Nano-periodic structure formation on titanium thin film with a Femtosecond laser

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Periodic nanostructures were observed on the Ti thin film surface after irradiation with a focused beam of femtosecond Ti:sapphire laser. It has been found which, on the ablated Ti thin film surface, the linearly polarized femtosecond laser pulses produced arrays of ripple-like periodic nanostructures that were oriented to the direction parallel to the laser polarization, and a net-like nanostructure was fabricated on the surface of Ti thin film by the technique of two linearly polarized femtosecond laser beams with orthogonal polarizations ablating material alternately. The period of self-organized ripple-like nanostructures can be controlled by the pulses energy and the number of irradiated pulses. The result suggests that the formation of periodicity can be attributed to the excitation of surface Plasmon polarizations which induce initial period distribution of the electron plasma concentration orientation parallel to the light polarization on the surface layer. The estimated field period was in general accord with the observed size of nanostructures.

Key-words : Femtosecond laser, Surface Plasmon, Nanostructures, Ti thin film

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1. Introduction

High power ultrashort pulse lasers have opened new frontiers in technology of light–matter interactions, physics and chemistry fields. Its applications have expanded from coherent X-ray generation[1),2)] and nonlinear Thomson scattering[3)] to direct writing of 3D photonic structures.[4)–6)] One reason is femtosecond pulses, for direct writing and data storage, can rapidly and precisely deposit energy in solids[7),8)] in contrast with longer ones.

Laser-induced periodic surface structures on solids have been the subject of extensive theoretical and experimental study. Especially the nanostructure formation after ultrashort laser pulses treatment attracts a lot of interest. So far, there are many reports about laser-induced periodic surface structures on metals[9)] dielectrics and semiconductors.[9)–11)] For example, Vorobyev et al., has applied the femtosecond laser technique in generating laser-induced periodic surface structures on various metals,[12)–14)] and the forming of these nanostructures is generally believed to be the result of local periodic enhancement triggered by excitation of surface Plasmon polarizations in surface layer.[15)–17)] To the best of our knowledge, until now, all the reported nanostructures only mentioned the nanostructures perpendicular to the laser polarization direction. Here, for the first time, we report the controlled preparation of the nanostructures vertical or horizontal to the laser polarization direction by ablating once, and the combined nanostructures through ablating twice.

2. Experimental

Firstly, using an radio frequency sputtering (ULVAC, KIKO, Inc., RFS-200), we deposited a Ti thin film (200 nm thick) on one silicon wafer (1 cm thick) within pure N2 gas under bias voltage of 100 W. Then, for the ablation experiment, the laser radiation in Gaussian mode produced by regenerative amplified mode-locked Ti:sapphire laser (70 fs pulse duration, 250 kHz repetition rate) operating at a wavelength of 800 nm was focused via 20× (numerical aperture = 0:45) microscope objective into the silica glass samples placed on the XYZ piezotranslation stage. The beam was focused on the interface of Ti/Si. The laser writing parameters were controlled by an electronic shutter, a variable neutral density filter, and a half-wave plate placed in an optical path of the laser beam. We produce nanostructures over a line by scanning the sample across the laser beam, and the femtosecond pulse energy was set in a range of 0.008–0.064 µJ, and the number of irradiated pulses used was in a range of 30–102, corresponding to the scanning speeds of 10000–3000 µm/s. After laser irradiation, the surface of the irradiated sample was observed by scanning electron microscope (JEOL, model JSM-6700F). All experimental were performed in air.

3. Results and discussion

Figure 1 shows the SEM images of the Ti surface ablated by the femtosecond pulses (pulse energy 0.008 µJ and scanning speeds of 10000 µm/s of linearly polarized output at 800 nm) with p- and s-polarizations. After ablation, the linearly polarized pulses produce fine slender ripple-like framework on the Ti film. This structure, with an average spacing of about 105 nm between the ripples, is highly oriented to the direction parallel to the laser polarization, differing to the normal situation perpendicular to the laser polarization. The difference may be interpreted as follows: once a high free electron density is produced by multi-photon ionization, the material has the properties of plasma and will absorb the laser energy via one-photon absorption mechanism of inverse bremsstrahlung (joule) heating, and the light absorption in the electron plasma will excite bulk electron plasma density waves. These are longitudinal waves with the electric field component parallel to the direction of propagation. Such an

