RHEED patterns of 3 nm carbon layer coated Si(111) surface using Sputtering

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Abstract. In order to overcome the high cost of SiC substrates, researchers reacted carbon atoms and Si surface to obtain SiC layers on Si substrate since one decade ago. The SiC is the best substrate to grow the graphene. In this work, 3 nm carbon layer was coated on the Si(111) surface using the Sputtering method. After the RCA cleaning process, n-type Si(111) with resistivity 1.5-4.5 Ω.m was put into the load lock chamber then transferred into the deposition chamber after the vacuum condition was attained. The carbon source was evaporated with plasma energy of 150 watt for 3 min to obtain about 3 nm carbon layer on Si(111) surface. The samples were characterized using ex-situ the reflection high energy electron diffraction (RHEED), the scanning electron microscopy (SEM) and the Raman spectroscopy. The sample was annealed at RT-1400°C while the transition of RHEED pattern was observed using the cooled CCD camera. The amorphous pattern appeared at RT-800°C and finally Si(111)-7×7 appeared at over 1200°C. Dot patterns were investigated as SiC structures. From SEM images, it is confirmed that triangle SiC formed on Si(111) surface. In addition formation of SiC on Si(111) was observed by Raman spectroscopy.

1. Introduction

The graphene has the excellent physical and chemical properties [1]. Since one decade ago, many methods were proposed to obtain the graphene such as chemical vapor deposition (CVD) [2], micromechanical exfoliation of highly oriented pyrolytic graphite [3] and ultrahigh vacuum (UHV) annealing of silicon carbide (SiC) or graphitization [4]. Among these methods, graphitization of SiC has been promising in epitaxial graphene formation [5]. However, the high cost of commercial SiC and high-temperature procedures has been a barrier to graphene development. In order to overcome this obstacle then the growth of graphene on silicon (Si) through SiC attracted the attention of researchers because silicon-based electronic devices have been published since a long time ago [6]. In addition, graphene is also expected to overcome the limitations of silicon in the development of CMOS devices. Therefore, the growth of SiC on Si is essential to determine an epitaxial graphene layer on the silicon surface.

The previous study, we successfully grew SiC on Si(111) surface using CH4 and C2H6 gases as carbon source in the molecular beam epitaxy (MBE) chamber [7-9]. Pure SiC formed on Si(111) surface
at 800°C using CH$_4$ in increasing temperature (IT) method [7]. However, it is needed a tungsten filament at high temperature to break the stable CH$_4$ gas. In our MBE chamber system, the lighting of tungsten filament could disturb the reflection high energy electron diffraction (RHEED) patterns observation. In addition, the growth rate of SiC on Si(111) surface was very low. A 10 nm circular SiC was obtained when CH$_4$ was exposed on Si(111) surface for about 2 h. In this work, carbon solid is used as carbon source in Sputtering method to increase the growth rate of SiC. The growth of SiC on Si(111) is investigated by the RHEED pattern and confirmed by scanning electron microscopy (SEM) and Raman spectroscopy. The objectives of this study are to obtain the bigger SiC size on Si(111) surface using Sputtering method relative to the SiC size obtained by gas source-MBE method.

2. Experimental

An N-type (P-doped) 1.5–4.5 Ω-cm Si(111) single crystal wafer was used as the substrate. A clean Si(111) substrate was prepared by the RCA cleaning process. A substrate was immersed in NH$_4$OH:H$_2$O$_2$:H$_2$O in ratio 1:6:20, respectively at 40°C for 15 min. Then it was overflowed in H$_2$O for 10 min. Finally, it is drained by N$_2$ gas. The substrate was put on the sample holder into the load lock chamber. After the pressure between the load lock chamber and the deposition chamber was attained, the substrate was transferred into the deposition chamber. Ar gas was introduced into the deposition chamber and the pressure was maintained at 1 Pa. In the case of carbon sputter gun, radio frequency was set at 150 W. Carbon shutter was opened and evaporated-carbon attached on Si(111) surface. Schematic diagram of our experimental apparatus can be shown in Fig. 1.

To determine carbon rate, sputtered carbon coating on Si(111) surface for 139 min and then carbon layer thickness was observed by cross-sectional SEM. Fig. 2 shows a cross-sectional SEM image of carbon-coated Si(111) surface. The thickness of the carbon layer was about 145 nm. Thus, carbon rate was about 1.04 nm/min. Therefore, it is assumed that the thickness of the carbon layer on the Si(111) surface was about 3 nm if carbon is sputtered for 3 min.

Carbon-coated Si(111) was put into the MBE chamber equipped with RHEED analysis. The schematic diagram of the MBE apparatus used in this work can be shown in ref [9]. The explanation of RHEED apparatus used has been described elsewhere [10]. The substrate temperature was determined from its resistivity calibrated by an optical pyrometer. Incident electron energy used for RHEED measurement was 15 keV. The substrate temperature was increased to react carbon atoms and Si atoms. Formation of SiC could be observed using RHEED pattern and then SiC sample was confirmed by SEM and Raman spectroscopy.
3. Results and Discussion

Fig. 3 shows RHEED patterns at each substrate temperature. There are three patterns when the substrate is annealed from room temperature (RT) to about 1400°C i.e. halo, ring + dot, and dot patterns. Halo pattern (Fig. 3(a)) indicates that carbon atoms and silicon atoms have not reacted to form SiC at RT-800°C. Halo pattern also appears on an amorphous layer thus it is concluded that carbon layer remains amorphous at that temperature range. A dot and ring pattern emerges when the substrate is heated over 800°C as shown in Fig. 3(b). This indicates that carbon atoms and silicon atoms have reacted to form SiC. White circles are SiC spots while another dot is silicon structure. Mixed-SiC + 7×7 present at 850-1200°C is good agreement with the previous study when Si(111) surface was exposed to CH₄ gas at about 800°C [7]. Furthermore, when the temperature is increased over 1200°C, pattern change into the 7×7 structure (Fig. 3(c)). It is well known that Si(111)-7×7 structure is obtained by using the flushing method i.e. substrate temperature is maintained at 1250°C for several seconds and observed using RHEED pattern analysis. These treatments are repeated many times until 7×7 pattern appear. The 7×7
structure is obtained through the flushing method will produce a clean surface Si(111) which means that all carbon atoms desorb from the Si(111) surface.

![Figure 4. SEM image of the sample after annealing at 900°C. Right side image is enlargement on one of triangular SiC.](image)

Fig. 4 shows the morphology of the sample after heated at 900°C. Based on the RHEED pattern at 850°C-1200°C, there are two structures appear on the Si(111) surface i.e. 7×7 and SiC. Therefore, it is considered that the triangular shape as SiC. However, inhomogeneous triangular SiC form on Si(111) surface. The most significant size of SiC is 500 nm.

In order to confirm that the mixed 7×7 and SiC present on the Si(111) surface at 900°C, Raman spectroscopy was conducted. There are two peaks correlating Si at about 520 cm$^{-1}$ and SiC at about 940 cm$^{-1}$ as shown in Fig. 5.

![Figure 5. Raman shift of sample after heated at 900°C.](image)

4. Conclusion

SiC has been successfully formed on Si(111) surface at 850 – 1200°C using the Sputtering method. Inhomogeneous size of triangular SiC appear on Si(111) surface. The average size of triangular SiC is bigger than circular SiC which is obtained using gas source MBE.
Acknowledgments
Authors wish to thank PNB Universitas Sebelas Maret 2017 for financial support through Hibah Mandatory

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