intravascular brachytherapy, etc. [4,6,7]. Therefore, it is of 35 great theoretical and practical significance to develop a new type 36 of coronary stent, which has low restenosis rate and can prevent 37 38 late stent thrombosis.

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http://dx.doi.org/10.1016/j.ijleo.2016.02.075 0030-4026/© 2016 Published by Elsevier GmbH. In recent years, the studies showed that the biocompatibility of the materials could be increased by the biomimetic process of surface and coating [8–13]. Consequently, the preparation of bionic surface with regular geometric structure is beneficial to the rapid, directional and orderly adhesion and growth of endothelial cells, thus reducing the formation of restenosis and late thrombosis.

Laser interference lithography (LIL) has been applied in many fields, such as solar cells [14,15], photonic crystals [16], biosensors [17] and bionics [18,19]. And studies have shown that the minimum direct writing feature size of direct LIL can reach 27 nm (laser wavelength: 308 nm, pulse width $\leq 10 \text{ ns}$) [20], which is already fully meet the requirements of the processing in this paper. The technology of LIL, meanwhile, has the incomparable advantages in the fabrication of bionic micro nano structure. Compared with other approaches to the fabrication of periodic structures such as electron beam lithography, ion beam lithography and scanning probe lithography, which adopt the point by point writing strategy [21,22], LIL is a parallel technology which reduced the processing time. In addition, LIL has the advantages with long focal depth and no mask. These advantages reduce the flatness requirements of substrate and can be imaged in a non-planar without affecting the resolution and image contrast. Therefore, LIL is very suitable to process the coronary stent with the structure of mesh tubes, as shown in Fig. 1.

In this paper, LIL is used to modify the surface of coronary stent by imitating the water repellent surface of lotus leaf. Having run

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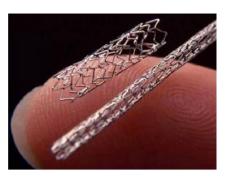


Fig. 1. Photography of the compressed and expanded coronary artery stents.

some tests, the processed stent showed good water repellency, which arrived the expected results. 65

2. Principle

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In the method of LIL, the three-dimensional laser etching of materials was based on the energy distribution of multi-laser beams interference on the materials surface [21]. The pattern generated by the intensity distribution of interference is transferred 70 to the material to produce periodic structures. By controlling the azimuthal angles, polarization directions, angles of incidence, laser fluences, exposure durations and other process parameters, we can utilize the LIL to obtain micro- and nanostructures of particular size on the material surface [23].

We can describe the three-beam interference with the super-76 position of electric field vectors of three laser beams, and it can be 77 expressed as 78

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$$\vec{E} = \sum_{i=1}^{3} \vec{E_i} = \sum_{i=1}^{3} A_i \vec{p_i} \cos\left(k\vec{n_i} \cdot \vec{r_i} \pm 2\pi\omega t + \phi_i\right)$$
(1)

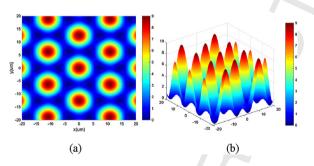


Fig. 2. (a) Two-dimensional and (b) three-dimensional plots of three-beam laser interference simulation results with the incident angle of 2.8° and the period of 12 µm.

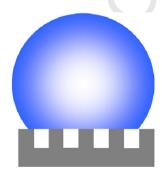


Fig. 3. Typical Cassie-Baxter model for wetting behavior of a water droplet on the rough solid substrate.

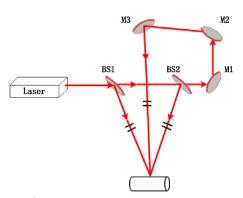


Fig. 4. Schematic of a three-beam laser interference system.

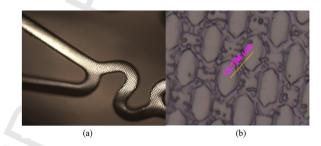


Fig. 5. (a) Scanning electron microscope images (low magnification) of the processed stent surface. (b) Close-up image of concave structure at high magnification.

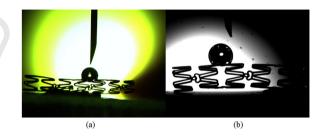


Fig. 6. (a) Photography of a spherical water droplet on the untreated stent surface. The corresponding water CA is 90°. (b) Photography of a spherical water droplet on the processed stent surface. The corresponding water CA is 120°.

and the interference intensity *I* can be calculated by

$$I = \left| \vec{E} \right|^2 = \sum_{i=1}^3 \sum_{j=1}^3 A_i \vec{p}_i \cdot A_j \vec{p}_j \cos \left[k \left(\vec{n}_i \vec{r}_i - \vec{n}_j \vec{r}_j \right) \right]$$
(2)

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where A_i (*i* = 1,2,3) is the amplitude, $\vec{p_i}$ (*i* = 1, 2, 3) is the unit polarization vector, $k = 2\pi\lambda^{-1}$ is the wave number, λ is the wavelength, \vec{n}_i (*i* = 1, 2, 3) is the position vector, and ϕ_i (*i* = 1,2,3) is the phase constant. When three laser beams were configurated symmetrically with the same incident angles and the TE-TE-TM polarization mode, Eq. (2) can be simplified as

$$= A^{2} \left\{ 3 + 2\cos(2kx\sin\theta) + 2\cos\left[2k\left(\frac{x}{2} + \frac{\sqrt{3}y}{2}\right)\sin\theta\right] \right\}$$

$$+2\cos\left[2k\left(\frac{x}{2}-\frac{\sqrt{3}y}{2}\right)\sin\theta\right]\right\}$$
(3) 90

where θ is the incident angle, *x* and *y* are the coordinates, and **Q4** 91 $A_1 = A_2 = A_3 = A$. 92

Fig. 2 shows the intensity distribution of the three-beam laser interference simulated by MATLAB.

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