Surface-polarity-dependent Raman spectra of ultrathin silicon carbide crystal

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Abstract

The surface-polarity-dependent Raman spectra of ultrathin silicon carbide crystal are reported.

The relative Raman intensity of the folded-transverse-acoustic phonon to the folded-transverse-optical phonon modes differs drastically between silicon-terminated face (Si-face) and carbon-terminated face (C-face) only for sample thickness below 150 nm. For samples thicker than 150 nm, the relative Raman intensity ratio takes an almost constant value for both Si- and C-faces.

These results indicate that the phonon modes confined in the near-surface region are the possible origin of the observed surface-polarity-dependent Raman spectra.

Raman scattering, which is the inelastic light scattering from materials, was first reported by Raman and Krishnan in 1928 [1]. Currently, Raman spectroscopy is being extensively used as a powerful tool for material characterization. The advantages of this method include nondestructive material characterization and high spatial resolution, down to the submicron scale. In addition, Raman spectrum measurement can be performed in ambient air without mechanical contact.

To characterize material properties, such as the crystallinity [2, 3] and free carrier concentration [4, 5], the center wavenumber and width of the Raman spectra are often discussed. However, the intensities of the Raman spectra have not been sufficiently utilized because the intensity calculation based on the Raman scattering formula, which includes the second-order quantum perturbation theory, is highly complicated and requires the precise structure of the electronic band state and the phonon-dispersion relationship of the target material. This prevents the quantitative understanding of the Raman intensity profiles. Nevertheless, approaches for calculating the Raman intensity profiles, considering the microscopic polarizabilities related to the atomic bonds in solids, have been examined for more than half a century. Nakashima et al. succeed in explaining the Raman intensity profiles of several types of layered crystals [6, 7] and silicon carbide (SiC) polytypes [2, 3] under off-resonant conditions, employing the bond-Raman polarizability concept. In addition, Tomita et al. introduced the concept of the resonance of the bond-Raman polarizability and succeeded in explaining the wavelength dependence of

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the Raman intensity profiles of various SiC polytypes [8].

In addition to the significant achievement of the bond-Raman polarizability concept of bulk crystals, the surface effect of Raman scattering is also being discussed. Nakashima et al. reported that the Raman intensities of 4H-SiC excited by deep ultraviolet laser beams (244 nm and 266 nm) strongly depend on the surface polarity, i.e, silicon-terminated face (Si-face), and carbon-terminated face (C-face) [9]. These results may indicate that the phonon modes observed for the two excitations are stuck at the surface, being confined in the near-surface region, which is comparable to the optical penetration depth of deep ultraviolet (DUV) light. This surface-polarity-dependent Raman spectra can be explained by the generation of surface-orientation-sensitive phonons, which are bound in the near-surface region and extend into the lattice to several hundred nanometers. It is worth noting that these surface-polarity-dependent Raman spectra are observed only for DUV light excitation, which has a penetration depth of approximately 200 nm. This is because the confined phonon mode is restricted near the surface, and visible light, which penetrates deeply into the sample, cannot efficiently detect the surface confined phonon mode.

Here, we work with the concept that the visible-light-excitation Raman spectrum from an ultrathin free-standing SiC crystal with a thickness comparable to the decay length of the surface confined phonon mode would provide information on the surface-polarity dependence. This is because the contribution of the surface confined phonon mode to the Raman intensity is

higher in an ultrathin crystal than in a bulk sample. Hence, we fabricated ultrathin SiC crystals and measured the Raman spectra using visible-light excitation. Experiments on ultrathin crystals with thicknesses of approximately 100 nm, using visible-light excitation, can provide fruitful information on light-matter interaction.

