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Evolution of microstructures on silicon induced by femtosecond laser with multiple pulses

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The effect of multiple pulses of Ti:sapphire femtosecond laser system on silicon wafer was investigated. Using the pulse energy exceed the threshold of silicon to investigate the evolvement of structures and found that exceed certain fluence no any periodic structure will appearance. For 1.91 J/cm^2, the pattern of columnar structure was formed in the central region of irradiation area. In further experiment, using the subthreshold multiple pulse femtosecond laser irradiation of 0.91 J/cm^2, the periodic ripple structures and nanohole array were presented in the whole irradiation area due to the incubation effection. Also, we obtained the threshold of nanohole array to be higher than that of the periodic ripple structures.

Keywords: femtosecond laser, evolvement, ripples, subthreshold, silicon.

1. Introduction

Nanostructuring of a variety of materials is gaining widespread importance owing to ever increasing applications of nanostructures in numerous fields. Silicon is an important material in the semiconductor industry and useful for microelectromechanical system (MEMS) devices. The laser processing of silicon has received significant attention in the last several decades because of its potential in a micromachining application. Laser-induced surface structuring in silicon has been extensively studied [1–5]. Compared to the long-pulse laser [6, 7], ultrashort pulsed laser radiation has been shown to be highly effective for precision material processing and surface micromodification due to minimal thermal and mechanical damage in various materials; in addition to these advantages, periodic nanostructures were self-organized in the femtosecond laser irradiated area [8–10]. Recently, the formation of microstructures (ripples, columns, and cones) on Si samples in the case of multiple pulse irradiations on stationary samples has been reported by several research groups [11].

Ripples or, in general, laser-induced periodic surface structures (LIPSS) have been observed substantially near the ablation threshold. Several mechanisms for the formation of ripples have been proposed, the acoustic wave mechanism [12, 13], surface tension gradient [14], interference between the incident light/surface wave and the boson condensation hypothesis [15]. The theory of interference between the incident light/surface wave was the most popular mechanism to interpret the formation of the periodic ripple structures [16]. The dependence of spacing of periodic ripples $\Lambda = \lambda/(1 \pm \sin\theta)$ has been found, where the plus and the minus refer to the downwards and upwards running surface wave on the inclined surface and the θ is the angle of incidence laser. Usually, LIPSS shows a regular groove structure with the period of incidence laser wavelength scale and the orientation of ripples is perpendicular to the polarization of the incident light. However, it was reported recently that nanostructures with period much shorter than the laser wavelength were formed on sample surfaces after irradiation with femtosecond laser pulses [17–19].

In this paper, we perform a detailed study of surface structures produced by femtosecond laser treatment of silicon surfaces. In order to investigate the dependence of the nanostructures on the number of the laser pulses and the pulse energy, a silicon (100) plate was irradiated by the femtosecond laser in the range of 1 to 1000 pulse, with the fluence in the range of 0.5–4 J/cm^2. New characteristics on the morphologies of silicon, such as a laser-induced periodic structure and the array holes were discussed.

2. Experimental setup

A global scheme is depicted in Fig. 1. In this experiment, we use an amplified Ti:sapphire laser system based on the chirped pulse amplification technique that generates 130 fs laser pulses at a 1 kHz repetition rate and with a central wavelength $\lambda = 800$ nm. The spatial profile of the beam is nearly Gaussian. The laser is running at a repetition rate of $f = 1$ kHz. The energy output was continuously controlled by an energy attenuator. A power meter is used to measure the average power of the pulses generated. Using a delay generator (Stanford Research, DG535) to control the interval time of femtosecond laser, then the number of pulses can be controlled accurately, we selected a predefined number N of pulses per spot (1, 10, 50, 200, 1000). The laser beam was focused on the surface of the specimen which was mounted on a computer-

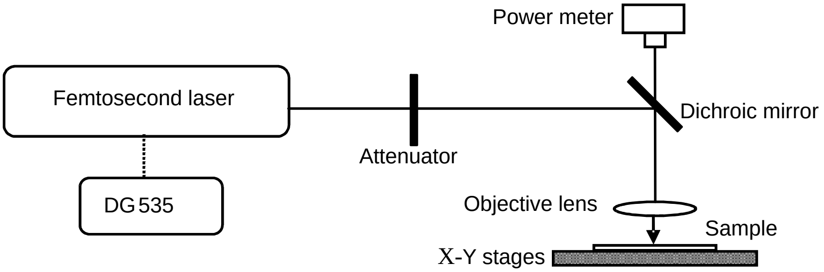

Fig. 1. Schematic diagram of the experimental setup.

