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Raman spectroscopic study of femtosecond laser-induced phase transformation associated with ripple formation on single-crystal SiC

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Abstract Raman spectroscopy was performed to investigate microscopic structural changes associated with a ripple structure formation initiated by femtosecond laser irradiation on the surface of single-crystal silicon carbide. The amorphous phases of silicon carbide, silicon, and carbon were observed. The intensity ratio between amorphous silicon carbide and silicon changed discretely at the boundary between fine and coarse ripples. The physical processes responsible for the formation of the ripple structure are discussed.

1 Introduction

Since high-intensity lasers have enabled the development of new applications of laser micromachining, material ablation with high-intensity laser pulse irradiation has been extensively studied. In particular, ultra-short-pulse laser technology has undergone rapid progress, and recent achievements have gathered much attention due to a wide variety of interesting phenomena induced by laser irradiation. Laser-induced periodic structures, in particular, known as 'ripples', which are spontaneously produced on a solid surface by laser irradiation, have attracted interest from both fundamental and practical points of view [1, 2].

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The first observation of ripple formation was reported by Birnbaum in 1965 [3]. Since then, the phenomenon has been reported for many kinds of solid surfaces. Most of the periods of the ripples, which were reported, were similar to the wavelength of the incident laser beam. Systematic experimental results and theoretical studies of ripples were reported two decades ago by Sipe et al. [4–6]. They concluded that the ripples are formed by the interference of the incident laser beam with the surface-scattered waves.

Recently, by femtosecond laser pulse irradiation, ripples with periods 1/3–1/10 times that of the wavelength of the incident laser beam have been reported [7–12]. These cannot be explained by Sipe's model. Here, the structure of the ripples can be roughly classified into two types, coarse and fine, according to their periods. Coarse ripples have a period close to the wavelength of the incident laser beam, and fine ripples have a period less than half of the laser wavelength; the latter are produced only by femtosecond laser irradiation. Some models have been proposed to explain the mechanism of fine ripple formation, such as interference between a laser beam and a plasmon wave [13], and self organization [11]. However, the mechanism is yet not fully understood and is still the subject of debate.

Although numerous studies have reported morphological changes with respect to the structures produced by femtosecond laser irradiation on solid surfaces, only a few have discussed the microscopic properties, such as crystallographic and chemical compositions [14]. Phase transformations from Si-I to the polymorphs Si-III, Si-IV, and Si-XII, and to amorphous silicon, in the irradiated spot, have been reported [15, 16]. But, single atomic systems do not provide sufficient information about atomic migration induced by laser irradiation. Recent results indicate that microscopic processes, such as lattice instability and self organization, may be related to ripple formation [15, 17, 18]. To

investigate the involvement of these processes, experimental studies of the microscopic structure of ripples, especially in well-defined diatomic systems, such as single-crystal silicon carbide, are essential. In this paper, we report a Raman spectroscopic study of the microscopic structure associated with the formation of a femtosecond laser-induced ripple structure on single-crystal silicon carbide (SiC) [19]. Micro-Raman spectroscopy is a useful, non-destructive tool which is used to reveal the crystalline structure of semiconductors with a spatial resolution of about 1 μm. We employed the surface analytical technique of micro-Raman spectroscopy to identify the chemical composition of the ripple structure. Based on these experimental data, we will discuss the physical processes responsible for the formation of the ripple structure.

2 Experimental

Ripple structures were produced by irradiating near-infrared femtosecond laser pulses from a Ti:sapphire regenerative amplifier system, based on chirped-pulse amplification (Spectra-Physics, Spitfire). The system emits a linearly polarized laser beam with a pulse duration of 130 fs at a central wavelength of 800 nm. We used a commercial single-crystal 4H-SiC wafer (Sterling Semiconductor, Inc.) having a thickness of approximately 100 μm. The surface of the sample was first cleaned with methanol and rinsed with distilled water. The laser beam was passed through a polarizing beam splitter and focused by a plano-convex lens ($f = 100$ mm) onto the (0001) surface of the 4H-SiC wafer to produce a ripple structure in air. The pulse repetition rate was 50 Hz and the accumulated number of pulses was 50 shots. Three samples, irradiated with different pulse energies (4 μJ, 5 μJ, and 20 μJ) were prepared. The diameter of the ripple structure was 20–40 μm.

In this study, we employed confocal micro-Raman spectroscopy to investigate the microscopic structures, such as the chemical composition and crystal structure of the ripples. Raman spectra which were obtained using a Renishaw in Via Raman system had a backscattering geometry with experimental polarization arrangement of $z(xy)z$. The system consisted of an optically pumped semiconductor laser (Coherent, Sapphire, 488 nm), edge filters to remove the scattered excitation light, a single monochromator, and a thermoelectrically cooled charge-coupled-device detector. An objective lens with a magnification of 50 was used to produce a focused laser spot approximately 1 μm in diameter and 2-μm deep. The position dependence of the Raman spectra was measured using a stepping XYZ stage with 0.1-μm resolution. Raman spectra were obtained across the ripple area by 1-μm step.