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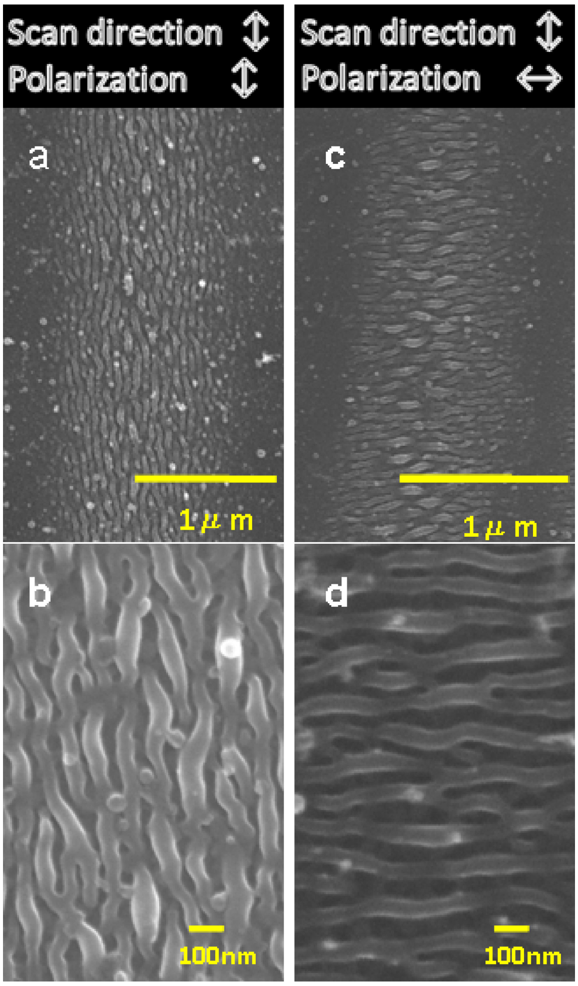

Fig. 1. (Color online) SEM images of the Ti surfaces ablated by the 800 nm femtosecond laser pulses with P-polarization (a, b), S-polarization (c, d). The magnification of the upper (a, c) and lower (b, d) images are 10000× and 50000×, repectively.

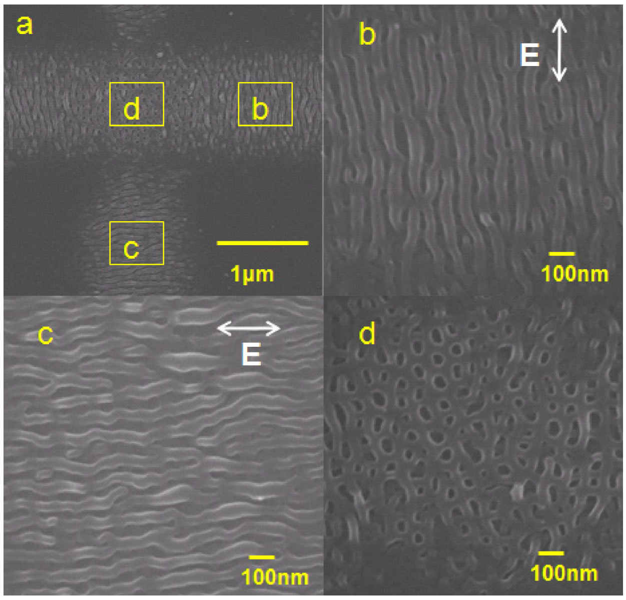

Fig. 2. (Color online) SEM images of a Ti surface ablated by the two-beam alternate ablation with scanning speeds of 10000 μm/s and laser power of 0.016 μJ: (a) overview. (b) ripple-like nanostructure in the area ablated by one beam with vertical polarization. (c) ripple-like nanostructure in the area ablated by the beam with horizontal polarization. (d) net-like nanostructure formed in the two-beam overlapping area. Double arrows: the polarizations of the incident laser.