-controlled *x*–*y* translation stage with a fused silica lens with 200-mm focal length. The silicon wafer, with a thickness of 400 μm, was subjected to different pulse fluences and different pulse number. All experiments were performed in air at normal incidence. The morphology of the periodic structures produced was examined using a scanning electron microscope (SEM) without further treatment.

3. Results and discussion

For a Gaussian spatial beam profile with a $1/e^2$ beam radius ω_0 being about 21.2 μm, which we had reported previously [20], the maximum laser fluence at the cross-sectional surface ϕ_0 is proportional to the incident laser pulse energy E which could be obtained as the following equation $\phi_0 = 2E/\pi\omega_0^2$. In this experiment, the pulse energies were: 70 μJ, 135 μJ, 200 μJ, 240 μJ, 325 μJ, with the respective fluence being 0.9 J/cm^2, 1.91 J/cm^2, 2.84 J/cm^2, 3.4 J/cm^2, 4.51 J/cm^2. COYNE *et al.* [21] analyzed the interaction of ultrashort pulses with wafer-grade silicon in air using an optical and electron microscope and suggested that the optimum fluence condition for precise and accurate machining of silicon is in the range of 0.8–1.5 J/cm^2.

Figure 2 shows the microphotographs of structure in the irradiation area at the pulse number of one with different pulse fluence. Images have been taken directly after processing without further cleaning. For a single laser pulse, surface damage morphology could be detected when the processed region was observed under SEM, it is due to the pulse energy exceeding the threshold of the silicon. As Fig. 2**a** shows, the irradiation area could be divided into three regions which was coincident with the energy distribution of Gauss pulse. Compared to Fig. 2**a**, with an increase of the pulse fluence, the ablated area was larger than the previous ones, as shown in Figs. 2**b**–2**d**. Figure 2**e** was the image of the silicon surface without any radiation.

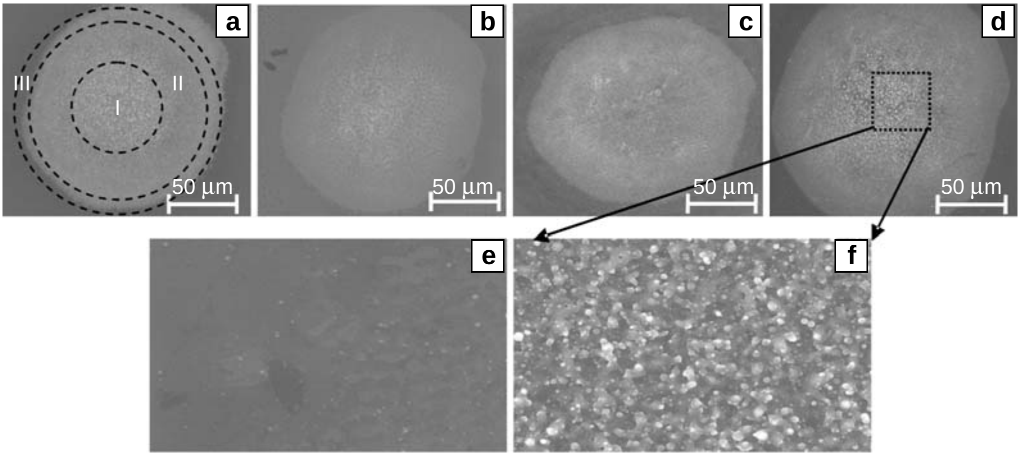

Fig. 2. SEM micrographs of the irradiation area at the pulse number of one with different pulse fluence, 1.91 J/cm^2 (**a**), 2.84 J/cm^2 (**b**), 3.4 J/cm^2 (**c**), 4.51 J/cm^2 (**d**), the surface of silicon unirradiated with laser pulse (**e**), magnified microstructure of central irradiation area of **d** (**f**).