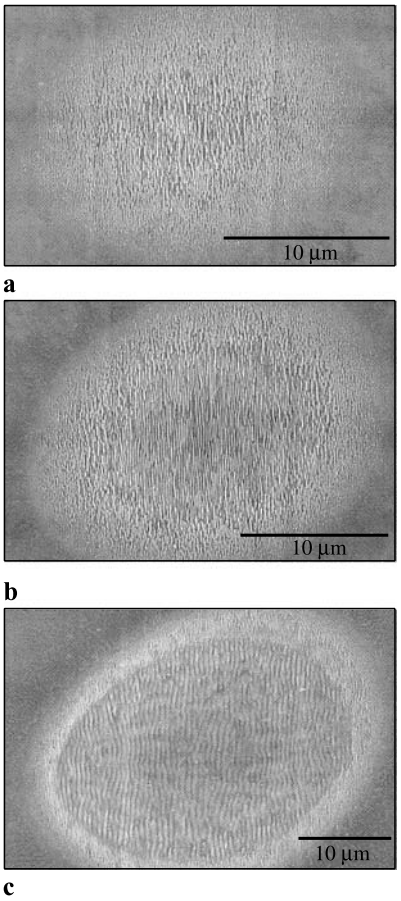

Fig. 1 Scanning electron microscope images of femtosecond laser-induced periodic structures on single-crystal 4H-SiC substrates. The pulse energies irradiated onto the surface were (**a**) 4 μJ, (**b**) 5 μJ, and (**c**) 20 μJ

3 Results and discussion

Figure 1a, b, and c show scanning electron microscope (SEM) images of the laser-irradiated spots with pulse energies of 4 μJ, 5 μJ, and 20 μJ, respectively. In Fig. 1a and b, only the fine ripple structure was observed, because the irradiated pulse energy was relatively low (4 and 5 μJ) [19]. In Fig. 1c, we observed fine and coarse ripple structures. The fine ripples were observed in the peripheral region, whereas the coarse ones were observed in the central region. The direction of both ripple structures was perpendicular to that of the electric field of the incident laser beam. The period of the fine ripples was about 250 nm and that of the coarse ripples was about 500 nm. A detailed analysis of the morphological features of such ripples was previously reported [19].

Figure 2a shows typical Raman spectra observed at the ripple structure (traces 1 and 2) and a non-irradiated area. Figure 2b shows a scanning electron microscope image of the laser-irradiated spot with a pulse energy of 20 μJ. The brighter area in the center corresponds to the region of the ripples. The Raman spectrum ‘1’ and ‘2’ shown in

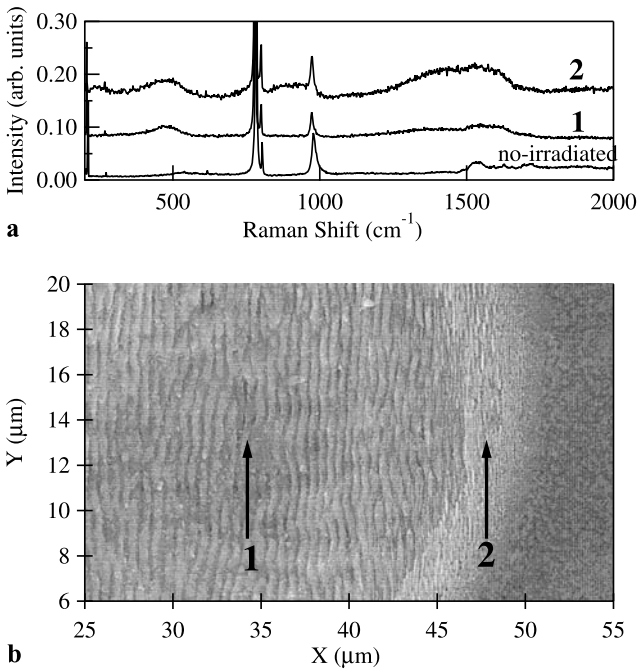

Fig. 2 (**a**) Raman spectra measured at '1', '2', and a non-irradiated surface region (no irradiation). The spectra are shifted on the ordinate for convenient display. (**b**) Scanning electron microscope image of the femtosecond laser irradiated spot. The positions where the Raman spectra were measured are indicated by *arrows*

