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Full Length Article

Manipulation of multiple periodic surface structures on metals induced by femtosecond lasers

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ABSTRACT

Under femtosecond laser pulse irradiation, the selective control of structural periods of low spatial frequency laser-induced periodic surface structures (LSFLs) is investigated on metals at large incident beam angles. As increasing the number of irradiating pulses, we produce three types of LSFLs, small-, dual-, and large-scale LSFLs, and find two kinds of structural period variations, the sequential structural variations from small- to dual- to large-scale LSFLs and the nonsequential variation directly from small- to large-scale LSFLs by controlling the laser fluence. Using the efficacy factor with the help of the Maxwell-Garnett theory, our study also shows that all three types of LSFLs can be understood by the interference between the incident beam and surface plasmon polaritons at the air-nanostructure composite and metal interface rather than the air-metal interface.

1. Introduction

Since their first observation, laser-induced periodic surface structures (LIPSSs) have been investigated on various materials by using numerous types of high power lasers over the past half a century, and it is now generally considered that the formation of LIPSSs following laser irradiation is regarded as one of universal phenomena in laser-matter interaction [1–14]. In the past decades, LIPSSs have been actively investigated with femtosecond (fs) laser pulse irradiation [11–22]. Compared to the LIPSSs produced with relatively long pulsed lasers, fs LIPSSs generally show significantly reduced periods, and typically have been categorized into two distinct types, high spatial frequency LIPSSs (HSFLs) and low spatial frequency LIPSSs (LSFLs), where their periods are less than λ/2 (λ :laser wavelength) and between λ/2 and λ at normal incidence, respectively [11,19]. Occasionally, fs LIPSSs with a period of larger than λ have been also reported [23]. For HSFLs, various formation mechanisms such as second/third harmonic generation [5,20,24], surface oxidation [20], self-organization [25], and cavitation instability [26,27] have been suggested on various materials depending on their periods and orientations [5,11,14,20,24–26]. Recently, due to the observations of near- and sub-100 nm HSFLs, the formation mechanisms of HSFLs are still actively investigated [11,20,26]. On the other hand, the formation mechanism of LSFLs on metals is rather well understood by nonuniform periodic heating of surface due to the interference between the incident laser pulse and the laser excited surface plasmon polaritons (SPPs) with the adjustments of dielectric constant by considering laser-induced carrier excitations for semiconductors [17,18,24] and extensive surface nanostructures including the groove of LSFLs itself for metals [15,16,18,22]. Currently, by using the two temperature model, more sophisticated simulations have been performed for LSFLs [21,28].

According to the interference mechanism, particularly at off normal incidence, LSFLs on metals can intrinsically have two distinguishable structural periods, large- and small-scale periods, depending on the propagating direction of SPPs that interfere with the incident beam [3]. In case the incident beam interferes with SPPs propagating along the incident beam, the period of LSFLs will increase with the incident beam angle, and decrease when SPPs propagate against the incident beam along the air-metal interface [3,16]. Previously at off normal incidence, the former type of LSFLs (large-scale LSFLs) was observed on metals by us [16], and several observations were available by others for both the former and latter types of LSFLs (small- and large-scale LSFLs) on metals and semiconductors with various incident beam angles [13,29–31]. Recently, we observed structures with dual periods, namely dual-scale LSFLs, where the former and latter types of LSFLs coexist at the surface of metals [32]. The control of incident beam angle can give us an additional degree of freedom to change the period of LSFLs [3,16]. With this capability, it is also expected to efficiently fabricate the surface of

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polymer with various optical and physical properties, since LSFLs on metals including Ni can be easily replicated at the surface of polymer [33]. Therefore, to fully make use of these benefits, it is necessary to have a capability of independently selecting either one or both of two structural periods. However, currently, it is not clear how to pick out a specific scale of LSFLs' period with the number of irradiating pulses.

In this paper, by irradiating femtosecond (fs) laser pulses on metals, we manipulate the structural period of LSFLs at large incident angles. By adjusting the number of irradiating fs laser pulses, we fabricate small-, dual-, and large-scale LSFLs on metals, and demonstrate two kinds of structural period variations, the sequential structural variations of these three types of LSFLs and the nonsequential variation directly from small- to large-scale LSFLs with the control of laser fluence. We also discuss that all structural periods of LSFLs described here are attributed to the interference between the incident beam and SPPs travelling in the two opposite directions along the air-nanostructure composite and metal interface.

2. Methods and materials

Our experiments employ a Ti:sapphire laser system that generates 120-fs with the maximum pulse energy of 5 mJ/pulse and operates with a central wavelength of 800 nm at a 1 kHz repetition rate. The samples used in our experiments were Ni foils with a thickness of 1 mm, and prepared by polishing the surfaces mechanically with 80-nm-grade colloidal silica, and the average roughness (Ra) of polished surfaces was 9.4 nm. P-polarized fs laser pulses were slightly focused onto the surface of samples with a lens with a focal length of 150 mm, and the sample was slightly moved towards the lens to minimize nonlinear optical effects of air. The sample was vertically mounted on a rotation stage to produce LSFLs at off normal incidence. The $1/e^2$ intensity spot size (radius) is used to estimate the fluence of laser. The number of irradiating pulses is carefully adjusted with an electro-mechanical shutter, and the laser fluence is controlled by using a polarizer and half wave plate assembly. All experiments are performed in ambient air, and the period and morphological profile of LSFLs are measured by using a scanning electron microscope (SEM) and atomic force microscope (AFM), respectively.