Figure 2**f** was the magnified microstructure of central irradiation area of Fig. 2**d**. It is obvious that there was a raindrop-like structure in region I and not any periodic characteristic.

Figure 3 shows SEM micrographs of the irradiation area at the pulse number of 10, 50, 200, 1000 with different pulse fluence of 1.91 J/cm^2, 2.84 J/cm^2, 3.4 J/cm^2, 4.51 J/cm^2, respectively. Along the level axes, the evolution of the structure depending on the pulse energy was obvious when with a fixed pulse number. Along the perpendicularity axes, it is the evolution of the structure as a function of the pulse number with pulse energy unvaried. Along the perpendicularity axes, the first list of Fig. 3 was

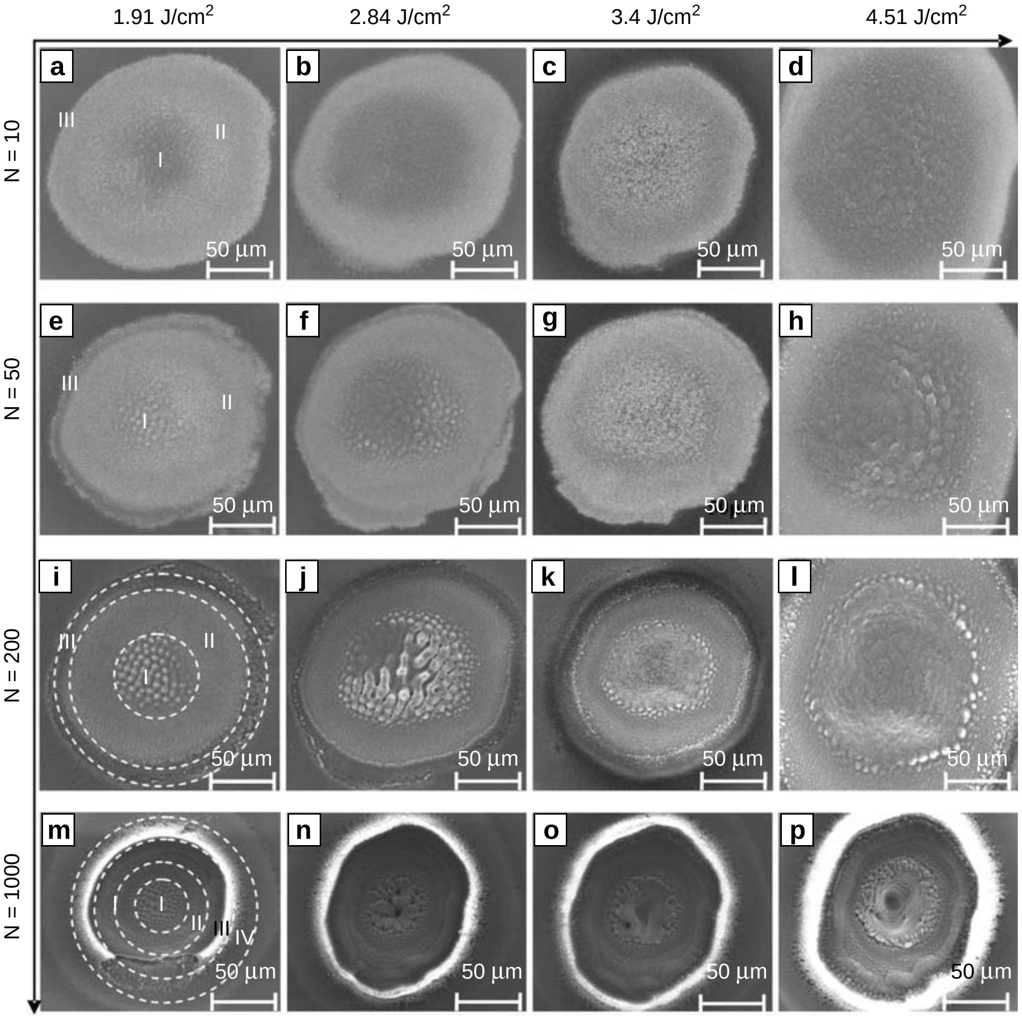

Fig. 3. SEM micrographs of the irradiation area at the pulse number of 10, 50, 200, 1000 with different pulse fluence of 1.91 J/cm^2, 2.84 J/cm^2, 3.4 J/cm^2, 4.51 J/cm^2, respectively.

