Correlation between the residual stress in 3C-SiC/Si epifilm and the quality of epitaxial graphene formed thereon

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Abstract. The quality of epitaxial graphene on silicon (GOS) is negatively correlated with the residual stress of the 3C-SiC films grown on the Si substrates. This has been systematically demonstrated by use of a series of 3C-SiC films formed on Si(110) substrates with varied residual stress. The residual stress of the 3C-SiC film and the grain size of graphene were estimated with Raman-scattering spectroscopy while the crystallinity of the 3C-SiC film was evaluated by x-ray diffraction. The more it reduces the residual stress the better the GOS quality it becomes. In particular, use of the rotated epitaxial film of 3C-SiC formed on Si(110) substrate, which gives the lowest residual stress, is found to produce a graphene with one of the best quality ever obtained in GOS. The revealed GOS quality improvement opens new opportunities for the production of high-performance GOS-based devices.

1. Introduction

Graphene, a single atomic layer of hexagonally arranged carbon atoms, is attracting much attention owing to its very interesting physical properties, such as the high electron mobility reaching up to \(~200,000\) cm\(^2/V\)s, anomalously quantized Hall effect [1-5], and spin polarization of the current [6]. These physical properties make graphene a promising material for future electronic devices.

Graphene can be formed by many ways. One can form graphene by micromechanical [1] and chemical [7] exfoliation of graphite as well as by CVD on metal substrates [8]. Among others, however, the industrially most practical way of forming graphene should be the epitaxial growth of graphene on surfaces of SiC crystals, which can be conducted on both bulk [9] and epitaxial films [10-11]. By simply annealing the SiC surfaces to desorb Si atoms therefrom, epitaxial graphene forms. The epitaxial graphene on SiC thin films, or further the epitaxial graphene on silicon (GOS), is especially intriguing in that it can enjoy various device technologies accumulated in Si devices in making graphene-based devices [11-12]. Field-effect transistors have already been demonstrated by using GOS [13].

The challenge for GOS production is its inclusion of defects [11], which is related to imperfections already present in the 3C-SiC films formed on the Si substrates such as stacking faults, misfit dislocations, antiphase boundary domains, surface roughness and cracks. For instance, Fukidome et al.
al. [14] have demonstrated that the quality of graphene is determined, at least partly, by the surface roughness of the SiC film used in the GOS [14] process. These imperfections in the SiC films used in GOS are somehow related to the large lattice mismatch (~20%) present between the 3C-SiC film and the Si substrate [11,15]. This large lattice mismatch induces a significant tensile stress accumulated in the SiC film. Little is known, however, about the relationship between the residual stress in the 3C-SiC film and the quality of GOS. We have prepared in this study four kinds of GOS samples with varying residual stresses in the 3C-SiC film.

We used Si(110) wafers as the starting substrates. The merit of using the Si(110) substrate is that we can widely change the residual stress in the 3C-SiC thin films on this surface. In particular, presence of the rotated epitaxy of 3C-SiC(111) on Si(110) [15-16] can greatly minimize the residual stress. In this rotated epitaxy, the accumulated stress in the film is minimized by forming a well-lattice-matched stacking of \( \overline{1}1\overline{0}0 \)Si/[\( \overline{1}1\overline{1}0 \)Si]3C-SiC and [001]Si/[\( \overline{1}1\overline{2} \)3C-SiC [15,17] orientation. In fact, it was experimentally demonstrated that the lattice constant anisotropy \( a_{\parallel}/a_{\perp} \) between the lateral and the growth directions is decreased by a factor of four from that of 3CSiC(111)/Si(111) in this rotated epitaxy [16]. We have conducted in this study x-ray diffraction (XRD) and Raman-scattering measurements on the four samples mentioned above, and have obtained correlations between the residual stress in the 3C-SiC film, crystallinity of 3C-SiC evaluated by the XRD-FWHM, and the domain size of the GOS film evaluated by the Raman analysis.

2. Experimental methods
An N-type Si(110) wafer with a resistivity of \( 1~20 \) \( \Omega \cdot \text{cm.} \), cut into 7×25 mm\(^2\) substrates, was used. In prior to growth, substrates were wet cleaned employing the RCA technique [18-19]. The growth was conducted by a gas-source molecular beam epitaxy (GSMBE) using monomethylsilane (MMS, \( \text{CH}_3\text{SiH}_3 \)) as a single source. After introduction to the GSMBE chamber, the sample was degassed at 600 °C and flash annealed at 1100°C for several times to clean the surface. MMS (Trichemical, 99.999%) was then introduced into the chamber. In the first step, a buffer-layer was formed at 600°C and flash annealed at 1100°C for several times to clean the surface. MMS (Trichemical, 99.999%) was then introduced into the chamber. In the first step, a buffer-layer was formed at 600°C [20] which was followed by the second step: formation of the 3C-SiC thin film [11-12]. After the 3C-SiC growth, graphene was formed on the SiC surface by annealing the sample at 1250 °C in vacuo [21-22]. Four GOS samples were prepared, whose preparation details are summarized in Table 1.

