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Fourier-transform Infrared Spectroscopy of Femtosecond Laser-modified SiC

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Characterization of femtosecond laser-modified areas on silicon carbide (SiC) was carried out through Fourier transform infrared reflectance spectra. The sample scanning was carried out during femtosecond laser irradiation to make larger modified area in order to evaluate the changes of the spectra by Fourier transform infrared spectrometer. The spectra were well fitted by the analytical function which is calculated through the dielectric functions of SiC including the effect from free carriers. The obtained parameters indicated that the enhancement of damping constant of longitudinal optical phonons after laser irradiation. This enhancement is due the degradation of crystallinity of SiC. The strong correlation between the direction of modified lines and the polarization of infrared probe light was found. This correlation opens the possible application of femtosecond laser-modification in SiC for control the optical properties in infrared region.

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1. Introduction

Femtosecond (fs) laser processing has potential application such as micro/nano micromachining, 3D microfabrication, and fabrication of photonic crystals. Fabrication of photonic crystals in infrared (IR) region is much easier than that in the visible region, because the wavelength, thus the required precision of processing, is far longer in IR region. In addition, recent increase in the interest for terahertz technology [1] requires further development of novel optical elements in this wavelength region and the interest is extending toward the higher frequency region, which corresponds to the frequency of optical phonons.

Silicon carbide (SiC) attracts much attention because of its excellent properties for the application to high power devices. Recently, high quality wafers of SiC are offered from many companies and the power devices consists of SiC have been demonstrated. If the control of electrical properties of SiC by fs laser irradiation is possible, the combination of fs laser modification technique and 3D modification technique inside transparent materials may offer novel device fabrication techniques of SiC. Thus, the characterization of electrical properties of fs laser modified areas is important. Non contact characterization of electrical properties on semiconductors is possible by measuring the infrared (IR) spectra.

Thus, in this report, we will report the result of optical characterization of femtosecond laser-modified SiC in the infrared region near the optical phonon frequencies.

2. Experimental

Light source used for laser modification is 1 kHz regenerative amplifier (Spectra Physics, Spitfire). The wavelength was 800 nm and the pulse duration was about 130 fs. The samples used in the experiment were semi-insulating and n-type SiC. To make larger laser-modified region, the samples were translated by the mechanical stage (Sigma, Mark-202) with the scan speeds of 200, 300, and 600 μm/sec. As shown in Fig. 1, laser irradiation was carried out on the whole area of sample surface (5 X 5 mm) with the line spacing of 20 or 30 μm (line spacing is shown by "d" in Fig. 1). After the laser modification, reflectance spectra were measured by Fourier-transform infrared (FTIR) spectrometers. We employed IR Prestige-21 (Shimadzu) for mid infrared region (350-1500 cm^{-1}), and Faris-1 (Jasco) for far infrared region (10-450 cm^{-1}). For the polarization dependence measurement, we employed wire grid polarizing filter to make linear polarized probe beam.

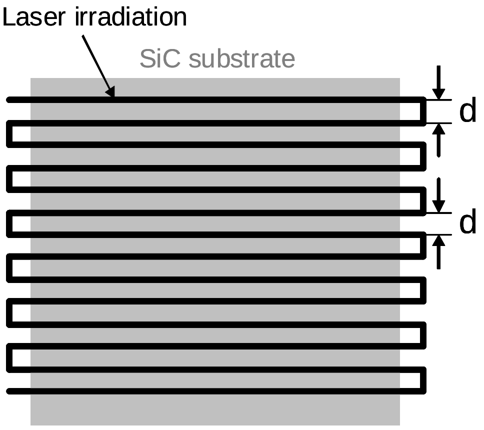

Fig. 1: The schematic illustration of laser scanning for laser modification of SiC

3. Results and Discussion

3.1 Spectral changes in IR region by femtosecond laser irradiation

After the laser irradiation, sample surface was observed by scanning electron microscope (SEM). On the surface, debris due to the laser irradiation was accumulated onto the sample surface. The surface was cleaned with acetone, ethanol, and water to remove the debris accumulated on the surface during laser irradiation. During the cleaning the sample surface was rubbed by a cotton swab to complete the cleaning. The cleaned sample surface was observed by scanning electron microscope and ripple structures was observed on the laser irradiated surfaces [2-5]. Signal to noise ratio of FTIR spectra was significantly improved after cleaning of the sample surfaces.