obtained with pulse fluence of 1.91 J/cm^2 and the pulse number was 10, 50, 200, 1000. It is obvious that with an increase of the pulse number the structure in the radiation area was varied. As Figs. 3**i** and 3**m** show, in region I, the columnar structure was formed. Column formation in crystalline silicon was observed in the past with different pulse duration, laser fluence, and ambient environment.

In recent work [22] on femtosecond laser with crystalline silicon, sharp spikes were observed when the material was irradiated in SF_6 or Cl_2 environment but not in vacuum, N_2 or He. The chemical reactions were suggested to be essential for formation of sharp spikes [22]. In region II of Fig. 3**i**, at the periphery there were many periodic ridge structures covered with periodic ripple structures. When increasing the pulse number to 1000, the structure of region II was more evident, and region IV produced oxidation and crack, as Fig. 3**m** shows. It is obvious that the area of region I was enhanced with decreasing the area of region II when the pulse energy or pulse number was increased as shown in Fig. 3. It is interesting that with increasing the pulse number the evolution of the structures occurred. However, with increasing the pulse fluence and keeping the pulse number constant, the structure in the central area of radiation was ablated gradually. The surface damage in Fig. 3 at different pulse fluences shows the incubation effect, *i.e.*, accumulation of energy, in material when irradiated with multiple pulses. This effect was observed in many materials for nanosecond, picosecond and femtosecond lasers [23–25]. JHEE *et al.* [26] observed this incubation effect on silicon irradiated with picosecond laser pulses. They suggested that damage precursors by multiple pulses were due to the long-lived excitations or accumulation of permanent states. They showed that there existed a multiple pulse damage threshold or fatigue limit below which no damage was supposed to occur even at an infinite number of laser pulses. In our experiment, the fluence exceeded the threshold of the silicon, with the incubation effect, there were no classical ripple structures (LIPSSs) in the radiation area. Also, with the pulse fluence exceeding 3.4 J/cm^2, regardless of the pulse number, there were not any periodic structures in the radiation area as shown in Figs. 3**c**, 3**g**, 3**k**, 3**o** and 3**d**, 3**h**, 3**l**, 3**p**.

Figure 4 shows the SEM micrographs of the irradiation area at the laser fluence of 0.91 J/cm^2 with different pulse number. In this experiment, the pulse energy was less than the threshold. For a single pulse, we did not observe any surface damage in the processed region on the silicon surface using SEM. Due to the incubation effect, with an increase in the pulse number to 100, there is a periodicity parallel ripple structure covered with nanohole array, which can be seen in Fig. 4**a** and the magnified image Fig. 4**h** of Fig. 4**a**. With increasing the pulse number, in the centre of the radiation area, the nanohole structures became more evident, and at the same time, the ripple structure disappeared gradually. These results indicate that the threshold of the laser fluence for the parallel periodic ripple structures formation was lower than that for periodic array nanoholes. With the classical theory of ripple formation [16] a good accuracy is achieved in forecasting periodic ripple structures formation. LIPSSs could be very simply interpreted as being produced by the interference between

