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Controlled assembly of high-order nanoarray metal structures on bulk copper surface by femtosecond laser pulses

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ABSTRACT

We report a new one-step maskless method to fabricate high-order nanoarray metal structures comprising periodic grooves and particle chains on a single-crystal Cu surface using femtosecond laser pulses at the central wavelength of 400 nm. Remarkably, when a circularly polarized infrared femtosecond laser pulse (spectrally centered at 800 nm) pre-irradiates the sample surface, the geometric dimensions of the composite structure can be well controlled. With increasing the energy fluence of the infrared laser pulse, both the groove width and particle diameter are observed to reduce, while the measured spacing-to-diameter ratio of the nanoparticles tends to present an increasing tendency. A physical scenario is proposed to elucidate the underlying mechanisms: as the infrared femtosecond laser pulse pre-irradiates the target, the copper surface is triggered to display anomalous transient physical properties, on which the subsequently incident Gaussian blue laser pulse is spatially modulated into fringe-like energy depositions via the excitation of ultrafast surface plasmon. During the following relaxation processes, the periodically heated thin-layer regions can be transferred into the metastable liquid rivulets and then they break up into nanodroplet arrays owing to the modified Rayleigh-like instability. This investigation indicates a simple integrated approach for active designing and large-scale assembly of complexed functional nanostructures on bulk materials.

1. Introduction

Production and engineering of metallic nanostructures is of great interest for many applications, including in plasmonics [1], sensing [2], magnetic recording [3], and catalysts for hydrogen energy [4]. Commonly, several nanofabrication techniques have been already developed, for example, on the uses of photon/charged-beam lithography [5,6], microcontact nano-imprinting [7], and laser directing [8]. Although these top-down approaches can be highly controlled in the creating of nanostructures, they often suffer from high cost, low throughout, or time consuming, thus not suitable for large scale production. In contrast, bottom-up methods which build nanostructures via self-assembly process, are usually characterized by the low cost and a large-area extension but in a weak controllable manner [9]. By combining the advantages of the two fabrication methods, a templated self-organization technique has been reported [10–13], in which the highly ordered arrays of nanoparticles are produced by dewetting of thin metal films on the pre-patterned surfaces via thermal and pulsed laser annealing, and their formation actually depends on both the film thickness and predefined structures [14,15]. Because the templates often have limitations in material types and structure profiles, integrating such multiple steps (top-down fabrication, metal film deposition, and dewetting process) into a simple industrial process is challenging especially for the emerging field of high-temperature nanophotonics [16]. Therefore, it is highly desirable to develop powerful and reliable techniques for the flexible fabrication of nanostructures on solid bulk targets.

Here we present a new one-step-process strategy by femtosecond laser pulses irradiating the bulk copper surface, to generate the composite nanoscale arrays of metal structures with uniformly distributed particle chains within the periodic grooves. Remarkably, the structure dimensions can be well controlled with the incident time-delayed dual-color femtosecond laser pulses. In physical essence, the self-assembly of such periodic nanostructures is originated from the excitation of surface waves on both the optically excited solid and the metastable liquid materials, namely, ultrafast surface plasmon and modified Rayleigh instability are responsible for the formation of nanoscale groove and particle arrays, respectively.

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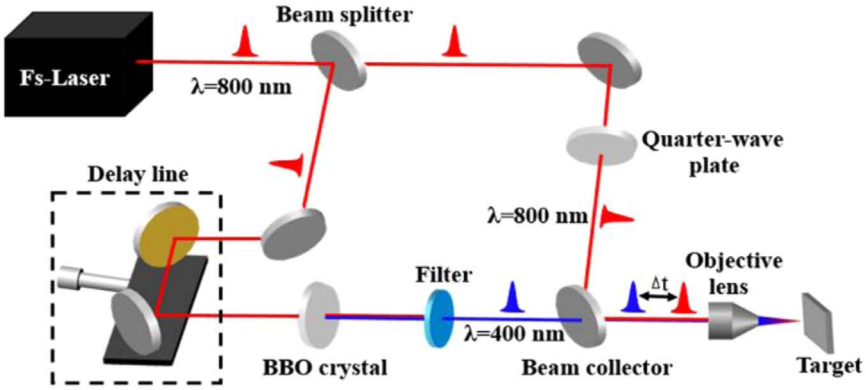

Fig. 1. A schematic diagram of the experimental setup for one-step assembly of high-order nanoarray metal structures on bulk copper surfaces by femtosecond laser pulses.