Figure 2 shows the FTIR reflectance spectra from 50 to 1500 cm^{-1}. The spectrum for a non-irradiated n-type SiC was shown by blue line and that for the laser modified one was shown by red line. The pulse energy, the scan speed and the line spacing was 7 μJ, 300 μm/sec, and 30 μm, respectively. The spectral was measured without the polarizer, i.e. the non-polarized infrared light was used. The 100% of the reflectance was calibrated by an Al mirror. The high reflectance band around 800-1000 cm^{-1}, observed on a non-irradiated sample, is so-called reststrahlen band. Reststrahlen band originates from the forbidden gap of the phonon modes between longitudinal and acoustic mode and the data obtained for the non-irradiated sample agrees well with the previously reported data by K. Narita and coworkers [6]. The increase of the reflectance toward the lower wavenumber was observed below 350 cm^{-1}. The energy position where the increase of reflection starts, which is shown by a green arrow in Fig. 2, is called plasma frequency. Plasma frequency is proportional to the square root of carrier density. For the laser-modified sample, the reflectance of the reststrahlen band shows the steep decreases toward the higher wavenumber. Any shift of plasma frequency was not observed after the laser irradiation. This means that the carrier density did not change by laser irradiation.

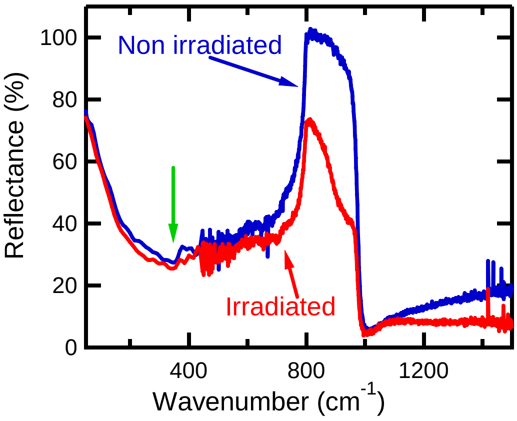

Fig. 2: FTIR reflectance spectra of laser modified (red line) SiC and the non-irradiated SiC (blue line). The pulse energy was 7 μJ/pulse and the scan speed of 300 μm/sec. The spacing between lines were 30 μm. IR probe beam used in this measurement was unpolarized one.

3.2 The analysis of spectral shape

Spectral shapes of FTIR spectra related to reststrahlen band and plasma frequency can be calculated though the dielectric functions including the effects of plasma and phonon oscillations. The dielectric function of SiC is strongly dependent on longitudinal optical (LO) phonon damping constant because the plasmon is overdamped and the LO-phonon frequency is much higher than the plasma frequency except for heavily doped cases. In this case, it is better to use the modified classical dielectric function (MDF) taking into the contribution of transverse optical (TO) phonon damping constant and the LO-phonon damping constant, independently [7-11].

$$\varepsilon(\omega)=\varepsilon_{\infty}\left(\frac{\omega_L^{\ 2}-\omega^2-i\Gamma_L\omega}{\omega_T^{\ 2}-\omega^2-i\Gamma_T\omega}-\frac{\omega_p^{\ 2}}{\omega(\omega-i\gamma_p)}\right)$$