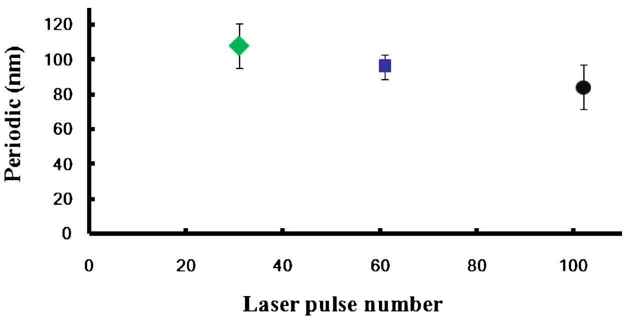

Fig. 3. (Color online) The dependence of the observed periodic nanostructures on the laser pulse number under a fixed pulse energy.

electron plasma wave could couple with the incident light wave only if it propagates in the plane of light polarization. Initial coupling is produced by inhomogeneities resulted from electrons' moving in the plane of light polarization, which leads to the initial period distribution of the electron plasma concentration orientation parallel to the light polarization.[18] According to other early studies, if the electric field intensity does not exceed certain threshold, the structure of initial period distribution can be maintained without the risk of rupture.[19] However, when the electric field intensity exceeds certain threshold, the further coupling is adequately increased by a periodic structure created via a pattern of interference between the incident light field and the electric field of the bulk electron plasma wave, resulting in the periodic modulation of the electron plasma concentration and the periodic structures oriented perpendicular to the light polarization.[18] Therefore, we have reason to consider this the ripple-like nanostructure oriented parallel to the light polarization was generated by the initial period distribution of the electron plasma concentration.

Figure 2(a) demonstrates a cross produced by two mutually perpendicular beams with scanning speeds of 10000 μm/s and laser power of 0.016 μJ. A closer observation shows that there are distinct morphologies in different ablation areas: the arms and the intersection. The same regular ripple-like nanostructures [as shown in Figs. 2(b) and 2(c)] with a periodicity of 91 nm exist in two arms areas, and the orientation of these ripple-like nanostructures are invariably parallel to the laser polarization. This result further confirms that the ripple orientation is strictly determined by the polarization of the incident laser. Figure 2(d) shows a net-like nanostructure fabricated in the two-beam overlapping area. The net-like structure can be referred to as the consequence of intercrossing of two orthogonal ripple-like nanostructures. This means that the morphological characteristics of the corresponding ripple-like nanostructure induced by the beam with a certain polarization can be maintained in the ablation using the two-beam alternate ablation process.

We found the period of ripple-like nanostructure is reversely related to the laser pulse number, as shown in **Fig. 3**. Under same pulse energy of 8×10^{-3} μJ, the periods of 108, 96, and 85 nm are observed for the number of laser pulses of 31, 61, and 102 corresponding to the scanning speeds of 10000, 5000, 3000 μm/s respectively. While fixing laser pulses number, the dependence of

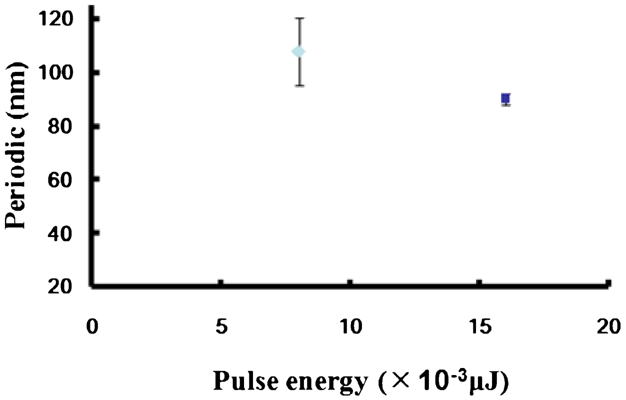

Fig. 4. (Color online) The dependence of the observed periodic nanostructures on the pulse energy under a fixed laser pulses number.

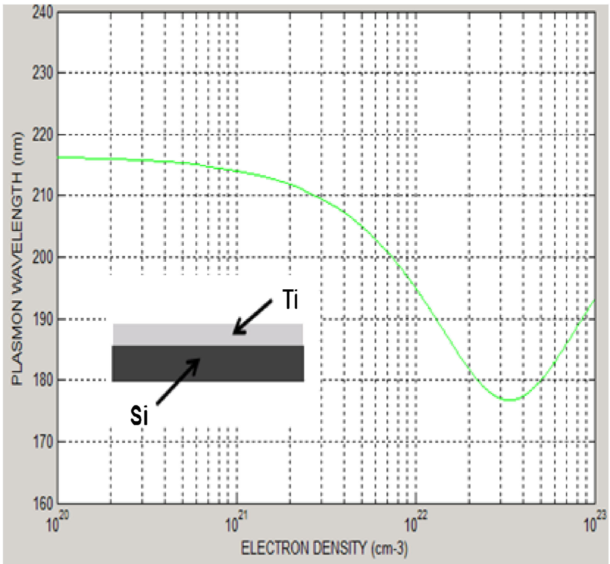

Fig. 5. (Color online) Plasmon wavelength calculated as a function of electron density for the Ti/Si interface.

