Applied Surface Science 359 (2015) 7–13

Contents lists available at ScienceDirect

Applied Surface Science

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

Tuning the optical reflection property of metal surfaces via micro–nano particle structures fabricated by ultrafast laser

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ARTICLE INFO

Article history:
Received 24 June 2015
Received in revised form
17 September 2015
Accepted 10 October 2015
Available online 22 October 2015

Keywords:
Metal
Optical properties
Micro–nano structure
Particle
Ultrafast laser processing

ABSTRACT

Optical functional surfaces are key components of nearly every optical device and they have become a special focus in both academia and industry. The no contact, one step, direct, and maskless laser surface texturing technique is one of the most encouraging approaches for realizing the surface functions. We use a high power and high repetition rate ultrafast laser system to produce micro–nano structures on metal surfaces. We demonstrate that metal surface micro–nano structures and correspondingly their optical responses can be facilely tailored by simple controlling the ultrafast laser processing parameters. Nano particles of tens to hundreds nm, sub-micro particles of 0.5–1 μm, fine-micro particles of 1–10 μm, micro particles of 10–50 μm, and coarse-micro particles larger than 50 μm have been fabricated on Cu surfaces. And surface reflection of copper surfaces has been tuned from 10% to 90% in spectra level and from UV to MIR in spectrum range, with unique optical properties like visible selective reflection, linear changing reflection, band reflection, and broadband absorption being achieved. The formation processes of those particle structures as well as the underlying mechanisms for their optical responses are discussed.

1. Introduction

Due to their great advantages in providing a profound effect on the overall properties of a product, but with dramatically reduced cost compared to their bulk counterparts, functional surfaces are becoming increasingly important for devices, components, and facilities of every description. Among that, optical functional surfaces are key components of nearly every optical device including various daily used lenses, screens, cameras, eye-glasses, window glasses, and different industrial implements like solar cells, light emitting diodes, infrared sensors, as well as some space-related equipment [1,2]. Thus, they have become a special focus in both academia and industry.

The research of optical functional surfaces origins from the investigations of the unique biological optical properties like the anti-reflection and night vision capability of the moth eye [3], the gorgeous colors of the butterfly wing [4], and the sensitive photoreceptor in brittlestar [5], *etc.* Meanwhile, inspired by nature, scientists have been dreaming to realize optical functional surfaces artificially. Basically to date, two technical routines have been developed, i.e., the coating techniques, and the micro–nano structure techniques. The research on coating techniques has started years ago and they have been well developed [2]. However, an inevitable disadvantage of the coating techniques lies in the fact that they usually face the problem of poor stability as well as poor durability. Compared to that, the in situ produced micro–nano structures have natural and stronger bonding with substrates, thus better stability and durability can be achieved. Besides, for metallic micro–nano structures specifically, unique responses to incident electromagnetic waves like plasmonic resonance can be aroused, which are usually favorable for surface optical functions demanding tunability in response wavelength [6]. Therefore, it has attracted worldwide research interests to develop and experimentally fabricate surface micro–nano functional structures with desired optical responses.

Among the variety of available micro–nano structuring techniques, laser surface texturing, which possess the processing advantages of no contact, one step, direct, and maskless, is one of the most encouraging approaches. Over the last two decades, laser surface texturing has been increasingly investigated to enable the tailoring of surface functions of various materials, including tribological properties [7,8], wettability [9,10], biological properties [11], and optoelectronic properties [12], *etc.* In particular for optical properties, Mazur [13] and Guo [14,15] conducted the pioneering

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http://dx.doi.org/10.1016/j.apsusc.2015.10.069

Table 1
Chemical composition of the oxygen-free copper investigated (wt.%).

Cu + Ag	P	Bi	Sb	As	Fe	Ni	Pb	Sn	S	Zn	O
99.97	0.002	0.001	0.002	0.002	0.004	0.002	0.003	0.002	0.004	0.003	0.002

work on tuning the optical reflection of semiconductor and metal surfaces by forming surface micro–nano structures under direct femtosecond laser irradiation, creating the so-called “black silicon” and “black metals”, respectively.

After that, tremendous research has been made on tailoring the reflection properties of solid surfaces with different laser systems [16–27]. Typical instances are listed as but not confined to the follows: Tang et al. [16] reported the blackening of copper surface with a nanosecond (12 ns) Nd:YVO_4 laser and constant absorption over 97% in the spectral range from 250 nm to 750 nm was realized via highly organized periodic microstructure arrays. Lasagni et al. [17] used a nanosecond laser interference structuring technique to fabricate periodic grating structures on stainless steel and copper surfaces, making their overall reflectance in spectrum of 250–2500 nm being reduced 15% and 20%, respectively. Nayak et al. [18,19] used femtosecond laser to structure Ti surface and produced self-organized micro conical pillars which are covered by nanoscale ripples, reaching a reflectivity below 5% in the wavelength range of 500–1000 nm. Paivasaari et al. [20,21] presented a four-beam interferometric femtosecond laser ablation method and formed hole-array structures on stainless steel, achieving almost total absorption in a spectrum band of 200–2300 nm. Yang et al. [22] studied both the laser direct writing technique with a 1064 nm laser and the laser interference lithography technique with a 325 nm laser to produce micro–nano structures on Si surface, reducing its reflection to below 1.0% within 300–1200 nm. Shah et al. [23,24] fabricated spectral selective coatings for solar thermal receivers by pulsed laser sintering of tungsten nano and micro particles on stainless steel substrate, which show solar absorptance of ~90% at room temperature and remain stable after heat treatment at 650 °C in air for at least 36 h.