The crystal used in this experiment was n-type 4H-SiC (TankeBlue, China). The ultrathin samples were fabricated by a pickup technique, using Ga^+-focused ion beam (FIB) micromachining. An FEI Quanta 3D 200i equipped with an Omniprobe pickup system was used. A small piece that was $10\times6\times2$ μm^3 in width, height and thickness was lifted off the crystal and fixed to a post of a grid in the flag position. Then the piece was thinned by FIB. We defined that the initial polarities of the surfaces (Si- and C-faces) were kept during the micromachining. After FIB micromachining, Ar-ion was irradiated onto the samples for removing the amorphous layer piled-up during FIB micromachining.

The thinned sample contained two areas; a thicker area near the post of the sample grid and a thinner area away from the post, as shown in Fig. 1. In order to study the effect of the sample thickness, we prepared three samples (Sample I to III) with different thicknesses; the details of the sample thickness are listed in Table 1. Micro Raman spectroscopy was carried out to measure the Raman spectra of the ultrathin SiC crystals, using a Renishaw inVia Reflex-S. The wavelength of the Raman excitation was 532 nm, and the excitation power was approximately 7.5 mW. The exposure time was 1000 s for each measurement point. The spectral resolution of

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the spectrometer used in the experiment is about 5 cm^{-1}. Thus, the spectral broadening of the phonon modes is mainly due the resolution of the spectrometer and is not due to the FIB micromichining. By changing the measurement point, the Raman spectra at different sample thicknesses can be obtained by assuming a trapezoidal cross section for both thicker and thinner areas in the sample.

The SiC crystal structure exhibits more than 250 polytypes [10]. The polytype, which shows the shortest unit cell, i.e, the longest Brillouin zone, is the 3C-SiC [10]. The dispersion curves for the other polytypes are expressed by the folding of the 3C-SiC dispersion curves. For example, the folded-transverse-optical phonon mode (FTO(2/4)) and the folded-transverse-acoustic phonon mode (FTA(2/4)) are observed in 4H-SiC [11]

Figure 2 shows the Raman spectra from a 90-nm-thick point, measured at the Si-face (blue line) and C-face (red line). These spectra are normalized to the peak intensity at 774 cm^{-1}. In these spectra, three broad peaks are found at approximately 200, 500, and 800 cm^{-1}, and are assigned to the amorphous phase [12], which remained even after Ar-ion cleaning. In addition to these broad peaks, two sharp peaks are observed at 206 cm^{-1} and at 774 cm^{-1}, which are assigned to the FTA(2/4) and FTO(2/4) mode, respectively. Both spectra did not show significant broadening due to sample thinning, indicating that the sample crystallinity in the ultrathin sample is similar to that in the bulk 4H-SiC crystal. In the Ref [9], the upper and the lower branches of the folded phonon modes were clearly resolved, however in this case they

cannot be resolved. Alternatively, the summation of the intensities of upper and lower branches of folded phonon mode can be used as the index of the Raman intensities. In order to discuss the intensity ratio between the FTA(2/4) and FTO(2/4) modes, the spectrum components corresponding to these sharp peaks were extracted and are depicted in Fig. 3. For the Si-face, the relative intensity of the FTA(2/4) mode normalized to FTO(2/4) is 3/5. On the other hand, for the C-face, the relative intensity of the FTA(2/4) mode normalized to FTO(2/4) is 1/4, with a clear difference in the intensity ratio. However, this could not be observed for a 180-nm-thick measurement point; the relative intensity of the FTA(2/4) mode normalized to FTO(2/4) was 2/15, both for the Si-face and C-face.

These results demonstrate the existence of a critical thickness, where the surface polarity dependence of the Raman spectra is observed. To discuss this point in detail, we measured the thickness dependence of the Raman spectra. The intensity of each Raman peak was obtained by the fitting according to Ref [13]. The relative intensity of the FTA(2/4) mode normalized to the intensity of the FTO(2/4) mode is plotted in Fig. 4, for sample thicknesses ranging from 80 to 440 nm. The surface polarity-dependence is negligible at thicknesses above 200 nm. On the other hand, the surface-polarity dependence is considerable at thicknesses below 150 nm. In addition, the surface dependence of the intensity ratio between the FTA(2/4) and FTO(2/4) modes was measured before and after Ar-ion cleaning. No significant difference was observed, before and after the amorphous removal by Ar-ion cleaning, indicating that the amorphous

layers piled on the sample surface are not the origin of the surface-polarity dependence in the ultrathin samples. Additionally, we considered the effect of thermal heating due to the laser irradiation. We varied the laser power from 0.75 to 7.5 mW, and determined that there was no significant dependence of the peak frequency of the FTO(2/4) mode, even for a sample thickness of 90 nm.