the observed periodic nanostructures on pulse energy reveals, shown in **Fig. 4**, that the periods drop with the decrease of pulse energy. Periods of 108, and 91 nm were measured at pulse energies of 8×10^{-3} μJ and 16×10^{-3} μJ, respectively, with a fixed number of laser pulses of 31.

For the simple Drude model[20] in which the damping is ignored, ε_1 in the laser field is given by

$$\varepsilon_1 = \varepsilon_0 \times \left[\varepsilon_{\mathrm{Ti}} - \left(\frac{\omega_{\mathrm{p}}{}^2}{\omega^2}\right)\right] \quad (1)$$

Where ε_0 and ε_1 are the dielectric constants of vacuum and the Ti thin layer including the effect of free electrons. And the $\varepsilon_{\mathrm{Ti}}$ is the static relative dielectric constant of Ti with $\varepsilon_{\mathrm{Ti}} = \mathrm{I} \times 25.7 - 5.78$,[21] and the ω is the angular frequency of the laser, respectively. The plasma frequency ω_{p} is given by

$$\omega_{\mathrm{p}} = \left[\frac{e^2 N_{\mathrm{e}}}{\varepsilon_0 m}\right]^{\frac{1}{2}} \quad (2)$$

where e is electron charge and m is mass.

The free electrons are predominantly produced in the Ti thin layer to induce a large change in ε_1. For simplicity, we assume that the film surface before ablation consists of two layers of the upper Ti and the lower Si, as illustrated in the inset of **Fig. 5**. When the surface is weakly corrugated through laser ablation, the surface Plasmon polarizations can be excited at the interfaces between the Ti and Si. The dispersion relation k_{sp} satisfied for the surface Plasmon polarizations excitation was given by

$$k_{\mathrm{sp}} = k_0 \left[\frac{\varepsilon_{\mathrm{a}}\varepsilon_{\mathrm{b}}}{\varepsilon_{\mathrm{a}} + \varepsilon_{\mathrm{b}}}\right]^{\frac{1}{2}} \quad (3)$$

where k_{sp} and k_0 are the wave vectors of the surface plasmon and the incident light in vacuum,[22] respectively, and ε_{a} and ε_{b} are the relative dielectric constants of two layers concerned. We calculated λ_{sp} for the Ti/Si interface, using $\varepsilon_{\mathrm{a}} = \varepsilon_1/\varepsilon_0$ for the Ti and $\varepsilon_{\mathrm{b}} = \varepsilon_2 = 13.67 + \mathrm{I} \times 0.05$ for the Si.[23] Figure 5 shows the results of λ_{sp} calculated as a function of N_{e} in the Ti layer. It is noted that the estimated electron density Ne leads to λ_{sp} (176–216 nm) for the Ti/Si interface, The local ablation would be initiated at a period d $\sim \lambda_{\mathrm{sp}}/2$ with the help of the local field periodically enhanced by the surface Plasmon polarizations. The period d (88–108 nm) calculated for the Ti/Si interface is in almost agreement with the observed size of nanostructure.

4. Conclusion

In conclusion, periodic nanostructures were controlled fabricated on the Ti thin film surface after irradiation. We also found that, on the ablated Ti thin film surfaces, the linearly polarized femtosecond laser pulses produce arrays of ripple-like periodic nanostructures which are oriented to the direction parallel to the laser polarization, and a net-like nanostructure was fabricated on the surface of Ti thin film by a technique of two linearly polarized femtosecond laser beams with orthogonal polarizations ablating material alternately. And then the period of self-organized ripple-like nanostructures would be controlled by the pulse energy and the number of irradiated pulses. The estimated field period was almost in agreement with the observed size of nanostructures.

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