Quantum Electronics **35** (10) 943 – 946 (2005)

PACS numbers: 42.65.Ky; 42.65.Re
DOI: 10.1070/QE2005v035n10ABEH013011

Third harmonic generation from a silicon surface structured by femtosecond laser pulses

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Abstract. **Periodic microstructures – ripples oriented perpendicular to the direction of radiation polarisation are produced by irradiating crystalline silicon with the (100) orientation of the surface by femtosecond laser pulses. The behaviour of the third-harmonic signal is studied in these microstructures. It is shown that the orientation dependences of the third-harmonic signal for optically induced ripples are determined by the morphology of the latter on the irradiated silicon surface, which allows the *in situ* diagnostics of these microstructures.**

Keywords: *femtosecond pulses, microstructuring, third harmonic generation, interaction of radiation with matter.*

Femtosecond laser irradiation is a promising method for processing solid surfaces because ablation causes only a weak thermal damage of the surface and produces a minimal amount of spatter and debris from a melt [1]. Precision laser drilling [2] and formation of two- and three-dimensional submicrostructures [3] are spectacular examples of the application of this technology for micromachining of materials. It is also known that by irradiating the surface of a solid by femtosecond laser pulses, it is possible to produce high-quality periodic microstructures on the surface due to interference of the incident and surface waves [4 – 8]. From the point of view of fundamental studies, the temporal separation between the interaction of laser radiation with matter and the appearance of phase transitions in the irradiated material makes femtosecond laser irradiation of solids important for understanding the electron – phonon interaction and studying nonequilibrium hydrodynamic processes in solids.

Of special interest is the formation of ordered microstructures on the silicon surface exposed to femtosecond laser pulses [6 – 8]. Silicon microstructures fabricated by various methods are promising for the development of new optical and electronic devices. The high birefringence of gap silicon structures [9] allows one to control, for example, a liquid on the surface of microstructure silicon [10]. Nonequilibrium processes during phase transitions in the near-surface region of silicon induced by femtosecond laser pulses can give rise to nanostructures, which opens up new possibilities for silicon optoelectronics and the development of silicon lasers [11]. In this connection the *in situ* control of structures being formed and the determination of the distribution of a local electromagnetic field on the microstructure silicon surface become urgent.

An efficient tool for detecting microstructures on the surface of crystalline silicon is the method of third harmonic generation (THG). Because the THG intensity is proportional to the six power of the local field strength near the surface, this method is very sensitive to variations in the local field on the anisotropic microstructure surface. This method was successfully used for determining the disorder and amorphous state of near-surface silicon layers [12 – 14]. Note also that THG is a local method. In this paper, we performed polarisation-sensitive measurements of a nonlinear-optical response during THG on the surface of anisotropic microstructure silicon.

Microstructuring of the silicon surface and its diagnostics were performed using THG in a laser system shown schematically in Fig. 1. Femtosecond output pulses of a 1.25-μm Cr^{4+} : forsterite master oscillator amplified in the stretcher – regenerative amplifier – compressor system were linearly polarised, had the 80-fs duration, ~250-μJ energy, and a repetition rate of 10 Hz. A half-wave plate and a Glan prism served as an optical attenuator to control the energy of a laser pulse incident on a sample, thereby passing from the regime of microstructure formation to the regime of THG diagnostics of nonlinear optical properties of microstructures. The intensity of radiation transmitted through this attenuator during microstructuring was maximal. Diagnostics was performed by reducing the intensity of incident laser pulses by an order of magnitude, when the sample surface was no longer modified.

Microstructures were produced by irradiating crystal silicon plates with the surface orientation (100) by femtosecond laser pulses. The normally incident laser beam was focused on a sample by a lens with a focal length of 5 cm. The light beam diameter on the irradiated surface was ~100 μm and the energy density was 3 J cm^{-2}. The exposure time was varied from a few seconds, when the appearance of an optically induced ripples was distinctly observed, up to 2 min. Microstructures with the maximum contrast of inhomogeneities were formed during irradiation

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Received 5 July 2005
Kvantovaya Elektronika **35** (10) 943 – 946 (2005)
Translated by M.N. Sapozhnikov