### Table 1. Summary of the multi-step growth method for growing graphene with varying stresses and crystal qualities.

| Sample Name | Step 1 | Step 2 | Step 3 | Step 4 |
|-------------|--------|--------|--------|--------|
| Thickness:  | Buffer layer: | SiC Growth: | SiC Growth: | Graphene Growth: |
| Sample (a)  | PMMS=4×10\(^{-3}\)Pa | T=600°C | P\(_{\text{MMS}}\)=4×10\(^{-2}\)Pa | T=1250°C |
| ~78 nm      | t\(_{\text{depo}}\): 5 min | T=1050°C | T=1050°C |
| Sample (b)  | PMMS=5×10\(^{-3}\)Pa | T=600°C | P\(_{\text{MMS}}\)=2.5×10\(^{-2}\)Pa | T=1250°C |
| ~108 nm     | t\(_{\text{depo}}\): 15 min | T=1000°C | T=1000°C |
| Sample (c)  | PMMS=1.25×10\(^{-3}\)Pa | T=600°C | P\(_{\text{MMS}}\)=5×10\(^{-2}\)Pa | T=1250°C |
| ~111 nm     | t\(_{\text{depo}}\): 5 min | T=1000°C | T=1000°C |
| Sample (d)  | PMMS=1.25×10\(^{-3}\)Pa | T=600°C | P\(_{\text{MMS}}\)=5×10\(^{-2}\)Pa | T=1250°C |
| ~83 nm      | t\(_{\text{depo}}\): 15 min | T=1000°C | T=1000°C |

The thickness of the 3C-SiC thin film was determined by ex situ spectroscopic ellipsometry (SE) (SpecEL-2000, Mikropack GmbH, Germany). The crystal orientation and the crystallinity of the 3C-
SiC films were characterized by x-ray diffraction (XRD) using a diffractometer (RINT2000, Rigaku Corp., Japan) with a monochromatic CuKα x-ray source operated at 40 kV and 30 mA. The stress in the 3C-SiC thin film and the graphene quality were characterized using a Raman-scattering microspectroscopy apparatus (RM1000, Renishaw plc, UK) with an Ar⁺ laser (wavelength: 514 nm, power: 10 mW being used as the excitation source.

3. Results & discussions

The XRD patterns of the 3C-SiC films on Si are shown in Fig. 1. The peak at 47.34° corresponds to the Si(220) planes originating from the substrate. The peak at 35.75° is attributed to the diffraction due to the rotated 3C-SiC(111) planes with its second-order 3C-SiC(222) peak appearing at 75.6°. The peak at 60.05° corresponds to the non-rotated 3C-SiC(220) planes. The sample (a) is thus a rotated 3C-SiC(111) thin film on Si(110), while sample (b)-(d) are non-rotated SiC(110) thin films on Si(110) but with different residual stresses as we will see shortly. The impact of the growth parameters on the rotation/non-rotation nature of the 3C-SiC/Si hetero-epitaxy is itself an interesting topic, which is currently investigated separately. The full widths at half maximum (FWHM) values of the 3C-SiC peaks of the samples are listed in Table 2. As we can see, the qualities of the 3C-SiC thin films, judged from the FWHM values, are in the order: (a) > (d) > (c) > (b).

![Figure 1. XRD patterns of graphene on 3C-SiC/Si films. Patterns (a)-(d) corresponds to samples (a)-(d), respectively.](image)

| Sample Name | 3C-SiC FWHM  |
|-------------|-------------|
| Sample (a)  | 0.25°±0.012°|
| Sample (b)  | 0.5°±0.012° |
| Sample (c)  | 0.45°±0.012°|
| Sample (d)  | 0.4°±0.012°  |

The residual stress accumulated in the 3C-SiC film can be estimated from the peak frequency of the transverse-optical (TO) phonon mode of 3C-SiC since the TO peak is quite sensitive to the stress in the crystal [23]. Figure 2 shows the Raman spectra of the samples in the low-frequency regions where the TO mode appears. In the spectra, two peaks can be seen, one at ~790 cm⁻¹ [24-25] and the other at 820 cm⁻¹ [27]. The former is attributed to the TO mode of 3C-SiC because this peak is absent in the
spectrum of the Si substrate (top). The TO peaks of 3C-SiC are redshifted from that (796 cm$^{-1}$) of bulk 3C-SiC crystals [26] and varies with the process condition. This indicates that the residual stress in the 3C-SiC film varies with the process condition as well. Quantitatively, the residual stress can be estimated using the empirical formula obtained by Olee et al. [28], where the measured TO phonon energy $\omega_{TO}$ in cm$^{-1}$ is described in terms of the stress $P$ (GPa) as

$$\omega_{TO} = (796.2 \pm 0.3) + (3.88 \pm 0.08)P - (2.2 \pm 0.4) \times 10^{-2} P^2. \quad (1)$$

The results obtained using Eq. (1) are summarized in Table 3. The minus signs of the pressure indicate that the stresses in the present 3C-SiC epilayers are of tensile ones. This result is consistent with the smaller lattice constant of 3C-SiC as compared to Si ($a_{SiC}=0.436$ nm, $a_{Si}=0.543$ nm) as well as the $\sim$8 % larger thermal expansion coefficient of 3C-SiC [26].