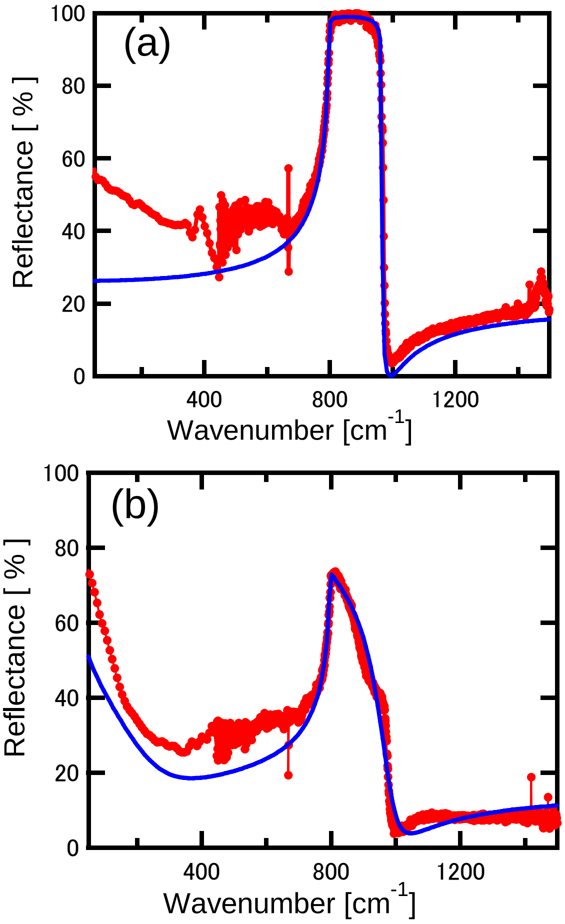

Fig. 3: Fitting results to the experimentally observed FTIR spectra (red lines) are shown by blue lines. (a) non irradiated semi-insulating 4H-SiC (b) The laser irradiated n-type 4H-SiC. The irradiation was carried out with the pulse energy of 7 μJ/pulse and the scan speed of 300 μm/s. The spacing between lines was 30 μm. IR probe beam was unpolarized one.

Where ε_∞ is the optical dielectric constant, ω_T and ω_L are TO and LO phonon frequencies, Γ_T and Γ_L are the TO and LO phonon damping constants, ω_p is the plasma frequency, and γ_p is the free-carrier damping constant.

The refractive index and the extinction coefficient can be connected with the dielectric function as follows;

$$\varepsilon(\omega) = (n + ik)^2 .$$

Here, n represents the refractive index and k means the extinction coefficient. The reflectance spectra can be calculated from the following function using the refractive index and extinction coefficient;

$$R(\omega) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} .$$

The fitting was carried out to by using spectrum analyzing software (Igor Pro, Wavemetrics, Ver. 5). The variable parameters used in the fitting procedure are ω_p , γ_p , and Γ_L . From plasma frequency (ω_p), carrier density (N) is obtained from the following equation.

$$\omega_p = \left(\frac{Ne^2}{m^* \varepsilon_\infty} \right)^{1/2}$$

Here, m^* and e is the effective mass and the charge of electron, respectively. The electron mobility also be estimated from the damping constant of plasma.

$$\mu = \frac{e}{m^* \gamma_p}$$

Figure 3 shows the fitting results for non-irradiated semi-insulating 4H-SiC ((a)) and the laser irradiated n-type 4H-SiC ((b)). The pulse energy, the scan speed, and the spacing was 7 μJ/pulse, 300 μm/s, and 30 μm, respectively. The red line shows the experimental results and the blue line shows the fitting results. The fitting results reproduce well with the experimental results, whereas the small deviation from the experimental results was observed in the lower frequency region. Although the origin of this smaller estimation of the reflection in the lower frequency region is not clear now, it is possible that the reflectance was increased due to the ripple formation associated with the laser irradiation.

The fitting results showed that the values of plasma frequency (ω_p) and the damping constant (γ_p) do not change. The experimental data was fitted well by only changing the value of LO phonon damping constant (Γ_L). The obtained damping constants of LO phonon of n-type SiC for the fixed scan speed 600 μm/s (which correspond to about 33 shots/spot) of was 28, 60, and 73 cm^{-1} for non-irradiated, 5 μJ, and 7 μJ, respectively. The damping constant of LO phonon obtained from fitting for various irradiation conditions for semi-insulating and n-type SiC are plotted in Fig. 4. The results shows that the damping constant of LO phonon increases as the pulse energy of irradiation increases for n-type SiC, whereas clear difference was not found between 5 and 7 μJ irradiation for semi-insulating SiC. The increase of the damping constant of LO phonon indicates that the shortening of LO phonon lifetime, and thus indicates the degradation of crystallinity due to the laser modification.