2. Experimental methods

A schematic diagram of our experimental setup is shown in Fig. 1, where a chirped-pulse amplification of Ti: sapphire laser system (Spectra Physics HP-Spitfire 50) was adopted as a light source, and it delivers linearly polarized 50 fs laser pulse trains at a repetition rate of 1 kHz with the central wavelength λ=800 nm. The output laser pulse was then split into two beams with a conventional Michelson interferometer, in one arm of which the laser is frequency-doubled by a beta-barium-borate (BBO) crystal and spectrally filtered to the central wavelength of λ=400 nm, while in another arm the laser is transformed into a circular polarization state via a quarter-wave plate. After passing a beam collector, the two-color femtosecond laser pulses were spatially overlapped into a collinear propagation and focused by an objective lens (4×, N. A=0.1) at normal incidence to the polished surface of a single-crystal Cu plate < 110 > (1 mm thickness), which was fixed on a three-dimensional (x-y-z) translation stage (New Port UTM100 PPE1). The roughness (Ra) of the polished Cu surface is less than 5 nm. To avoid serious ablation damages, the sample surface was placed about 400 μm away before the focus, where the laser spot exhibits a Gaussian fluence distribution with a ($1/e^2$) diameter of approximately 40 μm. The experiment was carried out with a line-scribing method at a scanning speed of 0.1 mm s^{-1} under the fixed irradiation of the laser pulses, resulting in 800 partially overlapped pulses within a beam spot. A temporal delay Δt between the two-color laser beams was able to adjust within a range of 0–140 ps via a high precision optical delay line. Positive time delays indicate the arrival of infrared laser pulse prior to the blue one. The laser energy in each interferometer arm was individually controlled via the neutral attenuators.

3. Results and discussion

First, a single blue femtosecond laser beam of the linear polarization was only used to irradiate the sample by shading the optical path of infrared laser beam in the interferometer, and the obtained morphologies of the laser irradiated surface are displayed in Fig. 2 for two different energy fluences of F_{blue}=0.059 J cm^{-2} and 0.1 J cm^{-2} (It is noted here that the measured threshold fluence for the single-pulse ablation of the polished Cu surface was 0.16 ± 0.02 J cm^{-2}.). Clearly, they present a fascinating composite nanostructure: Besides a typical pattern of the periodic grating oriented perpendicular to the laser polarization, a linear row of tiny grains appears to distribute within each grating valley region. Their zoom-in pictures demonstrate that the massive particles, like condensed droplets of the molten material, have nearly smooth round profiles and line up regularly along the groove direction. Under conditions of the two different laser fluences, the available groove periodicity is Λ_g=275.5 ± 12.1 nm and 268.7 ± 12.8 nm, much smaller than the incident laser wavelength of 400 nm, and the groove width approximates 95.7 ± 6.8 nm and 114.3 ± 13.7 nm, respectively. On the other hand, the measured average particle spacing is Λ_p=181.8 ± 20.5 nm and 201.1 ± 18.7 nm, and the particle diameter is about d=111.8 ± 17.8 nm and 132.1 ± 12.3 nm, respectively. The results are much different from those of the previous study on the silicon surface [17], wherein the observed nanoholes present empty cavity profiles, in particular, the distance between the two neighboring nanoholes was measured to be ~0.72 μm and the nanohole chains were separated by ~2.0 μm. Actually, such hybrid periodic surface structures, also the so-called high-order nanoarray metal structures on the copper surface, can be extended into a large two-dimensional (2D) areas through the sample scanning with other higher laser fluences even up to F_{blue}=0.139 J cm^{-2}.

In order to exploit transient physical properties of the metal for manipulating laser processing results, we began to introduce a circularly polarized infrared femtosecond laser pulse before the blue laser pulse reach the target. The temporal delay between the two-color laser pulses was Δt=+28 ps and the sample scanning was kept at the speed of 0.1 mm s^{-1}. The infrared laser fluence was selected so delicately that its individual irradiation cannot generate any periodic surface structures. Fig. 3 shows the surface structures obtained by two-color femtosecond laser pulses with variable energy fluences. Compared with the above experiment with the single blue femtosecond laser beam, the laser exposed surfaces by two-color beams can also provide the nanoscale periodic groove-particle composite structures. Under such circumstances, however, the top-view profiles of the nanoparticles located in the grating valley regions become more circular in accompany with the decreasing in either the diameter d or the spacing Λ_p. Moreover, the groove width turns to be narrower. In other words, a pre-incident infrared laser pulse enables to modify the formation of the high-order periodic nanostructures on the copper surface.

To quantitatively evaluate the effects of the pre-incident infrared femtosecond laser pulse, we summarize the measured data of the surface structures in Fig. 3. As shown in Fig. 4(a), for a given energy fluence of the blue femtosecond laser pulse, the available groove width appears to reduce with gradual increasing the infrared laser fluence within a range of 0–0.13 J cm^{-2}, in sharp contrast to the usual expectation of larger interaction regions for the increased dose of the laser exposure [18]. For instance, at F_{blue}=0.1 J cm^{-2}, the groove width, being about 114.3 nm without the infrared laser pre-irradiation, violently decreases down to only about 59.1 nm at $F_{infrared}$=0.08 J cm^{-2}. This result indicates a new potential method for the nanoscale processing metals with double time-delayed femtosecond laser pulses. On the other hand, for a given energy fluence of the pre-incident infrared laser pulse, the groove width is likely to enlarge with higher fluences of the blue laser. Fig. 4(b) illustrates the variations of the particle diameter as a function of the pre-incident infrared laser fluence. It is revealed that the diameter of the particles resting in the valley regions decreases with higher fluences of the pre-incident