3. Results and discussion

By irradiating the surface of Ni with fs laser pulses at a fluence (F) of 0.11 J/cm^2, we produce LSFLs at an incident angle of 65°. Following 10 pulses of irradiation, LSFLs form only in a small area within the beam spot. The period of LSFLs is about 415 nm, and the grating vector of LSFLs is parallel to the tangential component of laser polarization, as shown in Fig. 1. The structured area continuously expands with the number of irradiating pulses. Depending on the number of pulses, the period of LSFLs observed within the spot is in a range of 310–415 nm. The period decreases with the number of irradiating pulses, as described in Figs. 1 and 2. The LSFLs are covered with a large amount of nanoscale surface structures. These are consistent with the previous observations at normal incidence [15,18]. Comparing Fig. 1 with Fig. 2, we also notice that the shape of nanoscale structures covering LSFLs is changed from randomly oriented nanostructures (nanoscale protrusions, rims, and spheres etc.) to smaller porous type surface structures with the number of pulses.

Next, the fluence of laser is elevated to 0.17 J/cm^2 by increasing the pulse energy while other conditions are fixed, and the evolution of LSFLs is monitored with the number of irradiating pulses. At this fluence, the period of LSFLs is distributed in a range of about 350–415 nm, and the orientation of LSFLs is the same as that of LSFLs produced at lower laser fluence. The type of nanostructures on LSFLs is randomly oriented nanostructures, and the size of these nanostructures tends to increase with the number of pulses, as shown in Fig. 3(a)–(e). At this fluence, the change of nanostructure type to the porous type surface

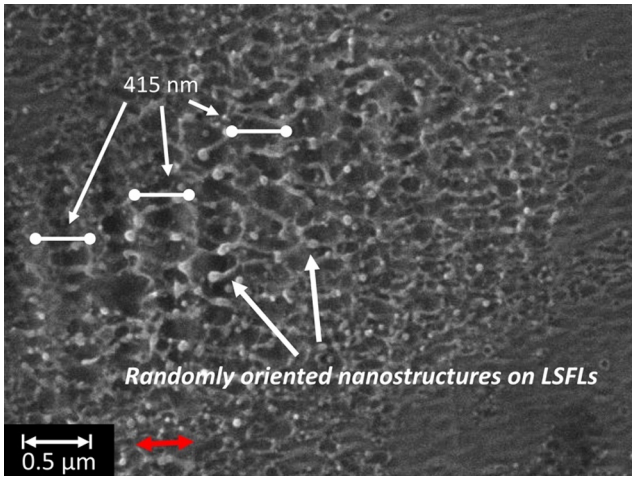

Fig. 1. SEM images of small-scale LSFLs on Ni produced at a fluence of 0.11 J/cm^2 and an incident angle of 65° with 10 pulses of irradiation. Double-headed arrows (red) indicate the orientation of polarization.

structures observed at $F = 0.11$ J/cm^2 slightly appears only at 50 pulses of irradiation, as shown in the inset of Fig. 3(b); however, with larger pulse numbers, this change is not shown. No significant change in the LSFLs' period is also observed up to 100 pulses of irradiation, as shown in Fig. 3(a)–(c); however, as the number of pulses reaches 250 pulses, the first structural period variation starts to happen, and large-scale LSFLs come into view along with small-scale LSFLs initially produced at lower pulse numbers. The period of large-scale LSFLs is in a range of 2.1–2.9 μm, more than 5 times larger than that of small-scale LSFLs, as described in Fig. 3(d). Until the number of pulses reaches 500, both small- and large-scale LSFLs, namely dual-scale LSFLs, clearly coexist on Ni, as shown in Fig. 3(d) and Ref. [32]. We also perform the similar experiments on Cu and Ag at larger incident angles of 70° and 80°, and observe dual-scale LSFLs on these metals. With additional 500 pulses of irradiation, dual-scale LSFLs on Ni experience another structural variation, resulting in vanishing small-scale LSFLs, and large-scale LSFLs are covered only with randomly oriented nanostructures, as shown in Fig. 3(e). By increasing the number of pulses, we can observe the sequential structural variations of small- to dual- to large-scale LSFLs within a fluence range of 0.14–0.17 J/cm^2.

We further increase the fluence of laser to 0.24 J/cm^2. In the beginning with low pulse numbers, the period of small-scale LSFLs is around 370–420 nm. Compared with LSFLs at $F = 0.17$ J/cm^2, no clear difference in the shape and orientation of small-scale LSFLs is observed below 100 pulses of irradiation; however, with more pulses of irradiation, the small-scale LSFLs start losing their periodic nature, and are completely gone prior to the formation of large-scale LSFLs, as shown in Fig. 3(f)–(h). Due to this early disappearance of small-scale LSFLs with low pulse numbers, small- to large-scale LSFLs direct transition with no dual-scale LSFL stage, namely the nonsequential structural variation, occurs at relatively high laser fluence.

When we take a look at Fig. 3(a)–(d) and (f)–(h), there seem some nanoscale quasiperiodic structures oriented perpendicular to small-scale LSFLs. Combined with small-scale LSFL structures, these structures form an array of rectangular domain at the surface. However, under identical experimental conditions, the period of these structures varies a lot and is not well-defined. As shown in the insets of Fig. 3, the shape of these structures are very similar to randomly oriented nanostructures described in Fig. 1 and Ref. [34,35]. As discussed in Ref. [34], their average distance also tends to increase with the pulse number and laser fluence. Accordingly, it is expected that the formation of these quasiperiodic structures results potentially from squirting liquid metal within a pot of locally melted liquid metal due both to Marangoni force and recoil pressure [34,35]. The reason that these randomly oriented