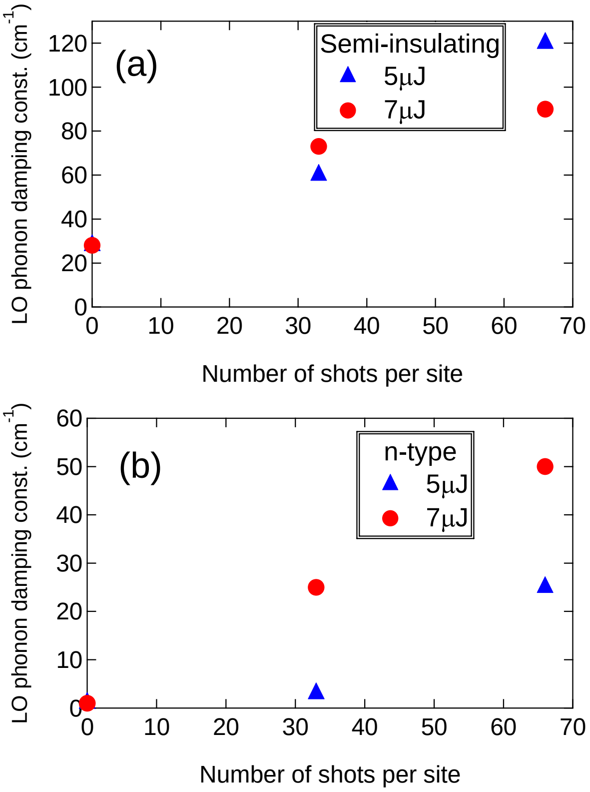

Fig. 4: Scanning speed dependence of damping constant of fs laser modified SiC. (a) semi-insulating SiC (b) n-type SiC

The obtained damping constants of LO phonon also increased as the scan speed decreases the for fixed pulse energy. The damping constants of n-type SiC for the fixed pulse energy of 7 μJ was 28, 73, and 90 cm^{-1} for non-irradiated, the scan speed of 600 μm/s (which corresponds to about 33 shots/spot), and 300 μm/s (66 shots/spot), respectively. This also indicates that the crystallinity of SiC is degraded as the scan speed of the laser beam is decreases.

The spectral analysis based on the dielectric function revealed that only the damping of longitudinal optical phonon was increased after the laser modification, and this means the crystallinity of the sample was decreased.

3.3 Polarization dependence of reststrahlen band

In the previous section, we discussed the FTIR spectra with un-polarized light because we could not observed significant polarization dependence for the lower irradiation conditions less than 7 μJ/pulse, whereas the slight polarization dependence was observed for the 20μm-pitched modified one. For the higher irradiation condition, however, we observed the strong polarization dependence of the FTIR spectra. Figure 5 show the FTIR reflectance spectra for various polarization configurations. The fluence and the repetition rate, line spacing, and the scan speed was 14 μJ, 1 kHz, 20μm, and 200 μm/sec, respectively. Figure 5 (a) shows the results for s-polarization. The angle of incidence was about 10 deg from the normal to the surface. The angle of the sample respect to the plane of incidence was varied.