Figure 2. Raman scattering spectra of GOS. The one from the Si(110) substrate is also shown as a reference. Spectra (a)-(d) correspond to samples (a)-(d), respectively.

Table 3. Peak positions of the TO-phonon mode of 3C-SiC and stress $P$ values estimated with Eq. (1).

| Samples  | TO peak (cm$^{-1}$) | $P$ (GPa)  |
|----------|---------------------|------------|
| Sample (a) | 792.41±0.78        | -0.824±0.05|
| Sample (b) | 791.84±0.16        | -1.261±0.05|
| Sample (c) | 791.72±1.63        | -1.188±0.05|
| Sample (d) | 791.34±0.53        | -1.160±0.05|

Figure 3 shows the XRD FWHM of the 3C-SiC thin films plotted against the estimated residual stress. The XRD FWHM increases with the stress. Namely, the 3C-SiC film crystallinity is negatively correlated with the 3C-SiC residual stress. This is consistent with the previous
experimental observations that the residual stress causes crystal imperfections such as cracks, misfit dislocations, micropipes, and voids [21,27-28].

It is quite natural and has been partially demonstrated [14] that the quality of GOS is strongly dependent on the quality of the 3C-SiC film inserted between the Si substrate and graphene. Figure 4 shows the Raman-scattering spectra from the samples. In all the spectra, three fundamental vibrational modes of graphene appear at ~1600 cm$^{-1}$ (G band), ~2700 cm$^{-1}$ (G’ band), and ~1360 cm$^{-1}$ (D band) [11,14,31]. The G band is the only band coming from a single-resonant Raman process, and is associated with a doubly degenerate (in-plane TO (iTO) and longitudinal optical (LO)) phonon mode ($E_{2g}$ symmetry) at the center of the Brillouin zone ($\Gamma$ point) [32-34]. The G’ (also known as 2D) band is due to an intervalley double resonant (DR) process involving excitation/de-excitation of an electron with wavevector $k$ in the vicinity of $K$ point and two iTO phonons with wave vectors $q \approx 2k$ [33-36]. Here, both $k$ and $q$ are measured from the Dirac $K$ point. The D band involves an electron transition at the wave vector $k$ in the vicinity of $K$ point and one iTO phonon with the wavevector $q \approx 2k$ [33-38]. It arises from an intervalley process, which occurs around two inequivalent $K$ points ($K$ and $K’$) at the corners of the Brillouin zone [33-38]. Since energy and momentum are not conserved within the simple electron-phonon scheme, the D band process is related to microscopic defects. The G’ band, on the other hand, is related to the intrinsic electronic structure of graphene [33-36,39], and is not related to any defects.

![Figure 3](image-url)

**Figure 3.** XRD FWHM values obtained for 3C-SiC vs. the 3C-SiC residual stress obtained by Raman scattering spectroscopy. The solid line is guide to the eyes.

A plot of the grain size ($L_a$) of graphene versus the residual stress is shown in Figure 5. The $L_a$ is empirically estimated from the ratio of the Raman scattering intensity of the D and G bands [40] as;

$$L_a = \frac{560}{E_{\text{laser}}^4} \left( \frac{I_D}{I_G} \right)^{-1},$$

where $E_{\text{laser}}$ is the excitation energy in eV used in the Raman scattering experiment, and $I_D$ and $I_G$ the intensities of the D and G bands, respectively. The result in Fig. 5 shows that $L_a$ is negatively correlated with the residual stress in 3C-SiC film. This indicates that the quality (grain size) of GOS is negatively affected by the residual stress of the 3C-SiC film at least on the Si(110) surface. It is
understood that the residual stress of 3C-SiC somehow influences the quality of the 3C-SiC film, which serves as the template for the epitaxy of GOS. In particular, the use of the stress-relaxed, rotated epitaxy of 3C-SiC(111)/Si(110) turns out to be quite effective in obtaining a high quality GOS.

4. Conclusions
By conducting XRD and Raman-scattering measurements on a series of samples with varied residual stress in the 3C-SiC films, a systematic study has been conducted to obtain relations amongst residual stress, the XRD-FWHM crystallinity of the 3C-SiC film, and the grain size of GOS. As far as the GOS on Si(110) substrates is concerned, clear correlations were found to exist among these three parameters. In particular, use of the rotated epitaxy, 3C-SiC(111)/Si(110), was found to be quite effective in obtaining stress-relaxed, high-quality 3C-SiC films and thus high-quality GOS films. This finding will serve to the production of high-performance GOS-based devices.

5. References
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Figure 5. The grain size $L_\alpha$ of GOS vs. the 3C-SiC residual stress both obtained by the Raman scattering spectroscopy.
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Acknowledgments
This work has been partly carried out at the Evaluation Division of Fundamental Technology Center, Research Institute of Electrical Communication, Tohoku University and supported by JSPS KAKENHI (21360017), Grant-in-aid for Young Scientist (B) (20760485), Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan, and the Tohoku University Electro-Related Departments Global COE Program.