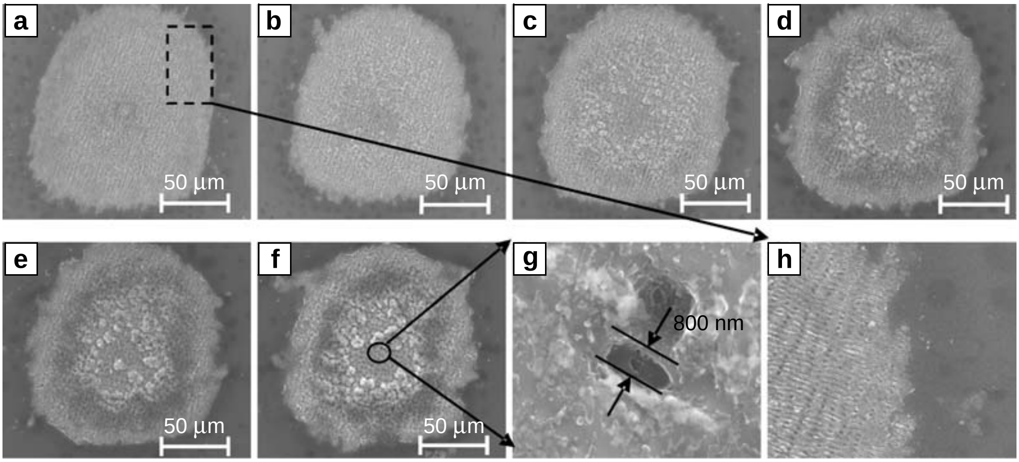

Fig. 4. SEM micrographs of the irradiation area at the laser fluence of 0.91 J/cm^2 with different pulse number 100 (**a**), 200 (**b**), 400 (**c**), 600 (**d**), 800 (**e**), 1000 (**f**); the magnified image of **f** (**g**); the magnified image of **a** (**h**).

the refracted radiation and the scattered waves parallel to the surface propagating in opposite direction. However, this theory cannot be applied in our case for results of nanohole array structures. Although there are many theories which explain how nanostructures are induced with ulrashort pulses, the formation mechanism of periodic nanhole has not been elucidated yet.

4. Conclusions

In this paper, we investigated the femtosecond laser-produced microstructures on the silicon surface. We studied the effect of pulse energy and pulse number on the formation of microstructure. Using the pulse energy exceeding the threshold of silicon to investigate the evolvement of structures we found that exceeding certain fluence no any periodic structure was present. For 1.91 J/cm^2, the pattern of columnar structure was formed in the central region of irradiation area. With further experiment, using the subthreshold multiple pulse femtosecond laser irradiation of 0.91 J/cm^2, the periodic ripple structures and nanohole array were presented in the whole irradiation area due to the incubation effection. Also, we have found that the threshold of nanohole array was higher than that of the periodic ripple structures. This is favorable for the formation of a certain kind of nanostructures.

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References

[1] Pedraza A.J., Fowlkes J.D., Lowndes D.H., *Self-organized silicon microcolumn arrays generated by pulsed laser irradiation*, Applied Physics A **69**(7), 1999, pp. S731–S734.

[2] Hommes V., Miclea M., Hergenröder R., *Silicon surface morphology study after exposure to tailored femtosecond pulses*, Applied Surface Science **252**(20), 2006, pp. 7449–7460.

[3] Bärsch N., Körber K., Ostendorf A., Tönshoff K.H., *Ablation and cutting of planar silicon devices using femtosecond laser pulses*, Applied Physics A **77**(2), 2003, pp. 237–242.

[4] Her T.H., Finlay R.J., Wu C., Mazur E., *Femtosecond laser-induced formation of spikes on silicon*, Applied Physics A **70**(4), 2000, pp. 383–385.

[5] Crouch C.H., Carey J.E., Warrender J.M., Aziz M.J., Mazur E., Génin F.Y., *Comparison of structure and properties of femtosecond and nanosecond laser-structured silicon*, Applied Physics Letters **84**(11), 2004, pp. 1850–1852.

[6] Petö G., Karacs A., Pászti Z., Guczi L., Divinyi T., Joób A., *Surface treatment of screw shaped titanium dental implants by high intensity laser pulses*, Applied Surface Science **186**(1–4), 2002, pp. 7–13.

[7] Trtica M., Gakovic B., Batani D., Desai T., Panjan P., Radak B., *Surface modifications of a titanium implant by a picosecond Nd:YAG laser operating at 1064 and 532 nm*, Applied Surface Science **253**(5), 2006, pp. 2551–2556.

[8] Bonse J., Wrobel J.M., Krüger J., Kautek W., *Ultrashort-pulse laser ablation of indium phosphide in air*, Applied Physics A **72**(1), 2001, pp. 89–94.