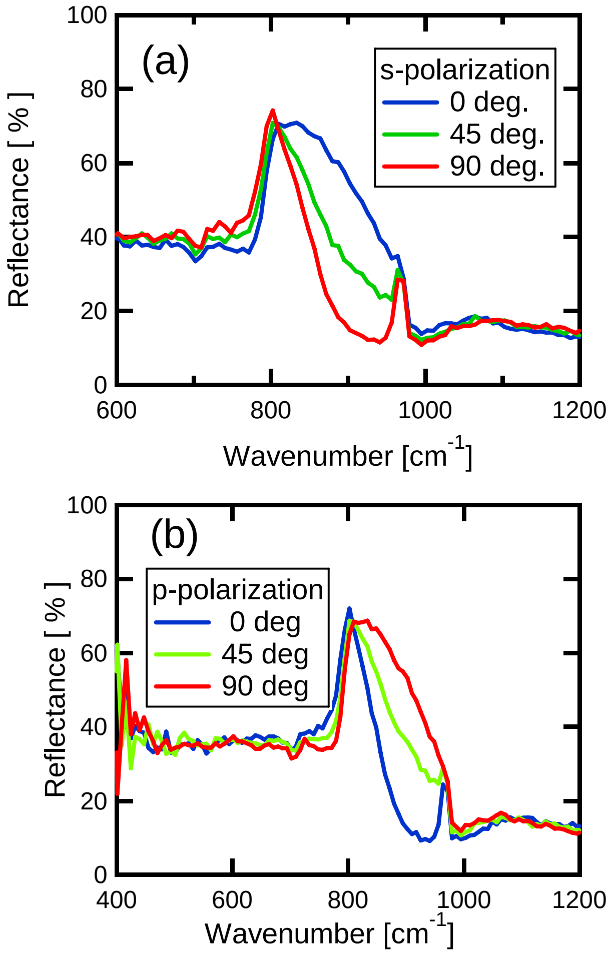

Fig. 5: Polarization dependence of FTIR reflectance spectra of laser modified SiC. The fluence and the repetition rate, line spacing, and the scan speed was 14 μJ, 1 kHz, 20μm, and 200 μm/sec, respectively.

The 0 deg means the plane of incidence is parallel to the scanning direction of the laser modification and 90 deg means that the plane of incidence is perpendicular to the scanning direction of the laser modification. The shapes of reststrahlen band drastically depend on the sample rotation. The reflectance of reststrahlen band for s-polarization in 0 deg configuration is higher, whereas that in 90 deg is very low. On the other hand, the results is opposite for the p-polarization. The reflectance of reststrahlen band for p-polarization in 90 deg configuration is higher, whereas that in 0 deg is very low. This means that the decrease of reststrahlen band in most pronounced when the scanning direction of fs laser beam is parallel to the polarization of the infrared probe beam. These polarization dependences are caused by the periodic modification effect such as photonic crystals in the visible region. The sharp peaks observed about 965 cm^{-1} are supposed to be the diffraction of the infrared beam due to the periodic modulation. At this point, further study about the dielectric function which includes the effects of periodic modification is needed. These findings can be applicable to control the reflectance properties of SiC near the terahertz radiation by fs laser modification technique, such as terahertz photonic crystals.

4. Conclusion

Femtosecond laser-modification on single-crystal SiC was investigated from the infrared spectroscopy. Femtosecond laser was irradiated whole area of the sample surface. FTIR spectra were changed after the femtosecond laser irradiation. The spectral analysis based on the dielectric function which includes the effect from the plasmon revealed that the change of plasma frequency and plasmon damping constant was not observed on n-type SiC. The damping constant of LO phonon was increases as the irradiation dose increases. This implies that the crystallinity of the SiC was degraded after femtosecond laser irradiation. The correlation between scanning direction of fs laser and the polarization of infrared probe light was found. The decrease of reststrahlen band is most pronounced when the direction of the scanning is parallel to the polarization of the probe beam. These findings may be applicable to control the optical properties of SiC near the terahertz region by fs laser modification technique.

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References

[1] K. Sakai (Ed.): TERAHERTZ OPTOELECTRONICS, (Springer-Verlag GmbH, 2005).
[2] J. E. Sipe, J. F. Young, J. S. Preston, and H. M. Driel, Phys. Rev. B 27 (1983) 1141.
[3] J. F. Young, J. S. Preston, H. M. Driel, and J. E. Sipe, Phys. Rev. B 27 (1983) 1155.
[4] J. F. Young, J. E. Sipe, and H. M. Driel, Phys. Rev. B 30 (1984) 2001.
[5] T. Tomita, K. Kinoshita, S. Matsuo, and S. Hashimoto, Jpn. J. Appl. Phys. 45 (2006) L444.
[6] K. Narita, Y. Hijikata, H. Yaguchi, S. Yoshida, and S. Nakashima, Jpn. J. Appl. Phys. 43 (2004) 5151.
[7] E. Neyret, G. Ferro, S. Juillaguet, J. M. Bluet, C. Jaussaud and J. Camassel: Mater. Sci. & Eng. B 61–62 (1999) 253.
[8] S. Nakashima and H. Harima: J. Appl. Phys. 95(2004) 3541.
[9] S. Perkowitz: Optical Characterization of Semiconductors ed. N. H. March (Academic Press, London, 1993) p. 36.
[10] S. Perkowitz and R. T. Thorland: Solid State Commun. 16 (1975) 1093.
[11] R. T. Holm, J. W. Gibson and E. D. Palik: J. Appl. Phys. 48 (1977) 212.

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