Finally, we compared the relative intensity between the sample with the thickness greater than the critical thickness and the bulk substrate. However, we could not observe significant difference between them. This means that the Raman intensity variation arises from the surface confined phonons.

It is widely accepted that the localized phonon mode exists in the vicinity of the heaver atom-terminated surface (so-called Wallis mode [14, 15]). This phonon mode lies between the center of the energy gap between TO and LO phonon modes. By observing this phonon mode from the both surfaces, the novel phonon profiles are observed. In our case, the phonon mode similar to the Wallis mode exists between the upper and lower branches of the folded phonon modes. Thus, it is supposed that the intensity variation between Si- and C-terminated surface is observed in the same manner as in Wallis mode.

The surface confined phonon mode is fixed to the surface and decays exponentially toward the opposite side within several hundred nanometers. In our experiment, the energies of the Raman peaks did not depend on the sample thickness. This means that the surface confined

phonon mode does not reach to the opposite side with the significant amplitude.

In conclusion, the surface-polarity-dependent Raman spectra of ultrathin SiC crystal were reported. Ultrathin samples with thicknesses ranging from 80 to 440 nm were fabricated by the FIB method, from a 4H-SiC bulk crystal. The Raman spectra of these samples were measured at both Si- and C-faces, with an excitation wavelength of 532 nm. The relative Raman intensity between FTA(2/4) and FTO(2/4) was drastically different between the Si- and C-faces, which was significantly observed only for thicknesses below 150 nm. It is supposed that the variation in the intensity ratio between the traveling phonon mode and the surface confined mode is the possible origin of the surface-polarity-dependent Raman spectra.

Acknowledgment

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure Captions

Fig. 1 (a) Bird's-eye view of the sample fixed to a post of a grid. Top-view (b) and side-view (c) scanning electron microscope images of Sample I.

Fig. 2 Raman spectra from a 90-nm-thick point, measured at the Si-face (blue line) and C-face (red line). These spectra are normalized to the peak intensity at approximately 774 cm^{-1}. The spectrum for Si-face is shifted by 0.1 along the ordinate for a convenient display.

Fig. 3 Spectrum components in Fig. 2, extracted for comparison. The intensities of the FTA(2/4) and FTO(2/4) peaks are depicted both for the (a) Si-face and (b) C-face. It is clear that the intensity ratio between them drastically changes between the Si- and C-faces.

Fig. 4 Sample-thickness dependence of the intensity ratio between the FTO(2/4) and FTA (2/4) modes. The intensity ratio for the Si-face is depicted by blue-circle points and that for the C-face by red-triangle points.

Table 1 Details of the thicknesses for each sample.

Sample	Thicker area		Thinner area	
	Minimum (nm)	Maximum (nm)	Minimum (nm)	Maximum (nm)
I	90	340	80	200
II	230	480	150	420
III	200	480	150	440

(a)

Top view

Post of sample
grid

[0001]

Pt

SiC

Side view

(b)

Thicker area

Thinner area

C-face

Si-face

5 μm

(c)

Pt protective film

SiC

[0001]

5 μm

Fig. 1

Fig. 2

(a) Si-face

FTA (2/4)
206 cm^{-1}

FTO (2/4)
776 cm^{-1}

3 : 5

Intensity

200   800

Raman shift [cm^{-1}]

(b) C-face

FTA (2/4)
206 cm^{-1}

FTO (2/4)
776 cm^{-1}

1 : 4

Intensity

200   800

Raman shift [cm^{-1}]

Fig. 3

Fig. 4