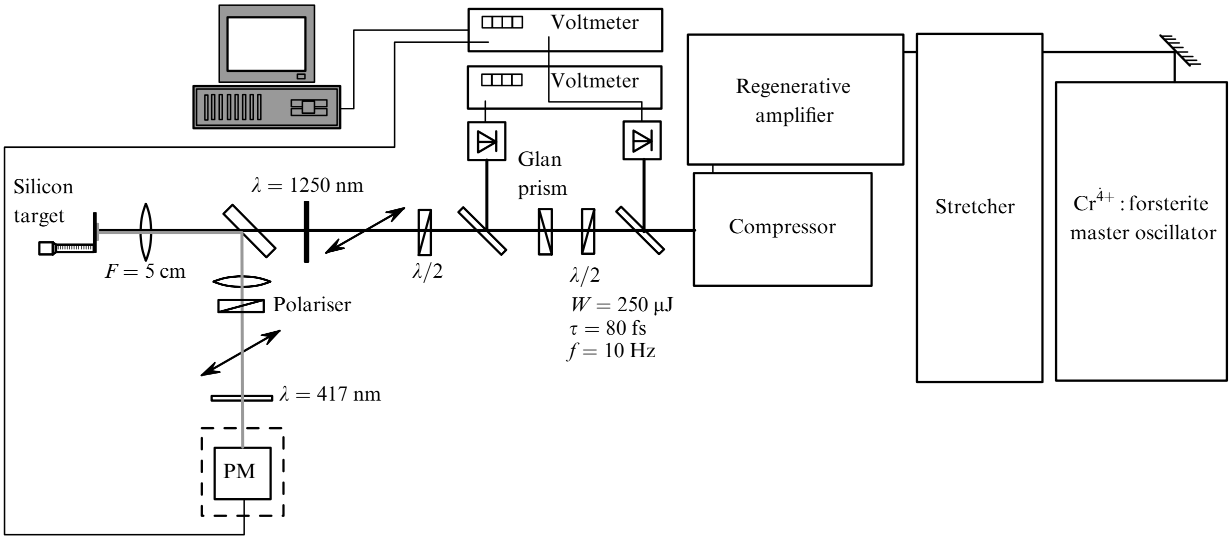

Figure 1. Experimental setup for the microstructure production and diagnostics by the THG method.

for 2 min (1200 pulses). After a longer exposure, microstructures were destructed and disappeared.

The data obtained in the THG regime were accumulated with an automated detection system consisting of a photomultiplier (PM), a photodiode controlling the pump, a synchronising avalanche photodiode, a PC, and two stroboscopic voltmeters (boxcars) for recording THG and pump pulses. To reduce the influence of intensity fluctuations on the detected THG signal, the latter was normalised to a factor proportional to the third power of the pump power. The orientation dependences of the THG signal were measured by rotating simultaneously the polarisation plane of the pump (by the half-wave plate) and a polariser for the third harmonic mounted in front of the photomultiplier so that the polarisation plane of the THG signal remained parallel to the polarisation plane of the pump radiation.

Figure 2 shows the typical scanning electron microscope image of the microstructure silicon surface irradiated by 1200 laser pulses. The optically induced ripples with a period of 1 μm is oriented perpendicular to the polarisation plane of laser radiation. The modulation depth of the ripples is also of about 1 μm. Our experiments showed that the rotation of the polarisation plane of structuring laser radiation causes the rotation of the ripples by the same angle irrespective of the initial crystallographic orientation of a sample. We also studied microstructuring of silicon with the surface orientation (110) and obtained similar results. Therefore, optically induced ripples are produced in our experiments by a periodically modulated interference light field near a sample surface [15].

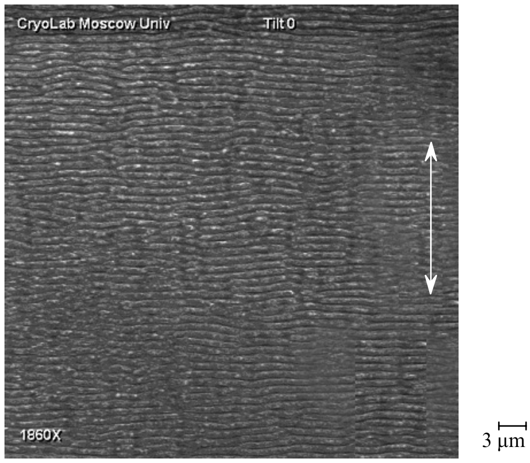

Figure 2. Scanning electron microscope image of the silicon surface irradiated by 1200 pulses. The direction of polarisation of structuring laser radiation is shown by the arrow.

We studied the formation dynamics of microstructures *in situ* by measuring the orientation dependences of the THG intensity obtained from the microstructure silicon surface at different exposure times. Typical orientation dependences for crystalline and microstructure silicon are presented in Fig. 3. The mutual arrangement of ripples and crystallographic axes for these dependences is shown in the insert in Fig. 3. The [010] and [001] crystallographic axes are oriented at an angle of ±45° to the direction of polarisation of structuring radiation, and the angle between the direction of the lines of ripples and the direction of polarisation of probe radiation is 135°. This geometry is most convenient for discriminating the components of the third harmonic generated by the microstructure and crystalline silicon itself.