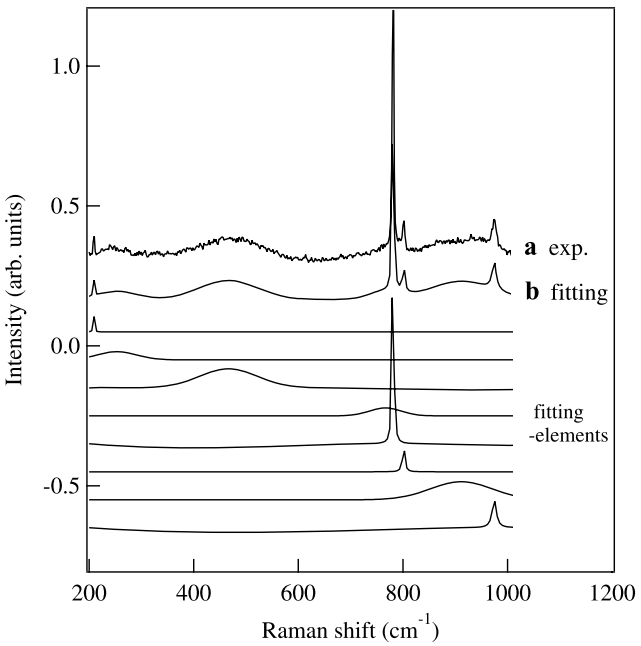

Fig. 3 Fitting results of the Raman spectrum for the fine ripples (pulse energy: 20 μJ/pulse) based on the functions in (1) and (2). Spectra are displayed with the decomposed elements shown at the bottom: four Lorentzian functions (peak energies at 210 cm^{-1}, 780 cm^{-1}, 800 cm^{-1}, and 970 cm^{-1}) and four Gaussian functions (peak energies at 260 cm^{-1}, 480 cm^{-1}, 770 cm^{-1}, and 880 cm^{-1})

Fig. 2a were obtained at the points labeled '1' and '2' in Fig. 2b, respectively. The 'no-irradiation' spectrum was obtained at the non-irradiated region of the surface, far from the laser spot, which was considered as a point of reference. All spectra were normalized at an intensity of 780 cm^{-1} peak, which can be assigned to the first-order transverse optical (TO) phonons. Sharp peaks (∼200 cm^{-1}, ∼780 cm^{-1}, ∼800 cm^{-1}, and ∼970 cm^{-1}) originate from acoustic/optical phonons produced in the single-crystal 4H-SiC (c-SiC). Their energy positions and spectral shapes reflect c-SiC structure, thereby allowing identification of the crystal structure, as either polytype or amorphous [20–22]. A non-folded mode of the longitudinal optical (LO) phonon peak appeared at approximately 970 cm^{-1}. As shown in Fig. 2a, broad peaks were observed around 260 cm^{-1}, 480 cm^{-1}, 770 cm^{-1}, and 880 cm^{-1} in the ripple structure. In general, the broad bands of the Raman spectra of a solid originate from a broad isotropic distribution of bond lengths and angles. The Raman spectra related to amorphous silicon have been previously reported [23]. The breakdown of the momentum selection rule in SiC phonon dispersion causes the appearance of a broad Raman peak around 800 cm^{-1}. Hence, the 260 cm^{-1} and 480 cm^{-1} peaks can be attributed to amorphous silicon (a-Si), and the 770 cm^{-1} and 880 cm^{-1} peaks to amorphous SiC (a-SiC) [24]. The bands of amorphous graphite also appear around 1350 cm^{-1} (D-band) and 1590 cm^{-1} (G-band).

The measured Raman spectrum of the ripple structure on SiC over the frequency range from 200 cm^{-1} to 1100 cm^{-1} was decomposed into peaks expressed by model functions. We used four Lorentzian functions (1) for the 210 cm^{-1}, 780 cm^{-1}, 800 cm^{-1}, and 970 cm^{-1} peaks, and four Gaussian functions (2) for the 260 cm^{-1}, 480 cm^{-1}, 770 cm^{-1}, and 880 cm^{-1} peaks:

$$f_{\text{Lorentzian}}(\omega; I_i, \omega_i, \Delta\omega_i) = I_i \frac{\sqrt{\Delta\omega_i/2}}{((\omega-\omega_i)^2 + (\Delta\omega_i/2)^2)}, \tag{1}$$

$$f_{\text{Gaussian}}(\omega; I_i, \omega_i, \Delta\omega_i) = I_i \exp\left(-4\ln 2\left(\frac{\omega-\omega_i}{\Delta\omega_i}\right)^2\right). \tag{2}$$

Twenty-four parameters (eight parameters each for peak position (ω_i), intensity (I_i), and width ($\Delta\omega_i$)) were individually adjusted to attain the minimum chi-square value using Levenberg–Marquardt nonlinear least-square optimization. An example of fitting to the Raman spectrum of a fine ripple is shown in Fig. 3. Curve (a) of Fig. 3 shows typical Raman spectra data at the ripple, and curve (b) shows the fitting result to curve (a). The model function reproduced the experimental data quite well. In addition, the fitting elements used are shown at the bottom. Similar qualities of fitting results were obtained for all spectra measured in our study.