However, there have been few reports which systematically investigate the sequential evolution of surface structures throughout both the micro and nano scales under laser irradiation. Furthermore, the relationship between the dimensions of surface structures and the spectral regions where they can respond to the incident light has not been sufficiently established. In our research, we use a high power and high repetition rate ultrafast laser system to produce micro–nano structures on metal surfaces. We demonstrate that metal surface micro–nano structures and correspondingly their optical reflection responses can be facilely tailored by simple controlling the ultrafast laser processing parameters. Specifically, we focus on the particle structure as a typical instance. Nano particle, sub-micro particle, fine-micro particle, micro particle, and coarse-micro particle structures have been successfully fabricated, with unique optical properties like visible selective reflection, linear changing reflection, band reflection, and broadband absorption being achieved.

2. Experimental

The most commonly used oxygen-free copper (approx. C10200 Grade in ATSM Standards) was chosen as the target substrates in this research for investigating the ultrafast laser micro–nano structuring technique, of which the chemical composition was given in Table 1. Because of its high purity and the resulting high thermal as well as electrical conductivity, the oxygen-free copper is the preferred material in many fields including solar energy absorbers, thermal radiation sources, radiative heat transfer facilities, and optoelectronic devices *etc*. And tuning the surface optical absorption/reflection properties of the oxygen-free copper surfaces can have essential importance in improving their practical application performance.

The experiments were conducted using an Edgewave picosecond laser with an amplified Nd:YVO_4 laser system, which can generate 10 ps laser pulses at a maximum repetition rate of 2 MHz and a maximum average power of 100 W. The central wavelength is 1064 nm. Before laser processing, the Cu samples with a dimension of $25 \times 25 \times 3\ mm^3$ were polished and cleaned ultrasonically with ethanol to remove the oxide and grease on their surfaces. An x–y galvo and an f–θ lens were used to scan and focus the laser beam onto the copper surfaces in a pattern of cross or parallel lines in atmospheric environment. The diameter of the focused spot (D) defined by an intensity drop to $1/e^2$ of the maximum value was approximately 30 μm. After laser processing, the sample surfaces were ultrasonically cleaned with ethanol again.

The surface micro–nano structures of the laser processed samples were studied with a LEO-1530 scanning electron microscope (SEM). Optical reflectance measurements on ultrafast laser structured Cu surfaces were conducted using two optical measurement systems. The wavelength dependence of the overall reflectance in the UV, visible (VIS), and near-IR (NIR) regions (250–2250 nm) was characterized with a Lambda 950 spectrophotometer incorporated with an integrating sphere of 150 mm in diameter. And a Bruker Tensor-Fourier transform infrared (FTIR) spectroscope with an A562 type integrating sphere was used for measuring the wavelength dependence of the overall reflectance in the mid-IR (MIR) region (2–25 μm or 5000–400 cm^{-1}).

3. Results and discussions

Several parameters are involved during laser micro–nano structuring including the laser average power (P), the pulse repetition rate (f), the scanning speed (V), the interval between two adjacent scanning lines (I), and the process repeat number (n), *etc*. Overall, all these parameters will take effect via two technological issues, i.e., the laser pulse energy (E) and the pulse input number (N) at one particular surface spot. Here, N was calculated by

$$N = \frac{D}{V} \times f \times \frac{D}{I} \times n$$

For laser scanning in a pattern of parallel lines, the calculated N above is right the final pulse input number; while for laser scanning in a pattern of crossed lines, N should be doubled because the laser scanning was conducted along both directions.

The pulse energy, the pulse input number, as well as the specific pulse input manner will all determine the produced surface structures by ultrafast laser. Through carefully adapting the combination of pulse energy and pulse input number, various surface micro–nano structures, e.g., particles, gratings, periodic cone arrays, *etc*., have been fabricated by the high power high repetition rate ultrafast laser system. Here, for more vividly demonstrating the processing capability of the ultrafast laser micro–nano structuring technique, we focus our discussions on one specific structure form, i.e., surface particle structures. Different kinds of particle structures with their sizes sequential changing from nano scale to micro scale have been successfully fabricated. According to their dimensional features, we classify them into five categories: the nano particles whose sizes vary from tens (~10^1) to hundreds (~10^2) nm, the