Vol 17 No 4, April 2008
1674-1056/2008/17(04)/1223-04

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Femtosecond pulse laser-induced self-organized nanostructures on the surface of ZnO crystal*

Zhong Min-Jian(钟敏建)[a)b)], Guo Guang-Lei(郭广磊)[a)], Yang Jun-Yi(杨俊毅)[a)], Ma Ning-Hua(马宁华)[a)], Ye Guo(叶 果)[a)], Guo Xiao-Dong(郭晓东)[c)], Li Ru-Xin(李儒新)[c)], and Ma Hong-Liang(马洪良)[a)b)†]

[a)] *Department of Physics, Shanghai University, Shanghai* 200444, *China*
[b)] *Instrumental Analysis and Research Center, Shanghai University, Shanghai* 200444, *China*
[c)] *State Key Laboratory of High Field Laser Physics, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai* 201800, *China*

(Received 14 June 2007; revised manuscript received 20 June 2007)

This paper reports self-organized nanostructures observed on the surface of ZnO crystal after irradiation by a focused beam of a femtosecond Ti:sapphire laser with a repetition rate of 250 kHz. For a linearly polarized femtosecond laser, the periodic nanograting structure on the ablation crater surface was promoted. The period of self-organization structures is about 180 nm. The grating orientation is adjusted by the laser polarization direction. A long range Bragg-like grating is formed by moving the sample at a speed of 10 μm/s. For a circularly polarized laser beam, uniform spherical nanoparticles were formed as a result of Coulomb explosion during the interaction of near-infrared laser with ZnO crystal.

Keywords: infrared femtosecond laser, ZnO crystal, nanograting, nanostructure
PACC: 3380K, 4280F

1. Introduction

Ultra-short pulsed laser radiation has been shown to be highly effective for precision material processing and surface micro-modification. During the last decades, special interest was paid to the potential of ultrashort laser pulses with durations in the picosecond to femtosecond domain with respect to laser-induced phase transitions[1−4] as well as the nanostructures,[5−8] precision material processing and surface micro-modification. The femtosecond laser can be used to generate a number of nonlinear effects by multiphoton absorption and avalanche ionization in the focusing area of materials. It was reported recently that nanostructures with period much shorter than the laser wavelength were formed on sample surface after irradiation with femtosecond laser pulses.[5−9] ZnO crystal, as an important material for the semiconductor industry, presents some specific characteristics when irradiating with ultra-short laser pulses at low fluence. Spontaneous nanostructure is observed. We present in this paper results of nanostructures obtained in air at a wavelength of 800 nm, a repetition rate of 250 kHz and a fluence of 0.5J/cm^2. We produce long-range Bragg-like nanogratings with period spacing of 180 nm for a linearly polarized femtosecond laser beam and uniform spherical nanoparticles with diameter of 150 nm for a circularly polarized laser beam by slowly scanning the crystal under a fixed laser focus.

2. Experiment

Figure 1 shows the experimental setup. Our experiments used a commercial regenerative Ti:sapphire laser system (RegA 9000, Coherent) with 120 fs, 800 nm pulses containing a peak energy of up to 6 μJ. A mechanical shutter was used to select laser pulses from a pulse-train with a repetition rate of 250 kHz. The Gaussian laser pulses were focused onto the surface of the sample with a spot size of approximately 2 μm by using an optical microscope (Olympus BX51) with a 20× objective lens and a numerical aperture of 0.46. We varied the average output power by at-

*Project supported by the Shanghai Leading Academic Discipline Project (Grant No T0104), the Shanghai Nano-technology Promotion Center and Science & Technology of Shanghai Municipality (Grant No 0652nm005) and Innovation Fund of Shanghai University, China.
†Corresponding author. E-mail: mahl@staff.shu.edu.cn

tenuating the laser beam with an absorptive neutral density filter. A $\frac{\lambda}{4}$ waveplate followed by a Glan polarizer was used to adjust the laser polarization direction. ZnO crystal polished on both sides was mounted on a motorized xyz-translation stage and positioned perpendicular to the direction of laser incidence. After irradiation, the surface morphology was examined under a scanning electron microscope (SEM) (JSM-6700F JEOL).