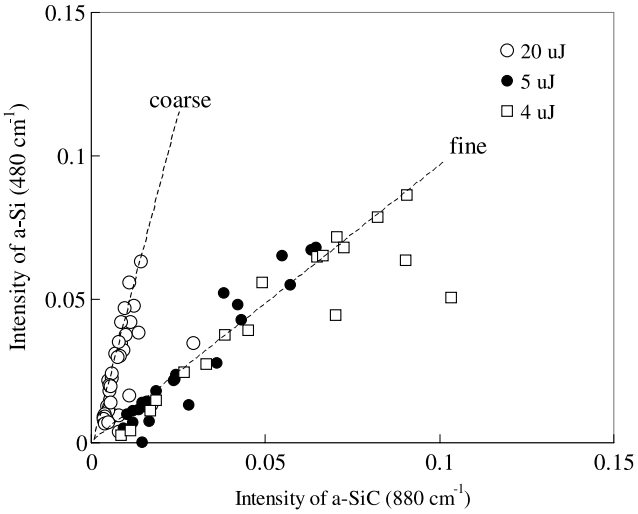

Fig. 4 Correlation between the intensities of the 480 cm^{-1} and 880 cm^{-1} peaks. The irradiated pulse energies were 4 μJ (*open square*), 5 μJ (*filled circle*), and 20 μJ (*open circle*). Two distinct linear relationships were observed

To discuss the origin of these amorphous peaks, the correlation between the intensities of the 480 cm^{-1} and 880 cm^{-1} peaks is plotted in Fig. 4. These intensities are determined by the ratios of a-Si and a-SiC to c-SiC in the volume area observed in the Raman measurement. This shows that the intensity of the 480 cm^{-1} peak and that of the 880 cm^{-1} peak obey a bilinear relationship. The two linear relations with different slopes correspond to the fine and coarse ripples. Jia et al. also observed weak broad bands of amorphous graphite and silicon in the Raman spectra of ripples on SiC. They concluded that these peaks correspond to Si and C clusters and originate from debris accumulated on the sample surface [25]. However, they did not discuss the difference in composition between coarse and fine ripples. Our results indicate that both the periodicity and chemical composition differ for the coarse and fine ripples.

The experimental results indicate that the initial c-SiC transforms into an a-SiC phase and then separates into a-Si and a-C with increasing laser fluence. The present results can be understood from atomic migration due to the femtosecond laser irradiation. A schematic illustration of the structural change caused by the laser irradiation is shown in Fig. 5. After laser irradiation, the single-crystal structure is destroyed and is transformed into an amorphous phase by atomic migration. With increasing laser fluence, the degree of atomic migration increases and phase separation into a-Si and a-C is induced. The time scale of atomic migration is an interesting topic, although it still unclear in this study. It has been reported that a pulse duration dependence of up to 2 ps on the surface morphologies could not be observed [26]. So, we speculate that this time scale is more than several ps. The observation of the broad Raman band of amorphous

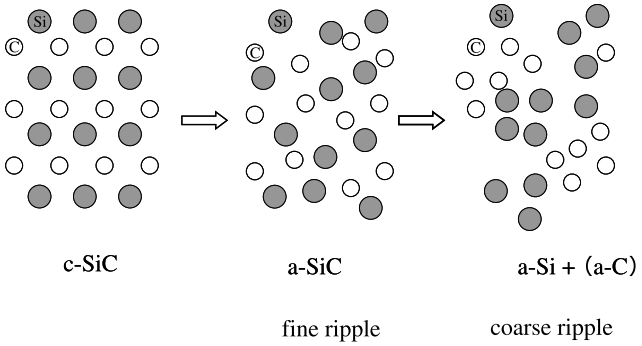

Fig. 5 Schematic illustration of atomic migration process associated with the ripple formation

graphite in Fig. 2 also supports this model of pair generation of a-Si and a-C. Therefore, these results indicate that the formation process of the ripple structure should be discussed in terms of phase transformation or atomic migration triggered by the interaction between light and the material, in addition to changes in the surface morphology such as the periodicities.

4 Conclusion

We have reported a Raman spectroscopic study of ripple patterns formed on silicon carbide (4H-SiC) by irradiation with femtosecond laser pulses. In the fine and coarse ripples, Raman bands corresponding to a-Si and a-SiC were observed. The intensities of the a-Si and a-SiC bands exhibited a bilinear relationship. Two linear relations with different slopes were found at the fine and coarse ripples. These results indicate that a structural change from c-SiC to a-SiC can occur at the initial stage of ripple formation, followed by transformation from a-SiC to a-Si and a-C. The phase transformation or atomic migration discussed in this study will play a vital role in understanding the formation process of ripple structures induced by femtosecond laser irradiation.

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