The orientation dependence of the third-harmonic intensity for crystalline silicon (Fig. 3a) was approximated by a curve calculated according to the known dependence [12, 13]

$$I_{\mathrm{TH}}(\psi) \propto \left|(3+\cos 4\psi)\chi^{(3)}_{1111} + 3(1-\cos 4\psi)\chi^{(3)}_{1122}\right|^2. \quad (1)$$

Here, $\chi^{(3)}_{1111}$ and $\chi^{(3)}_{1122}$ are the components of the cubic susceptibility tensor; ψ is the angle between the $\langle 100 \rangle$; direction and the direction of polarisation of probe radiation. The ratio $\chi^{(3)}_{1122}/\chi^{(3)}_{1111}$, obtained from the analysis of orientation dependences of the third-harmonic intensity for crystalline silicon, is 0.54 ± 0.05, which is close to the values presented in [12].

Figures 3b–d show the orientation dependences for silicon periodic microstructures formed after irradiation by 100, 300, and 1200 pulses, respectively. One can see

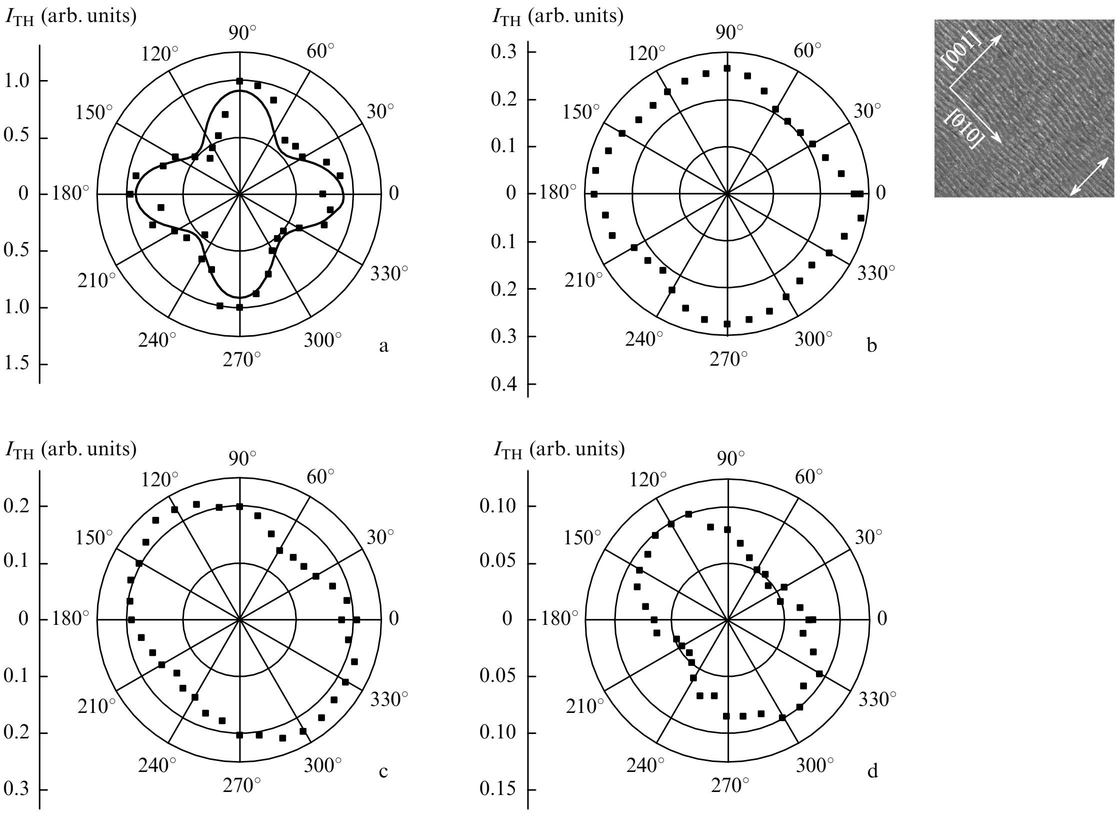

Figure 3. Orientation dependences of the third-harmonic intensity of crystalline silicon (a) and its microstructure surface after irradiation by 100 (b), 300 (c), and 1200 (d) pulses. The intensities are normalised to the maximum third-harmonic signal from crystalline silicon. The insert shows the directions of crystallographic axes and the direction of the optically induced ripples with respect to the direction corresponding to the zero angle.

that this dependence considerably changes with increasing number of pulses, while the third-harmonic intensity monotonically decreases. The four-lobe orientation dependence of the third-harmonic intensity for crystalline silicon (Fig. 3a), which is determined by the crystallographic orientation of a sample with respect to the direction of polarisation of structuring radiation, uniformly transforms to the two-lobe dependence (Figs 3c, d) with maxima in the direction perpendicular to the direction of polarisation of structuring radiation. Therefore, if silicon is irradiated for a minute (600 pulses) or longer, the shape of orientation dependences is determined only by the orientation of the ripples and is independent of the initial orientation of the crystallographic axes of the sample. The relation between the orientation dependences of the third-harmonic intensity and morphology of the surface of microstructure silicon becomes clear if we consider the distribution of a local field in the ripples.