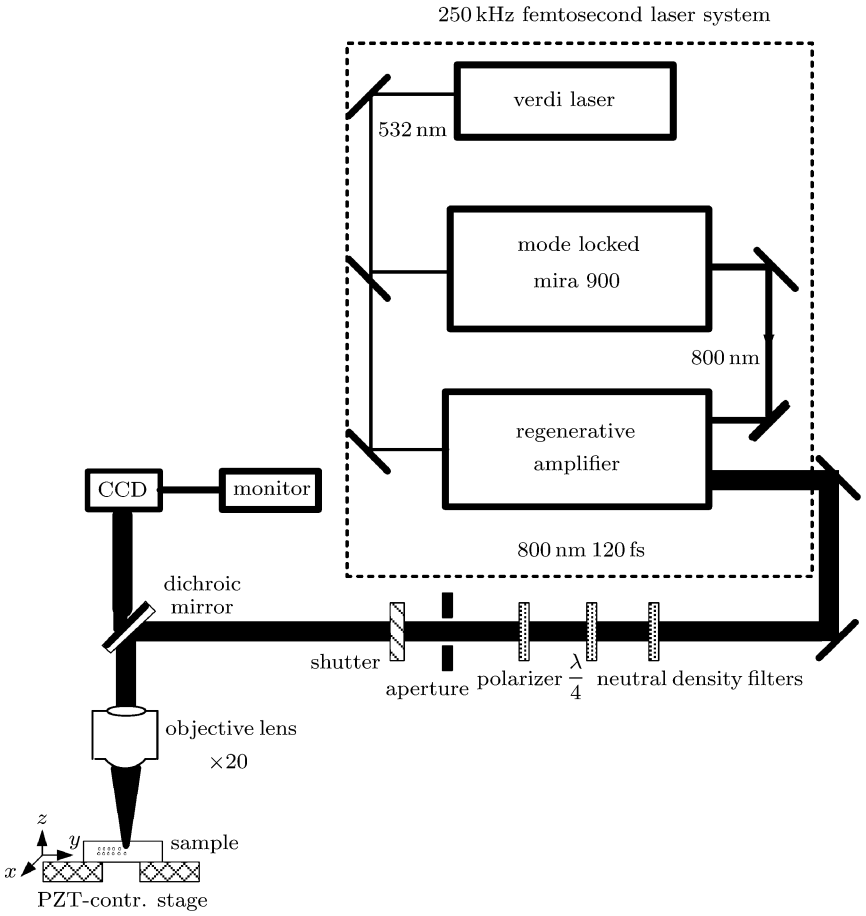


Fig.1. Schematic diagram of experimental setup.

3. Experimental results and discussion

SEM images of ZnO crystal surface after irradiation with 800 nm, 120 fs pulse laser in air with a 20× focusing objective are shown in Fig.2. Self-organized nanostructures are formed at the laser- irradiated craters. For a P-polarized femtosecond laser beam, the periodic nanogratings were perpendicular to the direction of laser polarization. The nanograting orientation rotates with laser polarization at 0° (a), 45° (b), and 90°(c). We observed that the grating period is around 180 nm. The orientation of nanogratings is perpendicular to the laser polarization direction. For a circularly polarized laser beam, uniform spherical nanoparticles, with diameter of 150 nm, is observed in Fig.2(d). We demonstrate directly that changing the polarization direction of the laser controls the orientation of the nanogratings.

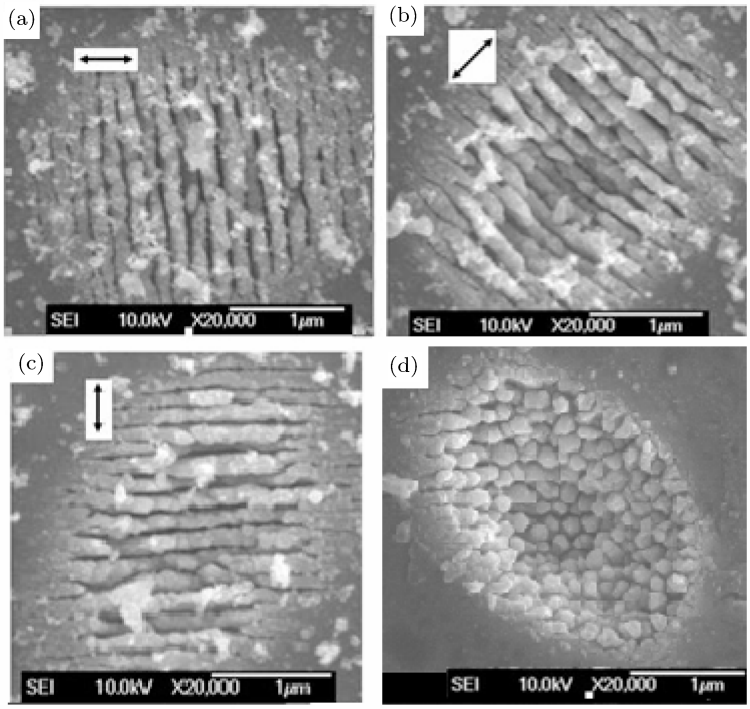


Fig.2. SEM images of the self-organized nanostructures of the irradiated craters formed in air after laser irradiation (250 kHz, 120 fs, 800 nm). The rotation of the nanograting direction with linearly polarized laser polarization at 0° (a), 45° (b), and 90° (c), its polarization direction is shown by the arrow. (d) For a circularly polarized laser beam.