[9] Borowiec A., Haugen H.K., *Subwavelength ripple formation on the surfaces of compound semiconductors irradiated with femtosecond laser pulses*, Applied Physics Letters **82**(25), 2003, pp. 4462–4464.

[10] Kautek W., Rudolph P., Daminelli G., Krüger J., *Physico-chemical aspects of femtosecond-pulse-laser-induced surface nanostructures*, Applied Physics A **81**(1), 2005, pp. 65–70.

[11] Costache F., Kouteva-Arguirova S., Reif J., *Sub-damage-threshold femtosecond laser ablation from crystalline Si: Surface nanostructures and phase transformation*, Applied Physics A **79**(4–6), 2004, pp. 1429–1432.

[12] Gorodetsky G., Kanicki J., Kazyaka T., Melcher R.L., *Far UV pulsed laser melting of silicon*, Applied Physics Letters **46**(6), 1985, pp. 547–549.

[13] Anthony T.R., Cline H.E., *Surface rippling induced by surface-tension gradients during laser surface melting and alloying*, Journal of Applied Physics **48**(9), 1977, pp. 3888–3894.

[14] Zhou Guosheng, Fauchet P.M., Siegman A.E., *Growth of spontaneous periodic surface structures on solids during laser illumination*, Physical Review B **26**(10), 1982, pp. 5366–5381.

[15] Jincheng Wang, Chunlei Guo, *Ultrafast dynamics of femtosecond laser-induced periodic surface pattern formation on metals*, Applied Physics Letters **87**(25), 2005, p. 251914.

[16] Ozkan A.M., Malshe A.P., Railkar T.A., Brown W.D., Shirk M.D., Molian P.A., *Femtosecond laser-induced periodic structure writing on diamond crystals and microclusters*, Applied Physics Letters **75**(23), 1999, pp. 3716–3718.

[17] Reif J., Costache F., Henyk M., Pandelov S.V., *Ripples revisited: Non-classical morphology at the bottom of femtosecond laser ablation craters in transparent dielectrics*, Applied Surface Science **197–198**, 2002, pp. 891–895.

[18] Le Harzic R., Schuck H., Sauer D., Anhut T., Riemann I., König K., *Sub-100 nm nanostructuring of silicon by ultrashort laser pulses*, Optics Express **13**(17), 2005, pp. 6651–6656.

[19] Venkatakrishnan K., Tan B., Stanley P., Lim L.E.N., Ngoi B.K.A., *Femosecond pulsed laser direct writing system*, Optical Engineering **41**(6), 2002, pp. 1441–1445.

[20] Yuan D.Q., Zhou M., Cai L., Shen J., *Micromachining of Au film by femtosecond pulse laser*, Spectroscopy and Spectral Analysis **29**(5), 2009, pp. 1209–1212.

[21] COYNE E., MAGEE J.P., MANNION P., O'CONNOR G.M., *Study of femtosecond laser interaction with wafer-grade silicon*, Proceedings of SPIE **4876**, 2003, p. 487.

[22] HER T.H., FINLAY R.J., WU C., DELIWALA S., MAZUR E., *Microstructuring of silicon with femtosecond laser pulses*, Applied Physics Letters **73**(12), 1998, pp. 1673–1675.

[23] BONSE J., BRZEZINKA K.W., MEIXNER A.J., *Modifying single-crystalline silicon by femtosecond laser pulses: An analysis by micro Raman spectroscopy, scanning laser microscopy and atomic force microscopy*, Applied Surface Science **221**(1–4), 2004, pp. 215–230.

[24] FAUCHET P.M., *Gradual surface transitions on semiconductors induced by multiple picosecond laser pulses*, Physics Letters A **93**(3), 1983, pp. 155–157.

[25] SMIRL A.L., BOYD I.W., BOGGESS T.F., MOSS S.C., VAN DRIEL H.M., *Structural changes produced in silicon by intense 1 μm ps pulses*, Journal of Applied Physics **60**(3), 1986, pp. 1169–1182.

[26] JHEE Y.K., BECKER M.F., WALSER R.M., *Charge emission and precursor accumulation in the multiple-pulse damage regime of silicon*, Journal of the Optical Society of America B **2**(10), 1985, pp. 1626–1633.

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