The simplest model allowing the qualitative analysis of the situation under study is a set of periodic air and silicon strips (Fig. 4). Because THG in the air can be neglected, only silicon makes a contribution to the third-harmonic signal. Therefore, it is sufficient to consider THG from silicon layers. If the electromagnetic field $\boldsymbol{E}_0$ outside the microstructure is directed along the strips simulating the optically induced ripples, it remains unchanged inside a silicon layer, and $\boldsymbol{E}_{\parallel} = \boldsymbol{E}_0$ [16]. The situation is different if the external field $\boldsymbol{E}_0$ is oriented perpendicular to the ripples and the field inside the silicon layer is $\boldsymbol{E}_{\perp} = \boldsymbol{E}_0 - 4\pi\boldsymbol{P}$, where $\boldsymbol{P}$ is the polarisation vector. In this case, the local field inside silicon strips is weaker than the external field. We also assume that the nonlinear optical response from microstructure silicon strips is isotropic because of the formation of defects on the surface and its amorphisation [8, 13, 14]. The same effect, which reduces the nonlinear effect and increases the scattering, can explain the decrease in the third-harmonic intensity approximately by an order of magnitude after two-minute irradiation (1200 pulses). Therefore, the orientation dependence of the third-harmonic intensity is determined only by the distribution of the local field on the surface. Because $|\boldsymbol{E}_{\parallel}| = |\boldsymbol{E}_0|$ and

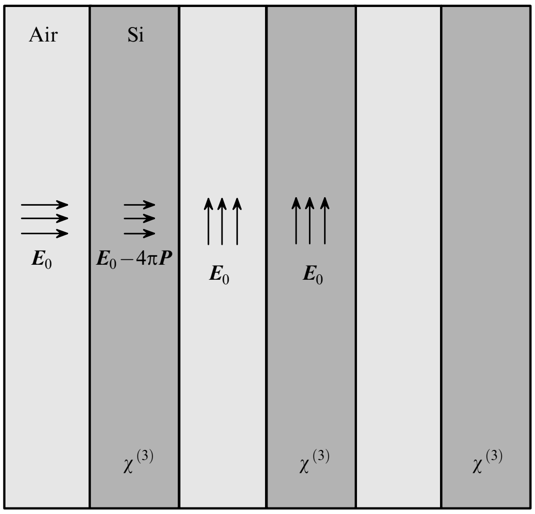

Figure 4. Model of the distribution of the electric field strength on the surface of microstructure silicon.

$|\boldsymbol{E}_{\perp}| = |\boldsymbol{E}_0 - 4\pi\boldsymbol{P}|$, and the intensity $I_{\mathrm{TH}} \propto |\boldsymbol{E}|^6$ (where $\boldsymbol{E} = \boldsymbol{E}_{\parallel} + \boldsymbol{E}_{\perp}$), the third-harmonic intensity achieves a maximum when the direction of polarisation of structuring radiation is parallel to the ripples, and this intensity is minimal when the direction of polarisation is perpendicular to the ripples.

Thus, we have shown that the morphology of ripples produced upon irradiation of silicon by femtosecond pulses is determined only by polarisation of structuring radiation and is independent of the crystallographic orientation of a sample. Electron microscope images show that the direction of silicon strips in optically induced ripples is perpendicular to the direction of polarisation of structuring radiation. The THG diagnostics of silicon microstructures has shown that the third-harmonic signal from the silicon surface irradiated for a longer time than a minute (600 pulses) also is independent of the mutual orientation of the crystallographic axes of a sample and the direction of polarisation of structuring radiation. In this case, the third-harmonic intensity is determined by the exposure time, while the direction of maxima in the orientation dependences is determined by the direction of polarisation of structuring radiation and is perpendicular to them, which is directly related to the distribution of local fields inside the optically induced ripples. It follows from the above said that femtosecond laser radiation is simultaneously an efficient tool for formation of optically induced surface microstructures of high quality and their *in situ* diagnostics, in particular, for determining the quality of ripples by their nonlinear optical response.

Acknowledgements. The authors thank V.I. Emel'yanov for useful discussions and V.S. Vlasenko for scanning electron microscope measurements. This work was supported by the Russian Foundation for Basic Research (Grant Nos 03-02-16617, 04-02-08083, 05-02-17035) and by programs of the Federal Science and Innovation Agency of the Russian Federation.

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