In order to further observe the nanostructures on the crystal surface induced by a linearly polarized laser beam and a circularly polarized laser beam, respectively, we tried to move the focal position of the femtosecond laser continuously by moving the ZnO crystal on the motorized xyz-translation stage. One line writing scan was performed at a scan speed of 10 μm/s and an energy pulse of 15 nJ. A fluence of approximately 0.5 J/cm^2 was achieved. Images have been taken directly after processing without further cleaning. Some recast or melted matter is observed on the sides of the channel. Figure 3(a) presents periodic structures known as ripples formed after linearly polarized laser. The average nanograting period is 180 nm±10 nm. Figure 3(a) shows a SEM image (viewed from the top of the sample) of modified planes obtained with laser polarization directed at 45° to the scan direction. A long-range grating pattern is formed over the entire 1mm writing range. The nanograting orientation is tilted with their normal aligned to the polarization direction. Figure 3(b) is a SEM image of modified plane obtained for circularly polarized laser. A long-range of uniform spherical nanoparticles is evident. The diameter is about 150 nm.

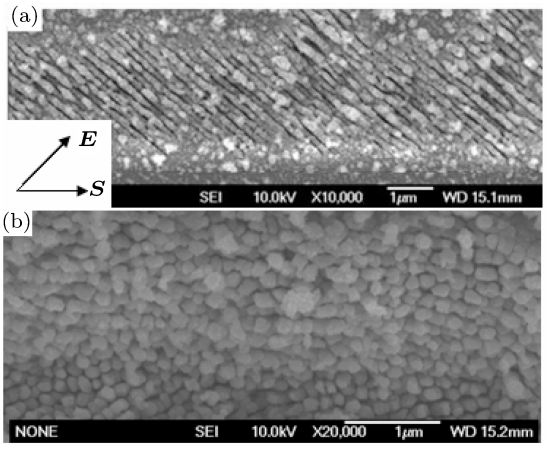


Fig.3. SEM images (viewed from top of the sample) of the long-range modified regions, (a) for a P-polarization laser beam with laser polarization $\boldsymbol{E}$ at 45° with respect to the scan direction $\boldsymbol{S}$, (b) for a circularly polarized laser beam.

For a linearly polarized laser beam, the nanogratings shown in Figs.2 and 3 are with same spatial periods. The formation of the nanograting is attributed to the interference between the surface scattered wave of 800 nm lasers and the scattered light.[10] For normal incident laser beam, the grating period Λ is $\Lambda = \lambda/2n \approx$182 nm ($\lambda$=800 nm, the fundamental laser wavelength; n =2.2 for 800 nm light, the refractive index of ZnO). For a circularly polarized laser beam, we observed the formation of uniform nanoparticles on ZnO crystal. Coulomb explosion is proposed to be responsible for the formation of nanoparticles.[11,12] The 'gentle' ablation was initiated by the two-photon absorption and dominated by Coulomb explosion.[13] The modification of crystal structure is attributed to lattice arrangement resulted from lattice heating accompanying Coulomb explosion.[11,12] The ultrafast laser pulse induces a repulsive electrostatic field, consisting of uncompensated positive charges due to the emission of electrons on the surface. The neutralization of positive charges directly ejects charges and indirectly ejects neutrals due to collision.

In conclusion, self-organized periodic nanostructures are observed on the surface of ZnO after irradiation by a focused linearly laser beam. The orientation of the gratings is adjusted by the laser polarization direction. The period of self-organized grating structures is about 180 nm. The phenomenon is interpreted in terms of interference between the incident light field and the surface scattered wave of 800 nm laser pulses. The long-range Bragg-like gratings were formed by moving the crystal under a fixed laser focus. For a circularly polarized laser beam, uniform spherical nanoparticles were formed as a result of Coulomb explosion during the interaction of near-infrared with ZnO crystal.

References

[1] Shank C V, Yen R and Hirlimann C 1983 *Phys. Rev. Lett.* **50** 454

[2] Ge Y C 2006 *Chin. Phys.* **15** 2909

[3] Yan L X, Zhang Y S, Zheng G X, Liu J R, Cheng J P and Lu M 2006 *Chin. Phys.* **15** 2271

[4] Ma H L, Yang J Y , Lu B and Ma G H 2007 *Chin. Phys.* **16** 3328

[5] Shimotsuma Y, Kazansky P G, Qiu J and Hirao K 2003 *Phys. Rev. Lett.* **91** 47405

[6] Bonse J, Munz M and Sturm H 2005 *J. Appl. Phys.* **97** 013538

[7] Ozkan A, Malshe A, Railkar T, Brown W, Shirk M and Molian P 1999 *Appl. Phys. Lett.* **75** 3716

[8] Ma H L, Ye G, Zhong M J and Li R X 2007 *J. Appl. Phys.* A **89** 707

[9] Reif J, Costache F, Henyk M and Pandelov S 2002 *Appl. Surf. Sci.* **197** 891

[10] Borowiec A and Haugen H 2003 *Appl. Phys. Lett.* **82** 4462

[11] Huang L, Callan J P, Glezer E and Mazur E 1998 *Phys. Rev. Lett.* **80** 185

[12] Kash J A, Tsang J C and Hvam J M 1985 *Phys. Rev. Lett.* **54** 2151

[13] Guo X D, Li R X, Hang Y, Xu Z Z, Yu B K, Ma H L and Sun X W 2007 *Mater. Lett.* **23–24** 4583